

**PROCEEDINGS OF THE THIRD INTERNATIONAL SYMPOSIUM  
ON ULTRA CLEAN PROCESSING OF SILICON SURFACES**



Marc Heyns (editor)  
Marc Meuris & Paul Mertens (co-editors)

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## Preface

The International Symposium on Ultra Clean Processing of Silicon Surfaces (UCPSS) is a bi-annual conference organized by IMEC. The first two editions were held in Leuven (Belgium) in 1992 and Bruges (Belgium) in 1994 respectively. The Third International Symposium on Ultra Clean Processing of Silicon Surface (UCPSS '96) was held in Antwerp (Belgium) on September 23-25, 1996. The issues which are addressed at this symposium cover all aspects of ultra-clean Si-technology, cleaning, contamination control, Si-surface chemistry and topography and its relation with device performance and process yield.

The scientific programme of UCPSS '96 consisted of 5 invited and 76 regular contributions which were selected out of 102 submitted abstracts. The meeting was attended by more than 300 scientists from 21 countries. The order and organisation of the presentations at the conference are maintained in these proceedings. Thanks are due to the programme committee for selecting the contributions and to the symposium authors and participants who made this symposium an informative and productive event.

At the symposium various authors discussed the delivery of ultra-clean chemicals and gases and the effect of contamination on processing characteristics. Important progress was reported on the understanding of the mechanism of Cu-outplating from HF-solutions and on the effect of Al and Fe on processing characteristics. Analytical techniques are a key issue in ultra-clean processing technology and novel analytical techniques for trace contamination detection in chemicals, on Si-surfaces and in gases were presented. Various new developments in dry cleaning were reported at the conference ranging from cryogenic aerosol cleaning to remote plasma cleaning, electric arc plasma jet and various gas-vapour based cleans for metal and native oxide removal. Despite the continuous progress in dry cleaning technology, wet cleaning seems to remain the dominant cleaning method. Various papers discussed results on diluted chemistries and simplified cleaning strategies aiming at the development of more cost-effective and environmentally-friendly cleaning techniques. The standard 'SC1-clean' also received a lot of attention and the characteristics of this cleaning mixture were discussed in great detail. Optimized chemistries, including the use of surfactants, were discussed for low-temperature epitaxy and for both front-end and back-end cleaning. Although all mechanisms involved in megasonic cleaning are not yet unravelled, a lot of advancement has been made in this area, illustrated by the papers presented at this conference. Another important topic that was addressed at the conference is the growth and characteristics of ultra-thin oxide layers. The effect of various processing parameters, including organic contamination, on the characteristics of these very thin oxide layers were discussed.

The success of the conference prompted us to start preparing for the Fourth International Symposium on Ultra Clean Processing of Silicon Surfaces (UCPSS '98). This will take place in Belgium between September 21 and 23, 1998. The enthusiasm created by the first three meetings makes us look toward the Fourth Symposium with great excitement.

Marc Heyns  
Conference Chairman

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## CHEMICAL MANAGEMENT FOR UHP WAFER FAB APPLICATIONS

Lindsey Hall, Jennifer Sees, and Ashutosh Misra  
Texas Instruments, Inc.  
Dallas, TX 75265

Wafer cleaning and etching applications in semiconductor manufacturing require ultrahigh purity (UHP) chemicals for acceptable device performance and yield. Over 50% of yield losses can be attributed to microcontamination remaining from inadequate cleaning processes.<sup>1</sup> Contamination remaining on a semiconductor surface is well known to cause a wide variety of adverse effects. For example, metallic impurities will contribute to leakage at the p-n junction, deterioration of minority carrier lifetime, and decrease of oxide breakdown voltage. Particulate impurities can lead to shorting and inadequate photolithographic processing.<sup>1,2</sup> For this reason, chemical specifications for critical chemicals are approaching 100 ppt each metal and 10 particles > 0.1  $\mu\text{m/mL}$  with typical impurity levels at least an order of magnitude less than specification. Delivering chemicals of this quality from the manufacturing site to fab point of use requires careful chemical management. Key issues include proper chemical production, transportation, and design and operation of chemical delivery systems.<sup>3</sup>

Most of the chemicals used in semiconductor manufacturing are toxic, corrosive, or otherwise pose severe safety hazards and must be properly handled to prevent operator exposure. During the early years of semiconductor device manufacturing, chemicals were stored and transported to the process equipment in glass or plastic bottles, posing both contamination and safety risks.<sup>4</sup> Chemical delivery systems were first introduced in the mid 1980s to eliminate the hazards of bottle delivery and fill. Since that time, it has been shown that properly designed chemical delivery systems with state of the art filtration technology are capable of providing chemicals to point of use (POU) with particle concentrations well below those in bottled chemicals.<sup>4,5</sup> In the absence of on-line purification, distribution systems must not add metallic contamination to process chemicals and distributed chemical purity at POU must match incoming purity. Recently, systems have been shown not to add measurable amounts of metallic extractables down to < 1 ppb total metallic contamination.<sup>4,6</sup>

In general, the chemical is pressurized or pumped from a bulk storage unit and transported to points of use within the fab through dual-contained distribution tubing, typically perfluoroalkoxy (PFA) or polytetrafluoroethylene (PTFE) for acid and caustic systems or stainless steel for solvent delivery. PFA and PTFE are desired because of their low metallic extractables.<sup>3,6</sup> Well designed systems insure that the chemical is in contact only with the fluoropolymer at all times. The most common bulk vessel for incoming chemical storage is the 55 gallon polyethylene lined stainless steel drum. Less frequently used, but higher volume, are 300 gallon

totes or 5000 gallon isotainers. All components in the system other than continuous runs of tubing are enclosed in cabinets or junction boxes.<sup>4,5</sup> Vacuum/pressure systems are desirable for their ability to provide constant flow, thereby avoiding particle release associated with sudden pressure surges. However, recent advances in pump technology allow for less than 1 psi pressure fluctuation. High volume chemicals such as  $\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{HCl}$  are the best candidates for chemical distribution.

Certification of chemical distribution systems involves several rigorous steps to insure sub-ppb chemical quality at startup. Certification involves a series of steps including a combination of nitrogen purges and DI water rinses until low particle counts are reached. Finally, the chemical for distribution is introduced and leaches the teflon until metallic and particulate contamination analysis results are within specification.<sup>3</sup> Routine monitoring programs including on-line particle counting and sampling along various points of chemical distribution and metals analysis are necessary for statistical process control and troubleshooting.

In terms of purity, the ultimate chemical delivery unit is the isotainer. Isotainers are 5000 gallon teflon lined vessels transportable by ship or truck. Isotainers provide purity benefits from several standpoints. They provide a lower surface area to volume ratio than drums (0.1 square feet/gallon vs. 0.4 square feet/gallon), thereby lessening the opportunity for contamination contributed by the container. Service with isotainers involves fewer handling operations, for example, dip tube insertions, connections made and broken, and chemical samples taken. Handling operations for 20,000 gallon/month chemical use would require in excess of 3000 such steps for drum fill vs. about 10 for isotainer fill. Additionally, isotainers are reusable, providing extensive leaching of the liner material with time and use. Drum usage does not afford this opportunity as new drums are often used with each delivery. Finally, one sample analyzed from an isotainer after delivery represents a 100% sampling plan, providing a high degree of assurance of chemical purity. Based on cost considerations, a comparable volume of chemical delivered in drums receives less than a 10% sampling rate, leaving the outside possibility of fab exposure to contaminated chemicals. Drum sourcing and handling must be carefully controlled in order to minimize variability. It is not economically feasible to analyze enough drums in a lot to adequately control variability due to contamination from the drum.

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## **DELIVERY OF HIGH PURITY CHEMICALS FOR THE MANUFACTURE OF SEMICONDUCTOR MICROCIRCUITS WITH SUB-0.5 $\mu\text{m}$ GEOMETRIES**

**Donald C. Grant, Wayne P. Kelly, Lisa Clark, David Schell, Don  
Winkelman, Travis Lemke, Wayne Falla and Norm Powell**

### **1. ABSTRACT**

Technological advances have allowed chemical management systems to meet the increasingly strict purity specifications for semiconductor process chemicals. Careful selection of system wetted materials has reduced metal extraction to analysis detection capabilities. Research on flow hydraulics has led to a better understanding of the behavior of particles in chemical delivery systems. A chemical management system installed at Motorola APRDL/MOS 13, assembled with high purity components, uses several advanced flow control techniques to minimize particulate contamination. This systems, which combines Advanced Stabilized Distribution™, fab-wide distribution and startup stabilization, delivers chemicals with very low particle concentrations ( $\leq 1$  particle/ml  $\geq 0.2 \mu\text{m}$ ) and has negligible metallic extractables.

### **2. INTRODUCTION**

The processes used to produce microcircuits with critical dimensions below  $0.5 \mu\text{m}$  are extremely sensitive to contamination. Both elemental contaminants, especially metallic species, and particulate contaminants are very detrimental to device yield and reliability. One source of these contaminants is the chemicals used in the cleaning, etching and stripping processes used to produce the devices.

Advances in chemical management technology have kept pace with the increasingly strict purity specifications for process chemicals. Careful selection of system wetted materials has reduced metal ion contamination [1]. Improved measurement tools and research on the effects of flow hydraulics on filter performance have led to a better understanding of the behavior of particles in chemical delivery systems [2]. Chemical delivery systems with Advanced Stabilized Distribution and startup stabilization have been designed to minimize particulate contamination through control of chemical flow.

Chemical delivery systems with Advanced Stabilized Distribution maintain a constant flow rate through system filters at all times. Both internal stabilization and fab-wide distribution can be maintained. In fab-wide distribution, chemical flows continuously through the system filters, past the fab points of use and back to a supply tank. When internal filter stabilization is used, chemical flowthrough the system filters and is returned to the supply tank. Chemical is supplied to the fab points of use through a line that branches from this loop downstream of the system filters. There is no flow through the branch except during a chemical demand.

Startup stabilization is used to control particulate contamination when a chemical delivery system is shut down for maintenance or for another reason. The system filters are subjected to a hydraulic shock upon startup, releasing a very large number of particles into the chemical [3]. Startup stabilization prevents these particles from reaching the points of use. The chemical is polished, that is, particles are removed by recirculating it through the system filters, prior to release to the fab.

Delivery systems incorporating both Advanced Stabilized Distribution and startup stabilization were designed to deliver the high purity chemicals needed to manufacture PowerPC<sup>®</sup> chips at Motorola APRDL/MOS 13. The chemicals delivered by these systems were 49% hydrofluoric acid, 37% hydrochloric acid, 29% ammonium hydroxide, 30% hydrogen peroxide, 96% sulfuric acid and isopropyl alcohol. Specifications for contaminant levels in incoming chemicals ranged from < 1 ppb to < 10 ppb. The systems were required to add < 1 ppb of total metallic contaminants to the delivered chemical. Particle specifications at the points of use ranged from < 2 to < 5 particles/ml ( $\geq 0.20 \mu\text{m}$ ).

### 3. SYSTEM METALLIC EXTRACTABLES

Each system was tested using the Dynamic Extraction<sup>™</sup> technique over a one-week period during which no chemical entered or exited the system. Concentrations of 34 elements were measured during this time using a combination of inductively coupled plasma-mass spectroscopy (ICP-MS) and graphite furnace atomic absorption (GFAA). Total elemental concentrations in the chemicals were essentially invariant over time. All the systems were able to achieve the specification of < 1 ppb of total metals added within three days of initial chemical contact and were predicted to add < 0.1 ppb of total metals within one month [4]. The systems typically met specification within one day, as shown in Table 1. The major element extracted was iron.

*Table 1.* Time required for chemical delivery systems to achieve selected extraction rates

| Chemical               | Time to < 1 ppb total metals added (days) | Time to < 0.1 ppb total metals added (days) | Main elements extracted |
|------------------------|-------------------------------------------|---------------------------------------------|-------------------------|
| 29% Ammonium hydroxide | < 1                                       | < 1                                         | None                    |
| 37% Hydrochloric acid  | 3                                         | 31                                          | Iron                    |
| 49% Hydrofluoric acid  | < 1                                       | < 1                                         | None                    |
| 30% Hydrogen peroxide  | < 1                                       | < 1                                         | None                    |
| 70% Nitric acid        | < 1                                       | < 1                                         | None                    |
| 96% Sulfuric acid      | 2                                         | 16                                          | Iron                    |

#### 4. SYSTEM PARTICLE CONCENTRATIONS

Particle concentrations were measured at the end of the distribution loop using an on-line laser optical particle counter. When the systems were operated under normal conditions, particle concentrations were well below design specifications, as shown in Table 2. Concentrations ranged from  $< 0.1$  to  $1.0$  particle/ml ( $\geq 0.20 \mu\text{m}$ ).

Table 2. Particle concentrations in delivered chemical under typical operating conditions

| Chemical               | Typical concentration<br>(#/ml $\geq 0.2 \mu\text{m}$ ) | Specification<br>(#/ml $\geq 0.2 \mu\text{m}$ ) |
|------------------------|---------------------------------------------------------|-------------------------------------------------|
| 29% Ammonium hydroxide | 0.5                                                     | $< 3$                                           |
| 37% Hydrochloric acid  | $< 0.1$                                                 | $< 2$                                           |
| 49% Hydrofluoric acid  | $< 0.1$                                                 | $< 2$                                           |
| 30% Hydrogen peroxide  | 1.0                                                     | $< 2$                                           |
| 96% Sulfuric acid      | $< 0.1$                                                 | $< 5$                                           |
| Isopropyl alcohol      | 1.0                                                     | $< 2$                                           |

Experiments were performed at APRDL/MOS 13 to verify the effect of startup stabilization on particle concentrations at the points of use. Three chemicals, sulfuric acid, isopropyl alcohol and ammonium hydroxide, were monitored for particle concentrations after startup. The duration of the startup stabilization time was varied from 0 to 20 minutes. Figure 1 presents the peak particle concentrations at the end of the distribution loop as a function of startup stabilization time. For all three chemicals, the peak concentration decreased as the startup stabilization time increased.

In addition, the length of time during which the particle concentrations were above specification decreased with longer startup stabilization time (Figure 2). These data indicate that chemical specifications can always be met for ammonium

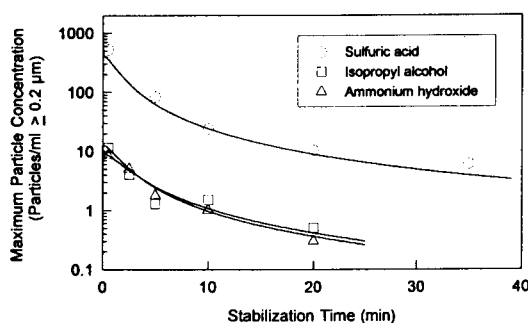


Figure 1. Effect of stabilization time on maximum particle concentrations

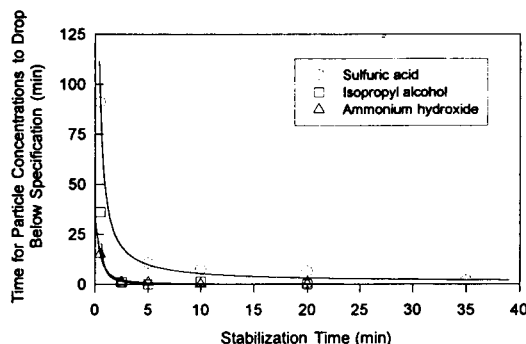


Figure 2. Effect of stabilization time on time for particle concentrations to drop below specification

hydroxide and isopropyl alcohol with a ten-minute delay in chemical availability following system startup. The startup stabilization time required for sulfuric acid is approximately 40 minutes.

## 5. CONCLUSION

The chemical management systems at Motorola APRDL/MOS 13 incorporate advanced particle and metal control features. The particle control features maintain constant flow through the system filters at all times (Advanced Stabilized Distribution) and prevent particles released during startup from reaching the points of use (startup stabilization). Metal control is accomplished by proper selection of system materials. These systems consistently deliver chemicals with  $< 1$  particle/ml ( $\geq 0.20 \mu\text{m}$ ) and add  $< 1$  ppb total metal ions within three days of chemical contact.

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<sup>TM</sup> Advanced Stabilized Distribution is a trademark of FSI International, Chaska, Minnesota.

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## EFFECT OF ANIONS ON COPPER OUTPLATING FROM HF SOLUTIONS

I. Teerlinck, P.W. Mertens, R. Vos, M. Meuris and M.M. Heyns

IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

### 1. INTRODUCTION

Copper ions present in aqueous HF solutions are known to plate out on Si wafer surfaces. We have shown that the semiconductor properties of the Si substrate play a very important role in the copper deposition process [1]. Illumination during immersion enhances the copper deposition due to the generation of minority carriers which are consumed in the deposition process. It has been reported that the addition of trace amounts of chloride to an HF solution increases the copper deposition [2]. In this paper we investigated the effect of the addition of different concentrations of chloride on the deposition process taking into account the illumination condition.

### 2. EXPERIMENTAL

Cz grown, p-type and n-type Si(100) wafers ( $10\text{--}20\ \Omega\cdot\text{cm}$ ) were precleaned by an IMEC clean. The HF-last wafers were immersed in a 0.5% aqueous HF solution at  $19^\circ\text{C}$  containing 100 w-ppb copper ions. Various amounts of HCl or KCl were added to the solution. The wafers were immersed in darkness or under illumination using a 35 W halogen lamp. The resulting copper surface concentration ( $[\text{Cu}]_{\text{surf.}}$ ) was measured by direct TXRF analysis performed on an Atomika XSA 8010 instrument, operated with a Mo anode at 50 kV and 40 mA. Some wafers were inspected by AFM using a Digital NanoScope Dimension 3000 instrument operated in "tappingmode".

### 3. RESULTS

The wafers were immersed for 300 s in the copper contaminated HF solution containing various amounts of HCl. Fig. 1 shows the  $[\text{Cu}]_{\text{surf.}}$  under different illumination conditions a.f.o. the w-concentration of HCl. We observe three different regions depending on the amount of HCl added. In the first region, up to 100 w-ppb, the copper deposition still increases by illumination by at least an order of magnitude. In the second region, between 100 w-ppb and 1000 w-ppm, and the third region, more than 1000 w-ppm, the effect of the illumination has disappeared. In the second region the  $[\text{Cu}]_{\text{surf.}}$  reaches the amount obtained under illumination without chloride addition. In the third region however, the copper deposition decreases to the level in darkness without chloride addition.

The effect of immersion time on the  $[\text{Cu}]_{\text{surf.}}$  in these three regions was investigated. Fig. 2 shows the results in the case of 10 w-ppb HCl addition (first region). In darkness the copper deposition is slightly increased. Under illumination a strong increase of the  $[\text{Cu}]_{\text{surf.}}$  is still observed with increasing immersion times.

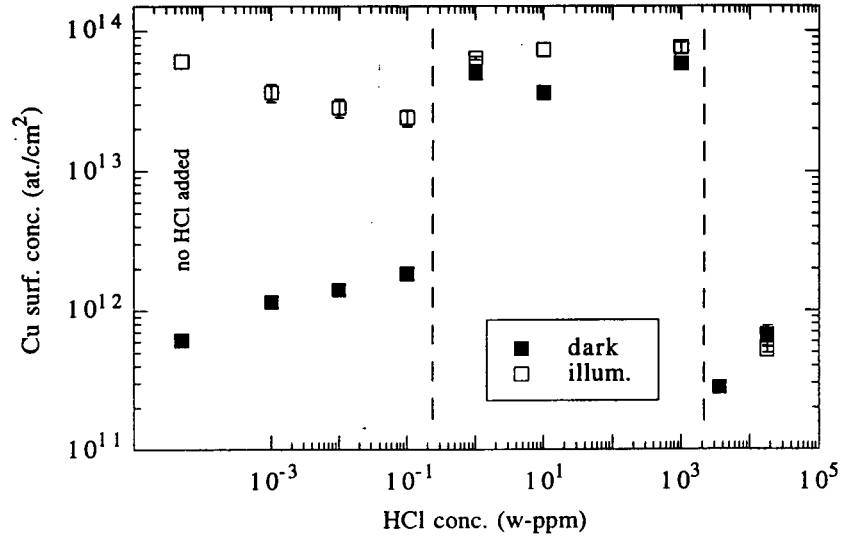


Figure 1. The  $[Cu]_{surf.}$  a.f.o. HCl addition in darkness and under illumination in a 0.5% HF solution containing 100 w-ppb of copper ions.

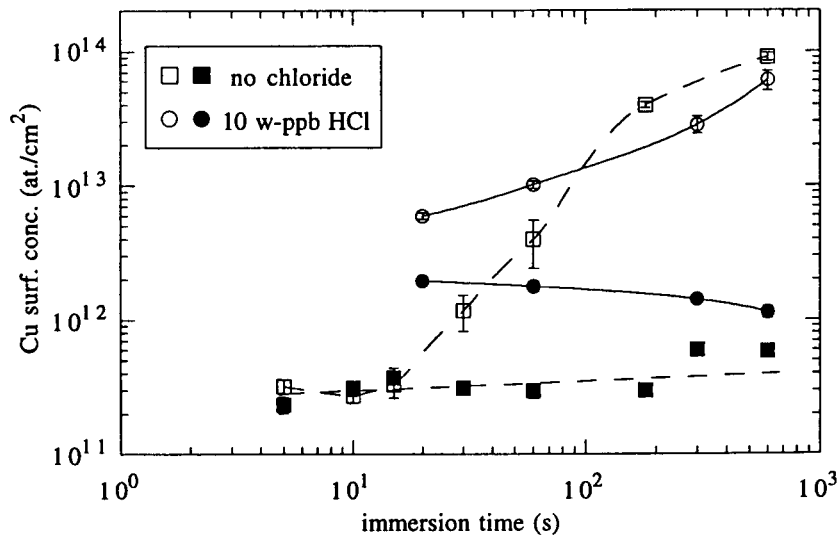


Figure 2. The  $[Cu]_{surf.}$  a.f.o. immersion time in darkness (full symbols) or under illumination (open symbols) in a 0.5% HF solution containing 100 w-ppb of copper ions and 10 w-ppb HCl. Also the experimental results without chloride addition are shown.

In Fig. 3(a) the results are shown when 10 w-ppm KCl or HCl (second region) is added. No difference is seen between HCl and KCl addition, indicating that the effect is due to the chloride. For the whole time frame investigated the effect of the illumination condition has disappeared. When 0.5 mole/l of HCl is added it is seen in Fig. 3(b) that the copper deposition is decreased.

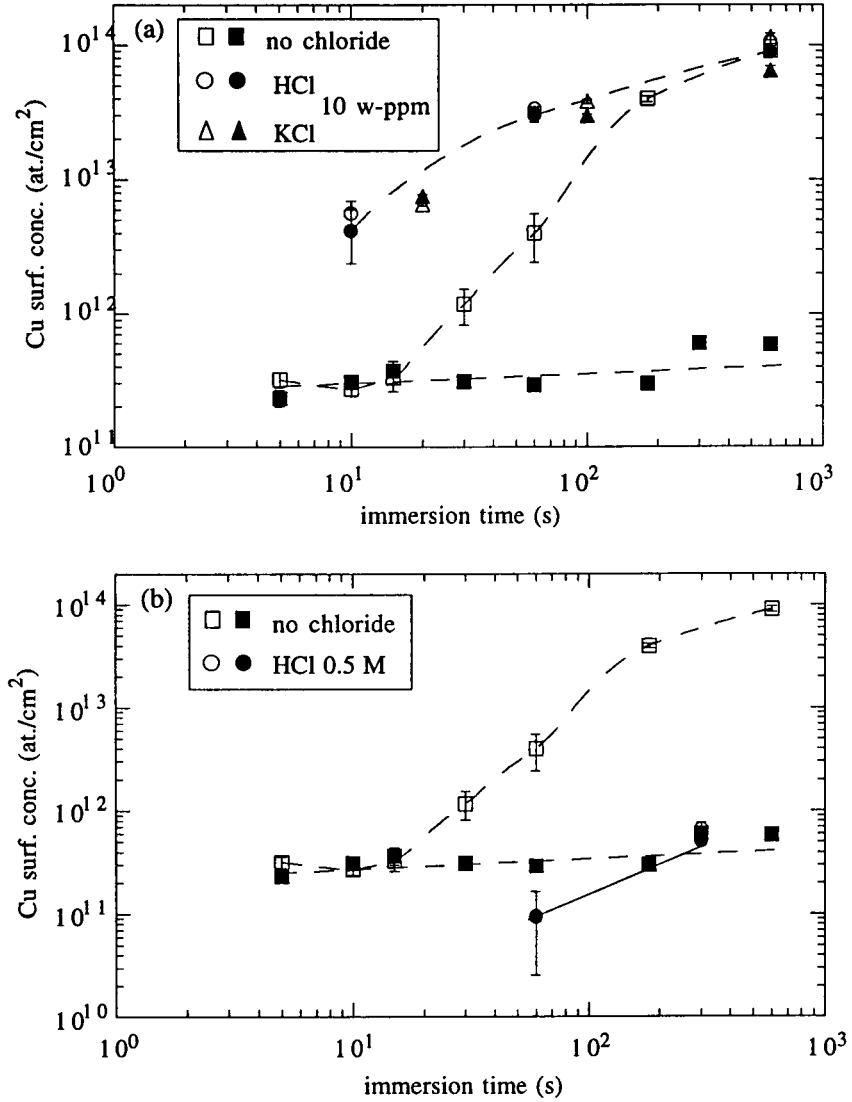


**Figure 3.** The [Cu]surf. a.f.o. immersion time in darkness (full symbols) or under illumination (open symbols) in a 0.5% HF solution containing 100 w-ppb of copper ions and (a) 10 w-ppm HCl or KCl and (b) 0.5 mole/l HCl. Also the experimental results without chloride addition are shown.

Fig. 4(a) shows a typical AFM result after a 10 min immersion in darkness in a solution containing 10 w-ppm HCl. We observe large copper deposits, similar to those observed after an immersion under illumination without chloride addition [1]. When 0.5 mole/l HCl is added, Fig. 4(b), no copper deposits are observed by AFM after 10 min immersion under illumination.

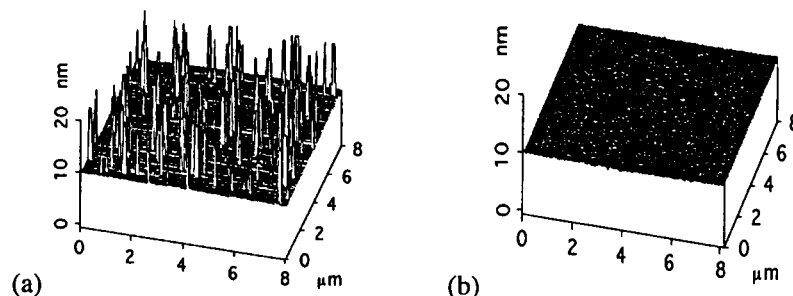


Figure 4. AFM plot of Si wafer surface after 10 min immersion in a 0.5% HF solution containing 100 w-ppb copper ions (a) in darkness with 10 w-ppm HCl and (b) under illumination with 0.5 mole/l HCl.

#### 4. DISCUSSION

The experimental results show that the presence of chloride ions in the HF solution strongly affects the copper deposition behaviour depending on the chloride concentration. Illumination increases the copper deposition in the case of chloride additions below 100 w-ppb. This is due to the increased concentration of minority carriers which are consumed in the electrochemical deposition process [1]. Trace amounts of chloride ions catalyze the  $\text{Cu}^{2+}/\text{Cu}^+$  reaction by a chloride bridged electron transfer pathway [3]. Furthermore chloride ions have a strong stabilizing effect on cuprous ions by the formation of cuprous chloride species. Small amounts promote the deposition as a result of  $\text{CuCl}$  formation:  $\text{Cu}^{2+} + \text{Cu} + 2\text{Cl}^- \rightleftharpoons 2\text{CuCl}$ . This deposition pathway does not involve the Si substrate and might therefore be independent of the illumination condition. However, for high chloride concentrations, soluble higher cuprous chloride complexes  $\text{CuCl}_{n+1}^{n-}$  are formed resulting in a decrease of the copper deposition. The same trends in copper deposition are expected in case of bromide or iodide addition since they also exhibit a stabilizing effect on cuprous ions and a catalysing effect by anion bridging.

#### 5. CONCLUSIONS

In aqueous HF solutions the copper deposition on Si surfaces is substantially affected by the illumination condition. The addition of chloride can suppress the effect of illumination. The copper deposition then depends on the chloride concentration. Small amounts of chloride increase the copper deposition due to a catalyzing effect and the formation of cuprous chloride. Large amounts of chloride addition suppress the copper deposition by the formation of soluble higher cuprous chloride complexes.

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## Effect of Al contamination on oxidation of silicon surfaces

\*T.Ohmori, \*N.Yokoi and \*K.Sato

Effect of Al contamination in SC-1(NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O) cleaning process on oxidation of silicon surfaces was studied. As a result, we found that oxidation of silicon surfaces was accelerated as Al impurities on silicon surfaces increased and its acceleration was more predominant in the initial stage of pyrogenic oxidation.

### 1. Introduction

As the degree of ULSIs increases, it becomes more significant to control many kinds of contaminants on silicon surfaces. In the ULSIs' fabrication process, particulate contaminants are especially harmful for ULSIs and reduce devices' yield and performance. The SC-1(NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O) has been used as a most efficient solution to eliminate particulate contaminants from silicon wafer surfaces. It has been also known that metallic contaminants such as Al and Fe adhere easily to silicon surfaces in SC-1 cleaning. Furthermore, as one of the influence by the metallic contaminants it has been reported that Al impurities on silicon surfaces retard oxidation rate in dry oxidation[1-2]. Figure 1 shows an effect of Al impurities on break-down voltage(Bvg) of silicon-dioxide films(nearly 10nm) formed with pyrogenic oxidation. We found that the Bvg shifted from 10V to 11V due to Al impurities ( $1 \times 10^{12}$  atoms/cm<sup>2</sup>) on silicon surfaces and this Bvg shift was caused by the increase of oxide thickness.

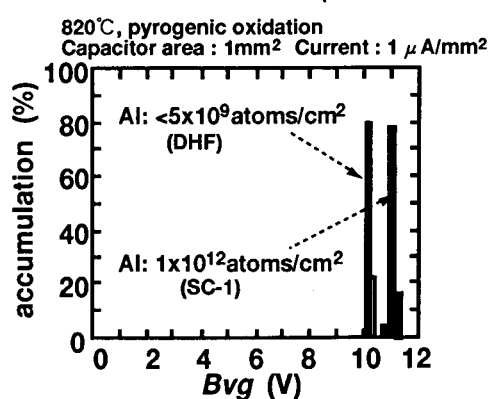


Fig.1 Effect of Al impurities on break-down voltage(Bvg)

\* Mizuhara4-1, Itami, Hyogo, Japan, ULSI Laboratory, Mitsubishi Electric Corp.

So we studied the influence of Al impurities on wafer surfaces on oxidation rate in pyrogenic oxidation. As a result, it was confirmed that oxidation of silicon wafers is accelerated as Al impurities increase and its acceleration is more predominant in the initial stage of pyrogenic oxidation. These results indicate that it is necessary to reduce Al impurities on silicon surfaces less than  $1 \times 10^{10}$  atoms/cm<sup>2</sup> to form thin silicon-dioxide films in good controllability.

## 2. Experimental

In order to investigate the influence of Al impurities on the oxidation rate the following experiments were done. The p-type <100> silicon wafers used in this work were initially treated with RCA cleaning (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>, HCl/H<sub>2</sub>O<sub>2</sub>, HF). Oxidation of the wafers was performed at 820°C in H<sub>2</sub> and O<sub>2</sub> ambient. The Al contaminated wafers with several levels of concentration in the range of  $10^{11}$  atoms/cm<sup>2</sup> to  $10^{13}$  atoms/cm<sup>2</sup> were prepared by means of SC-1 with different Al concentration following the RCA cleaning. Aluminum concentration on each silicon surface was analyzed by secondary ion mass spectroscopy and atomic absorption spectroscopy. At first we studied the influence of Al impurities on silicon surfaces. The Al contaminated wafers were oxidized with the reference wafers treated with RCA cleaning. Our study covered oxidation time of 1min to 65min, corresponding to oxide thickness of about 5nm to 60nm respectively. Next we studied the influence of Al impurities on pre-oxide films in order to understand the mechanism of accelerated oxidation caused by Al impurities. These pre-oxide films of 4nm and 7nm in thickness were formed with dry oxidation on the silicon wafers treated with RCA cleaning. The Al impurities were deposited on the outer surfaces of the pre-oxidie with SC-1 containing Al of 100ppb. The Al contaminated wafers were oxidized with the reference, clean pre-oxidized wafers. An ellipsometry was used for measuring oxide thickness.

## 3. Results and Discussion

### Al concentration vs. oxide thickness

The relation between Al concentration on silicon wafers and oxide thickness in the oxidation time of 5.5 min is shown in Fig.2. Al concentration on the reference wafers treated with RCA cleaning was below  $5 \times 10^9$  atoms/cm<sup>2</sup> and the oxide films formed on the reference wafers were  $10 \pm 0.2$ nm in thickness. While the oxide thickness increased with Al concentration in the range of  $10^{11}$  atoms/cm<sup>2</sup> to  $10^{13}$  atoms/cm<sup>2</sup>. The oxide films in the case of Al concentration of  $1 \times 10^{11}$  atoms/cm<sup>2</sup> was approximately 5% thicker compared to the reference wafers. It was confirmed that Al impurities make oxide thickness increase in pyrogenic oxidation.

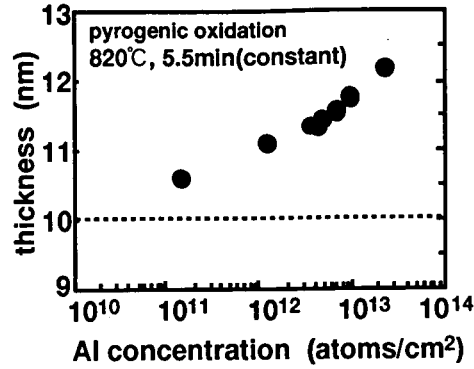


Fig.2 Influence of Al concentration on oxide thickness

#### Oxidation time vs. increased thickness

The relations between oxidation time and increased thickness on two different conditions of Al concentration are shown in Fig.3. Increased thickness ( $\Delta X$ ) shows the difference of the oxide thickness between Al contaminated wafers and the reference wafers. The increase of thickness occurred especially in the initial stage of oxidation. This tendency was observed in the both cases. The relation between oxide thickness and oxidation time is shown by the following formula, linear-parabolic model.

$$X^2 + AX = B(t + \tau) \quad (1)$$

where, X shows oxide thickness and t shows oxidation time, B is the parabolic rate constant and B/A is the linear rate constant. We calculated linear(B/A) and parabolic(B) rate constants in the case of each Al concentration by using the data of Fig.3. The linear rate constant(B/A) became bigger as Al concentration on silicon surfaces increased, while the parabolic rate constant(B) decreased(Fig.4). The oxidation of silicon wafers in this experiment was controlled by reaction of

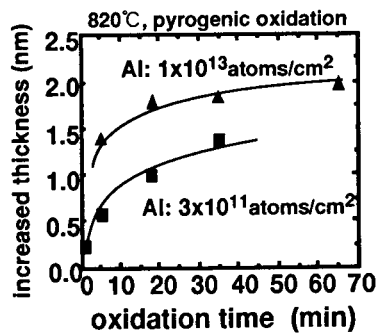


Fig.3 Increase of thickness in initial oxidation

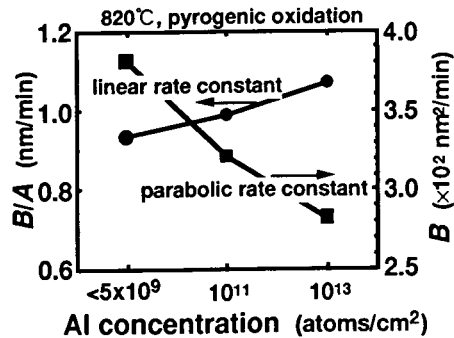


Fig. 4 Effect of Al concentration on linear and parabolic rate constants

H<sub>2</sub>O at the SiO<sub>2</sub>/Si interfaces and by adsorption of H<sub>2</sub>O at the outer surfaces of the SiO<sub>2</sub> layers rather than by diffusion of H<sub>2</sub>O in the SiO<sub>2</sub> layers. These results indicate that Al impurities accelerate oxidation rate in the initial oxidation.

#### Effect of Al impurities on thin SiO<sub>2</sub> films

The relations between oxidation time and increased thickness due to Al impurities on the outer surfaces of pre-oxide films are shown in Fig.5. Increased thickness ( $\Delta X$ ) shows the difference of the oxide thickness between Al contaminated wafers and the reference wafers on the same condition of pre-oxide thickness. It was observed that Al impurities on pre-oxide films, as well as on silicon surfaces, accelerated oxidation of silicon wafers. On the other hand we observed that almost all of Al impurities existed in the outer layer of oxide films after oxidation. These results suggest that Al impurities increase the adsorption of H<sub>2</sub>O at the outer surface of the oxide film.

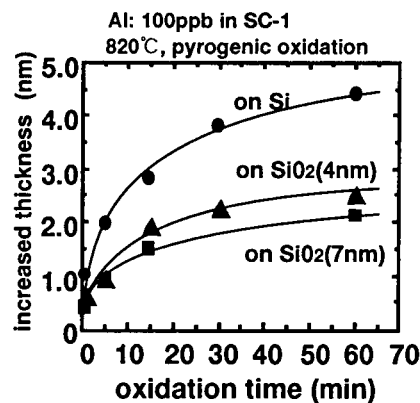


Fig. 5 Increase of thickness due to Al impurities on Si and SiO<sub>2</sub>

#### 4. Conclusion

In future ULSI devices, thinner silicon-dioxide films will be required. We studied the effect of Al contamination on oxidation rate. It was found that Al impurities accelerated oxidation of silicon wafers in the initial stage of pyrogenic oxidation controlled by reaction and adsorption of oxidants (H<sub>2</sub>O). The necessity of controlling Al contamination on silicon surfaces was definitely indicated.

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## Study of Cu particle growth with deposition condition of amorphous silicon

H.Morita, G.M.Choi\*, K.Sekine and T.Ohmi  
Department of Electronics, Faculty of Engineering  
Tohoku University  
Aza-aoba, Aramaki, Aoba-ku, Sendai 980-77, Japan

### Abstract

The purpose of this research is to reveal the growing behavior of Cu particle on amorphous silicon ( a-Si ) film, depending on deposition conditions. It was found that the characteristic of Cu adhesion depends on deposition film. It is supposed that un-activation of phosphorous in a-Si can suppress the rate of oxidation-reduction reaction. The etching rate of in-situ P-doped a-Si is smaller compared to un-doped a-Si. Therefore, we assume that it is really difficult to remove Cu impurity on un-doped a-Si than that of other surface conditions. In real mass production process, much care should be given to prevent un-doped a-Si substrate from being contaminated with Cu.

### 1. Introduction

As semiconductor devices are scaled down, ultra clean surface is essential. The metallic contamination on the Si surface can cause fatal effects on semiconductor devices. Especially, noble metals such as Cu, Ag and Au are likely to adhere to the Si surface in wet cleaning process[1,2] and can deteriorate device performance[3]. Figure-1 shows that SPM (  $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 4 : 1$  ) solution is not efficient in removing Cu impurity from amorphous silicon ( a-Si ), while it reduces Cu contamination on single crystal silicon ( c-Si ) to about  $1\text{E}+12$  atoms/cm<sup>2</sup>[4]. From this data, it is supposed that the removal efficiency of Cu impurity is strongly dependant on surface crystal structure. Our purpose is here to reveal the growing behavior of Cu particle on a-Si films on the base of crystal Si as mentioned former reseachers[5].

### 2. Experimental

Table-1 shows the deposition condition of the different kinds of substrates used in this research. They were all prepared in LPCVD system and PECVD system. First, we investigated the relationship between resistivity of in-situ P-doped a-Si and Cu contamination level. Then, the relationship between atomic H<sub>2</sub> ratio in un-doped a-Si and Cu contamination level was investigated. In these tests, wafers were dipped in 1ppm Cu ( using CuCl<sub>2</sub> ) spiked ultrapure water ( UPW ) or Cu spiked 0.5% HF solution. Dipping time was fixed at 3 minutes.

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\* Advanced Process Dept.2, Memory R & D Division, Hyundai Electronics Industries Co.,Ltd.  
P.O Box 1010, Ichon-si, Kyounggi-do, 467-701, Korea

Next, surface state of P-doped a-Si and un-doped a-Si films were investigated by SEM after contamination in Cu spiked 0.5% HF solution.

Finally, etching rate of these a-Si film after contamination of 1000ppm Cu in 0.5% HF solution were evaluated.

### 3. Results and Discussion

Figure-2 shows no dependance of Cu contamination on resistivity of P-doped a-Si, as contaminated from Cu spiked UPW solution or Cu spiked 0.5% HF solution. Figure-2 also reveals that Cu contamination on un-doped a-Si in UPW is about 1 order of magnitude higher than Cu contamination in 0.5% HF solution, regardless of H concentration in a-Si films.

Meanwhile, as can be seen from SEM images of figure-3, a-Si surfaces after contamination in 0.5% HF solution have many MIPs ( Metal Induced Pits ) irrespective of deposition condition of a-Si films. In the case of un-doped a-Si, wafer surface, except sites of pit formation, is not changed in comparison with that of in-situ P-doped a-Si.

The etching rate of a-Si film after contamination in 1000ppm Cu spiked HF solution is shown in figure-4. It is confirmed that the etching rate of un-doped a-Si is much higher than that of in-situ P-doped a-Si.

This result can be explained as follows.  $\text{Cu}^{2+}$  ion which features higher redox potential than Si, takes electrons from the substrates, reduces to become metallic Cu and deposits on the Si surface. When Si surface is contaminated by Cu impurity, the redox reaction is continued with successive the oxidation and etching of the surface in 0.5% HF solution[4]. It was reported that a-Si film has many defect sites like steps and microfacets, which are chemically unstable [6,7,8]. Also, it is a structure with short-range-order and elongated Si bonds. The difference of etching rate between c-Si and a-Si ( shown in figure-4 (2) ) is related to the structure of a-Si film as explained above. From a study of resistivity of a-Si with phosphorous doping level, it was estimated that phosphorous is inactive in in-situ P-doped a-Si. From SEM observations of figure-3, we believe that Cu particle can move all over the surface, as they proceed in UPW. Therefore, surface roughness is increasing without pits formation. Consequently, the etching rate of in-situ P-doped a-Si is reduced because the rate of oxidation-reduction reaction was suppressed by the effect of un-activated phosphorous in a-Si film.

### 4. Conclusion

The characteristic of Cu adhesion depends on the deposition film. It is supposed that un-activated phosphorous in a-Si can suppress the rate of oxidation-reduction reaction. The etching rate of in-situ P-doped a-Si is low compared to un-doped a-Si. Cu particle on P-doped a-Si can move all over the surface in 0.5% HF solution. Therefore, we assume that it is really difficult to remove Cu impurity from un-doped a-Si. In real mass production process, much care should be given to prevent un-doped a-Si substrate from being contaminated with Cu.

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**Table-1. Deposition condition of a-Si film used in our study**

| in-situ P-doped a-Si                                                 | un-doped a-Si                                                                                |
|----------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| 1.SiH <sub>4</sub> -base P-doped a-Si (550 C)<br>8.5E+3 Ω ·cm(LPCVD) | 4.SiH <sub>4</sub> base un-doped a-Si (550 C)<br>H <sub>2</sub> atomic % : below 0.5%(LPCVD) |
| 2.SiH <sub>4</sub> base P-doped a-Si (550 C)<br>1.5E+3 Ω ·cm(LPCVD)  | 5.SiH <sub>4</sub> base un-doped a-Si (250 C)<br>H <sub>2</sub> atomic % : 7% (PECVD)        |
| 3.SiH <sub>4</sub> base P-doped a-Si (550 C)<br>1.5E+2 Ω ·cm(LPCVD)  | 6.SiH <sub>4</sub> base un-doped a-Si (250 C)<br>H <sub>2</sub> atomic % : 13 % (PECVD)      |
|                                                                      | 7.SiH <sub>4</sub> base un-doped a-Si (250 C)<br>H <sub>2</sub> atomic % : 20 % (PECVD)      |

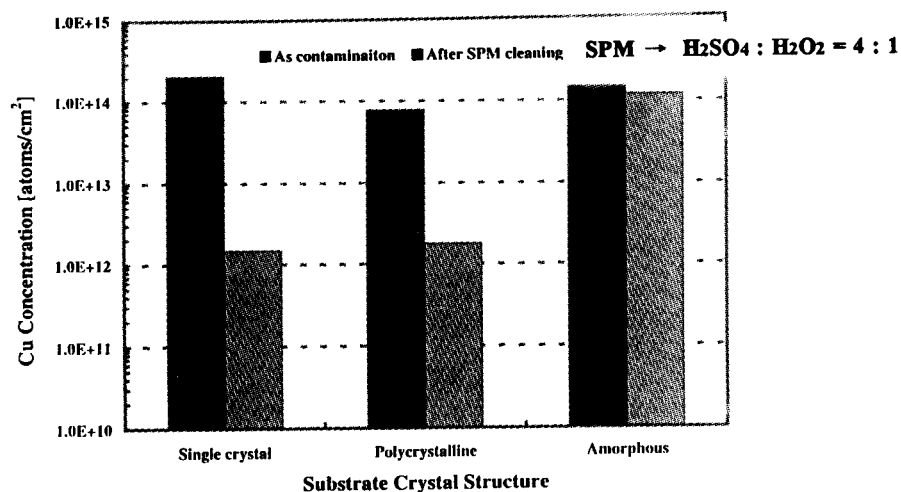


**Figure-1 SPM cleaning efficiency of Cu impurity on Si surface condition**

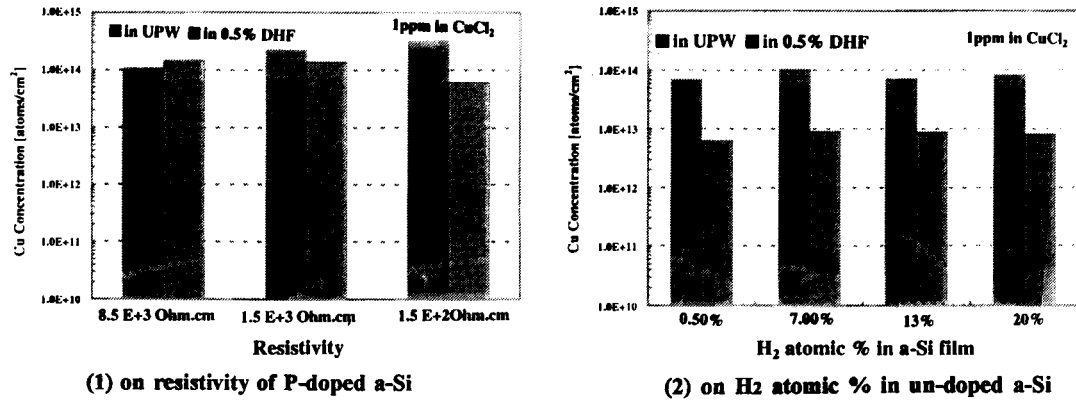


Figure-2 the amount of Cu contamination dependence



P-doped a-Si



un-doped a-Si

Figure-3 SEM image of a-Si surface after Cu contamination in 0.5% HF solution

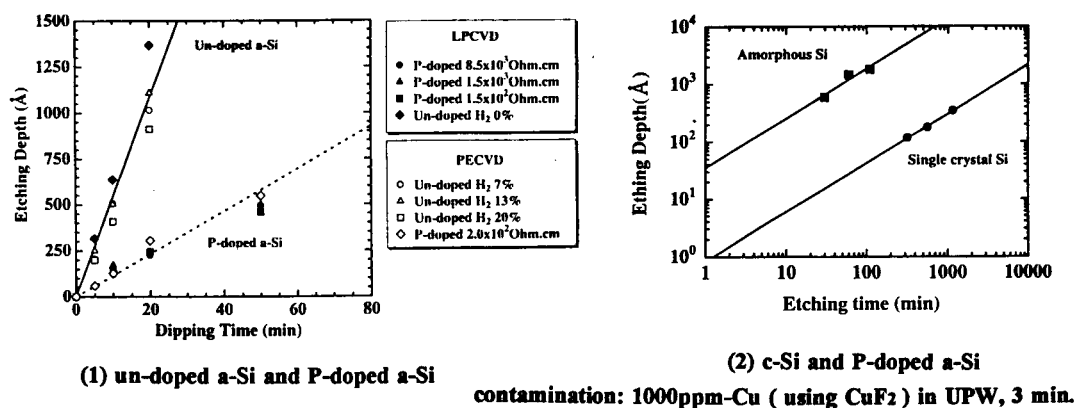


Figure-4 Etching rate of Si substrates in 0.5% HF solution

## EFFECT OF Fe CONTAMINATION ON 5 nm OXIDE - POLY SILICON GATE STRUCTURES

P.W. Mertens, S. De Gendt, M. Depas, K. Kenis, A. Opdebeeck, P. Snee<sup>a</sup>, D. Gräf<sup>b</sup>, G. Brown and M.M. Heyns

Imec, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>a</sup> on leave from Motorola, East Kilbriht Scotland

<sup>b</sup> Wacker Siltronic, Burghausen Germany

### 1. INTRODUCTION

The study of Fe contamination has received considerable attention. Fe contamination present on the wafer surface prior to the gate oxidation has been correlated with GOI degradation [1, 2]. The results reported in the literature have been obtained, however, on oxides with a thickness in excess of 10nm. The distribution of the Fe over the entire wafer structure is a key parameter that can be expected to contribute to a better characterisation of this degradation. The redistribution of Fe upon oxidation is relatively complex. Its relative distribution shifts by subtle changes in the treatment [3]. Metallic contaminants have been reported to affect the growth of poly silicon. Localised defects in the poly silicon layer have been observed when coarse metallic contamination was applied *onto* the gate oxide [4]. It has been reported that in case of Fe contamination deposited *prior to* gate oxidation, the concentration of Fe contamination measured with VPD-DSE-TXRF after gate oxidation, correlates with the thickness increase of the poly silicon layer [3].

The present study focuses on the effect of Fe contamination prior to gate oxidation on the GOI of 5nm oxides. Moreover the redistribution of the Fe contamination upon the growth of 5nm oxides is examined. The effect of the Fe contamination on the poly silicon growth is investigated in further detail. Furthermore, the impact of different furnace ambient during temperature ramp-up and stabilisation is evaluated.

### 2. EXPERIMENTAL CONDITIONS

Controlled Fe contamination was applied to wafers at different concentrations, prior to gate oxidation, by a 10 min immersion in selectively spiked SC1 or d-HCl. The target levels were either blank  $10^{10}$  or  $10^{12}$  Fe at./cm<sup>2</sup>. Table I shows the actual concentration determined with VPD-DSE-TXRF directly after the contamination. In all cases, the concentration of the other elements was found to be low, e.g. in case of Ca:  $< 2 \times 10^{10}$  at./cm<sup>2</sup>. 5 nm oxides were grown at 800°C in 100% O<sub>2</sub> ambient in approximately 30 min. Two different types of furnace ambient were used during temperature ramp-up and stabilizatoin. In one case 100 % N<sub>2</sub> was used, in the other case 5% O<sub>2</sub> + 95% N<sub>2</sub>.

Table I, Fe surface concentration measured directly after selective contamination, using VPD-DSE-TXRF.

| target conc.<br>( $10^{10}$ at./cm <sup>2</sup> ) | conc d-HCl<br>( $10^{10}$ at./cm <sup>2</sup> ) | conc. SC1<br>( $10^{10}$ at./cm <sup>2</sup> ) |
|---------------------------------------------------|-------------------------------------------------|------------------------------------------------|
| blank                                             | 0.17                                            | 0.37                                           |
| 10                                                | 20.5                                            | 9.5                                            |
| 100                                               | 79                                              | 117                                            |

The redistribution of the Fe contamination was evaluated. VPD-DSE-TXRF was used to measure the amount of Fe in or on the oxide layer. SPV measurements

were used to determine the concentration in the bulk of the wafer. The bulk concentrations were integrated over a half-wafer thickness in order to compare with the surface component.

After the gate oxidation, on a number of wafers, LPCVD poly silicon was deposited with a nominal thickness of 500 nm. The poly silicon surface topography was evaluated with light scattering using a Censor ANS100. The "haze" signal, i.e. the low spatial frequency component of the lightscattering map was used to characterize the roughness. In addition tapping mode AFM measurements were performed on the poly silicon surface. The RMS value obtained in scan areas of 5 by 5  $\mu\text{m}$  was extracted. Gate oxide integrity capacitor structures are prepared on different wafers. Capacitors with an area of 16  $\text{mm}^2$  were subjected to a ramped voltage stress from which the dielectric breakdown field was determined. The intrinsic Ebd yield was defined as the fraction of capacitors that survived a field stress of 12 MV/cm.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

#### 3.1. Fe-redistribution

Virtually independent of the ramp-up ambient, most of the Fe is found "in" the oxide layer. Only a smaller fraction is found in the bulk of the silicon wafer (Fig.1).

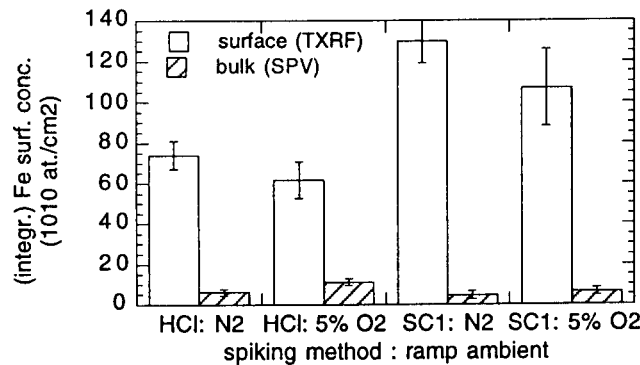


Fig. 1. Fe redistribution during 5nm oxide growth in 100% O<sub>2</sub> at 800°C on p-Cz wafers. The concentration "in" the oxide is measured with VPD-DSE-TXRF. The bulk concentration is determined with SPV and then integrated over half the wafer thickness.

This effect of the ramp-up and stabilization ambient on the Fe redistribution is distinctly different from that reported for the growth of 15nm gate oxides in 100% O<sub>2</sub> at 900°C, particularly in the case of inert ramp-up [3]. For the 15nm oxides a ramp-up in inert ambient resulted in a major part of the Fe to migrate into the bulk of the wafer, while for a ramp-up in 5% O<sub>2</sub> the major part of the Fe ended up "in" the oxide.

The presence of oxygen in the ambient in an early stage of the oxidation process results in a larger fraction of the Fe to be incorporated in the oxide layer. For the 15 nm oxides the oxidation temperature is 900°C. For 5nm the oxidation is performed at 800°C thus effectively suppressing the Fe migration into the bulk that could take place at temperatures in excess of 800°C. In addition the oxidation time for the 5 nm layers was shorter than for the 15nm layers. Since the diffusivity and solubility of Fe in Si increase very strongly with increasing temperature it is obvious that more Fe incorporation in the Si is to be expected than for the inert ramped 5nm oxides.

### 3.2. Poly silicon roughness

Elevated haze values are obtained when an oxidising ramp-up ambient was used for the gate oxidation process (Fig. 2). When the oxidation was done after an inert temperature ramp-up, the effect of the initial Fe contamination on the poly silicon growth is negligible. AFM measurements confirm the existence of roughness in case of  $O_2$  in the ramp-up ambient, as is shown in Fig. 3.

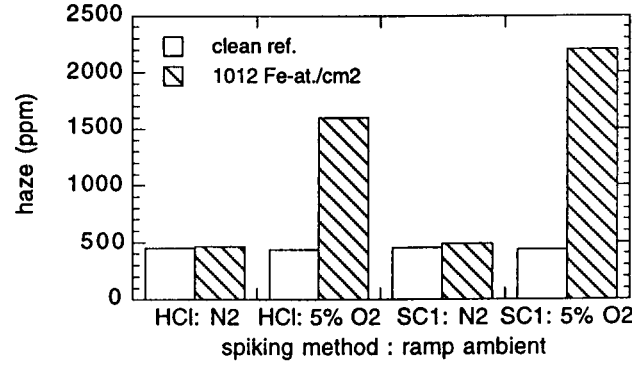


Fig. 2. The "haze" of the poly silicon surface shows that poly silicon growth is primarily disturbed by  $10^{12}$  Fe-at./cm<sup>2</sup> present before gate oxidation if the ramp-up for the oxidation contains  $O_2$ .

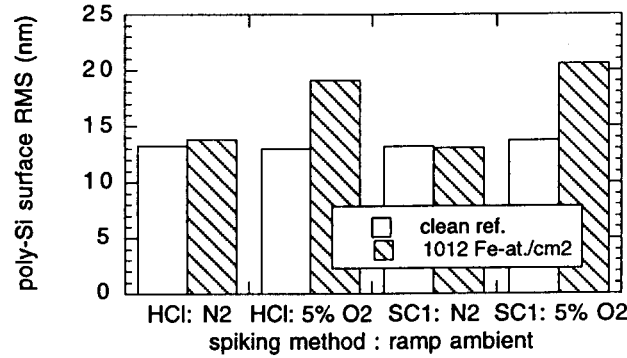


Fig. 3. RMS values of the cantilever tapping AFM measurements of the poly silicon surface in an area of  $5\ \mu\text{m}$  by  $5\ \mu\text{m}$ .

These results are consistent with earlier studies that reported anomalous poly silicon growth in similar circumstances [3]. The anomalous poly silicon growth is believed to be due to a catalysing effect of Fe on the LPCVD poly silicon process. The results presented here provide evidence that in case of ramp-up in 5%  $O_2$ , at least a significant fraction of the Fe is present at the very top of the gate oxide film, in agreement with earlier findings [5]. While it is not the case if the ramp-up was done in inert ambient.

### 3.3. GOI

The intrinsic Ebd yield did not show a systematic difference depending on wafer type nor on the solution used for contamination nor on the ramp-up ambient. A clear general dependence on the Fe concentration measured on the wafers prior to gate oxidation was observed (Fig 4).

It is interesting to consider the GOI results with regard to the results obtained for the poly silicon roughness. Both the Ebd yield and the Fe-induced surface

roughness of the gate poly silicon contamination decrease with decreasing partial pressure of  $O_2$ . Consequently, the Ebd degradation caused by Fe contamination cannot be attributed to the distortion it causes in the poly silicon structure.

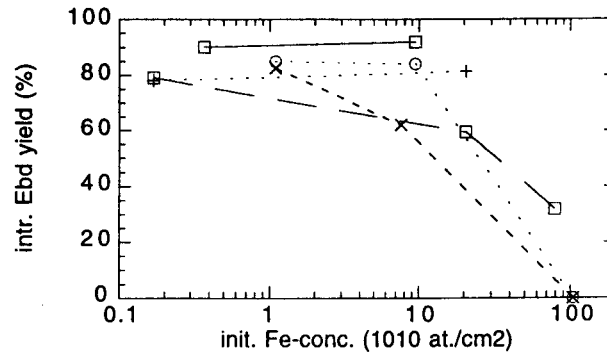


Fig. 4. Intrinsic ramped voltage Ebd yield for capacitors made with 5nm gate oxide grown on wafers that were contaminated with different concentrations of Fe and with different oxidation ramp-up ambient ( $A=16 \text{ mm}^2$ ).

#### 4. CONCLUSIONS

For the 5nm gate oxides grown at  $800^\circ\text{C}$ , virtually independent of the ramp-up ambient, most of the Fe is found "in" the oxide layer. Only a smaller fraction is found in the bulk of the silicon wafer. If the ambient prior to the oxidation step contains 5%  $O_2$  the presence of Fe results in a significant increase of the poly roughness. If the ramp-up is performed in 100 %  $N_2$  no additional poly silicon surface roughness is generated by the Fe. Because of the latter observation it may be concluded that although the overall amount of Fe "in" the oxide is the same for the two ramp-up ambients, in case of the ramp-up with 5% $O_2$  a much larger fraction of the Fe is expected to present at the very top surface of the gate oxide. The GOI degradation correlates with the Fe concentration irrespective of the ramp-up ambient. In the present study the threshold value for which the Fe contamination becomes the yield limiting factor lies in the range of  $10^{10}$  to  $10^{11}$  at./cm $^2$ . The GOI degradation does not correlate with changes in the poly silicon growth.

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## **Determination of PPB Anions in 49% Ultrapure Hydrofluoric Acid**

Jian-Ge Chen and ManLi Wu

Olin Research Center, 350 Knotter Drive, Cheshire, Connecticut 06117, USA

### **1. INTRODUCTION**

The purity of process chemicals plays an important role on device reliability in semiconductor production [1]. During the past years there has been a steady increase in the scale of integration for semiconductor devices. The trends lead to extreme requirements for high purity process chemicals and the need for monitoring trace levels of ionic contaminants.

PPB-level cationic contaminants in acids can be analyzed by ICP/MS [2]; however, PPB-level determination of anionic contaminants has been a difficult analytical challenge due to the presence of high concentration of anion matrix. In order to eliminate the matrix interference, samples of concentrated acids are often diluted, digested, or pretreated with off-line cartridges. The disadvantages are that dilution reduces the sensitivity of detection, and digestion or the use of cartridges can often introduce contaminants.

Ion chromatography (IC) has been applied successfully to the determination of ionic contaminants in a wide range of matrices [3]. The detection limits of common anions in strong acids have been reported to range from 100 ppb to 500 ppb. In this work we have developed a sensitive and reliable procedure for the analysis of chloride, sulfate, phosphate, and nitrate in concentrated hydrofluoric acid at low ppb level. This procedure employs a two-dimensional ion chromatographic system; one IC is used for pre-separating anionic contaminants from their matrix prior to the analytical separation by the other IC. This allows for the elimination of matrix and therefore better sensitivity for analyzing ppb levels of anionic contaminants in 49% HF.

In this work we have developed a two-dimensional ion chromatographic procedure for the analysis of chloride, sulfate, phosphate, and nitrate in concentrated hydrofluoric acid at 10 ppb level.

### **2. EXPERIMENTAL**

**Two-Dimensional Ion Chromatography** Figure 1 shows the block diagram of the instrumental setup. The approach here is to reduce the matrix, F<sup>-</sup> ion, by introducing the sample at percent levels directly onto the first IC system (preseparation system) where the anions of interest are separated from HF through this first separation. The effluent from the first IC that contains anions of interest and some F<sup>-</sup> is then fractionated using an automated switching valve and introduced onto the second IC (analytical separation system) for analysis of anions.

This approach significantly reduces the F<sup>-</sup> concentration and therefore allows for the analysis of anions with minimum matrix interference. This is clearly demonstrated in Figure 2. The top chromatogram obtained from the first IC shows the F<sup>-</sup> matrix severely interferes the anions of interest. With the use of the "heart-cutting" technique, a portion of the effluent which contained the anions as well as some part of F<sup>-</sup> were fractionated and retained on a collection column as is shown in Figure 1. The collected fraction was then flushed onto the second IC for the separation of anions as is shown in the bottom chromatogram obtained

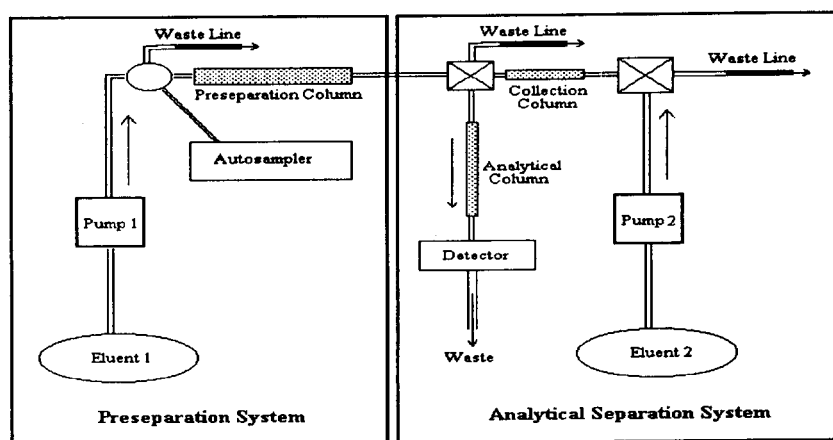


Figure 1. The block diagram of two-dimensional ion chromatography for ppb anions in 49% Hydrofluoric Acid

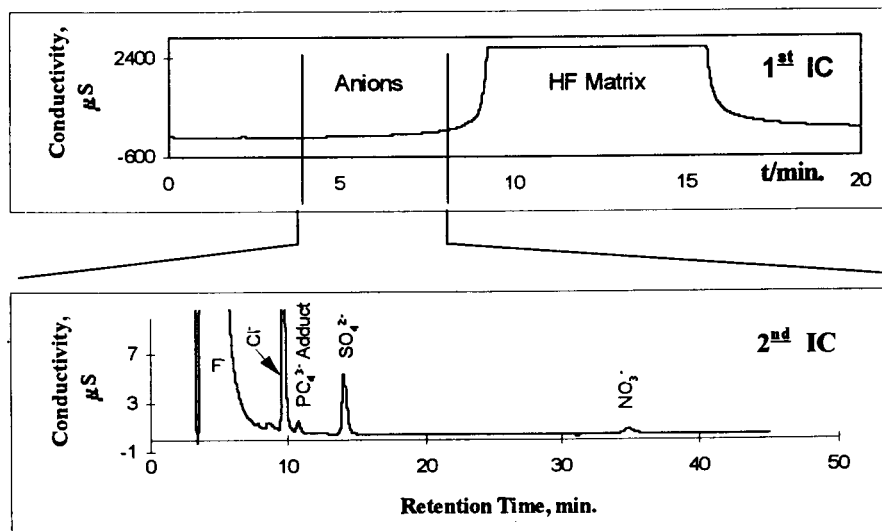


Figure 2. The separation of anionic contaminants in HF by first IC and second IC.

from the second IC. Since F<sup>-</sup> was significantly reduced from the first IC, the resolution of anions of interest from the matrix peak was achieved. This two-dimensional IC approach extends the separation power beyond one single system. It is also noted that in the concentrated HF matrix a phosphate adduct was detected rather than the phosphate ion itself.

**Optimization of Fractionation Interval** The fractionation time which is the total time that the effluent from the first IC is fractionated into the second IC is very critical to the reliability and the sensitivity of the analysis. The beginning of the fractionation was determined using a mixture of anion standards. The fractionation times ranging from 1.5 minutes to 5 minutes were studied and it was found that when the fractionation time extended beyond 3.5 minutes the improved sensitivity was sacrificed by the increase of F<sup>-</sup>. We therefore chose 3.5 minutes fractionation time for this study.

**Chloride Contamination** For trace analysis of chloride it is critical to minimize the contaminant that is commonly present in the air and glassware used for sample preparation. After a thorough cleaning and rinsing with ultrapure Mill-Q water, the chloride contaminant was still observed. The source of the contamination was studied. In that study HF was found to leach chloride out of the sample containers, flasks, and vials. The plasticware was pretreated prior to use. The results showed minimum chloride contamination from the plasticware.

**Influence of F<sup>-</sup> Concentration on Anion Analysis** Direct injection of concentrated HF (49%) can minimize the need for sample handling and improve sensitivity, however, it can overload the system hence decrease the resolution of HF from other anions. On the other hand, lower % HF injections might not give the desirable sensitivity for the analysis and require dilution of samples. In order to determine the optimum HF concentrations for the analysis, we have tested 49%, 24.5%, 12.25%, and 6.13% HF injections. It was found that the prolonged injections of 49% HF solutions caused significant bleeding of contaminants from the column and the injection vials as well as severe column damage. With lower concentrations of HF injected the detection limits of anionic contaminants, as are shown in Table I, were found to be adequate. The 24.5% injection provided the best detection limits and therefore was chosen for this study.

**Table I.** Detection limits of anions in 49% HF

| % HF<br>Injections | Detection Limits of Quantitation in 49% HF,<br>ppb |                               |                               |                              |
|--------------------|----------------------------------------------------|-------------------------------|-------------------------------|------------------------------|
|                    | Cl <sup>-</sup>                                    | SO <sub>4</sub> <sup>2-</sup> | PO <sub>4</sub> <sup>3-</sup> | NO <sub>3</sub> <sup>-</sup> |
| 24.5               | 2                                                  | 2                             | 10                            | 5                            |
| 12.25              | 5                                                  | 5                             | 20                            | 10                           |
| 6.13               | 10                                                 | 10                            | 30                            | 20                           |

### 3. RESULTS AND DISCUSSIONS

Once the optimized experimental conditions were defined, five 49% HF samples

from three different suppliers were analyzed and the results are listed in Table II. The results are the average of triplicate analyses. Average relative standard deviations of the analyses in all cases are below 10% and the day-to-day reproducibility of the method has been satisfactory. The anion concentrations in HF between suppliers appear to be significantly different. The HF sample from supplier B are found to contain much higher concentrations of chloride and nitrate.

**Table II.** Anionic contaminants in concentrated HF (49%)

| 49% HF, Lot#                 | [Cl <sup>-</sup> ],<br>ppb | [SO <sub>4</sub> <sup>2-</sup> ],<br>ppb | [PO <sub>4</sub> <sup>3-</sup> ],<br>ppb | [NO <sub>3</sub> <sup>-</sup> ],<br>ppb |
|------------------------------|----------------------------|------------------------------------------|------------------------------------------|-----------------------------------------|
| Supplier A <sup>a</sup> , #1 | 31                         | 34                                       | < 10 <sup>b</sup>                        | 15                                      |
| Supplier A, #2               | 31                         | 41                                       | 22                                       | 40                                      |
| Supplier B <sup>c</sup> , #1 | 90                         | 7                                        | < 10 <sup>b</sup>                        | > 250 <sup>d</sup>                      |
| Supplier B, #2               | > 250 <sup>d</sup>         | 13                                       | < 10 <sup>b</sup>                        | > 250 <sup>d</sup>                      |
| Supplier C <sup>c</sup> , #1 | 31                         | 30                                       | 27                                       | 10                                      |

<sup>a</sup> Supplier A is an overseas producer.

<sup>b</sup> Below the detection limit of quantitation

<sup>c</sup> Suppliers B and C are domestic producers.

<sup>d</sup> Too high a concentration to be analyzed by low standard spikes used in the analysis

#### 4. CONCLUSIONS

A sensitive and reliable procedure is demonstrated for the analysis of trace anion contaminants including chloride, sulfate, phosphate, and nitrate in ultrapure hydrofluoric acid. The technique allows for the direct injection of concentrated HF (24.5%) with minimum sample handling, allowing for lower detectability and better reproducibility for anion contaminants analysis. The detection limits of quantitation are 2 ppb for chloride and sulfate, 5 ppb for nitrate, and 10 ppb for phosphate in 49% HF. The spike recoveries at the 20 ppb level for chloride and sulfate and 10 ppb level for phosphate and nitrate are  $106 \pm 9.3\%$  (r.s.d.),  $107 \pm 11.2\%$ ,  $90.2 \pm 9.6\%$ , and  $121 \pm 1.3\%$ , respectively.

#### Acknowledgments

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## **VPD-Collecting-Efficiency-, Exchange Reaction- and Adsorption / Desorption-Studies on Silicon Surfaces Performed with TXRF and Radiochemical Analysis**

**G. Mainka, S. Metz, G. Kilian, S. Hohmann, A. Fester and B.O. Kolbesen\***

### **1. INTRODUCTION**

Radiochemical analysis is a powerful tool to investigate contamination and behaviour of metals on silicon surfaces as supplement to the standard investigations performed with TXRF. Radiochemistry e.g. for Fe shows contamination detection limits of down to  $E7 \text{ atoms/cm}^2$  and using  $\gamma$ -emitters the method is independent from the silicon surface conditions (roughness) [1].

VPD (Vapour Phase Decomposition) is one method to improve the TXRF detection limits from  $E10 \text{ atoms/cm}^2$  to the range of  $E8 \text{ atoms/cm}^2$  [2]. A problem of VPD is the collecting efficiency which depends on the type of metals and their chemistry and concentration on the surface. Part of this work deals with measuring these collecting efficiencies under various preparation conditions and to improve the results obtained with the VPD-TXRF method.

$\alpha$ -particle induced leakage current generation is a well known failure mode and reliability problem of DRAMs ( Dynamic Random Access Memories ). The sources of  $\alpha$ -particle emission are natural radionuclides like uranium and thorium which may be contained in trace amounts in packaging materials and chemicals used in device manufacturing. Low level  $\alpha/\beta$ -measurements were performed to investigate contamination mechanisms under various contamination conditions and improve cleaning procedures concerning metals emitting  $\alpha$ -particles.

### **2. EXPERIMENTAL**

100/150 mm silicon wafers (p-type CZ), orientation (100) and resistivity 0,67-1,33  $\Omega\text{cm}$  were (cut into quarters for U- and Th-studies) subsequently RCA cleaned and dipped in aqueous solutions containing metal contaminations in the ppb range ( 1-1000) and pH range from 1-10. For the exchange reactions and VPD experiments the wafers were first contaminated with Fe under SC1 conditions in the range of  $E12 \text{ atoms/cm}^2$ . For the exchange investigations the wafers were then immersed in a radionuclide solution (10  $\mu\text{Ci}$  Fe-59, Fe concentration  $< 100\text{ppt}$ , pH 1). VPD experiments were carried out with standard DSE ( Droplet Surface Etching ) solution  $\text{HF}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$  (100  $\mu\text{l}$ /350  $\mu\text{l}$ /9.55 ml). For standard TXRF measurements the DSE droplet was dried by using an IR-lamp or for comparison in vacuum without heating. For the  $\gamma$ -measurement the droplet was transferred onto an inactive Si-wafer piece and dried as above. In some special experiments the droplet was transferred into a cap. 20  $\mu\text{l}$  of this solution were taken out, deposited on a Si-wafer or a quartz substrate and dried as above.

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\* Johann - Wolfgang - Goethe University  
Institute of Inorganic Chemistry / Analytical Chemistry  
Marie Curie Str. 11, D-60439 Frankfurt/Main, Germany

Radiochemical analysis were performed with  $\alpha$ -particle 10 channel low-level proportional counter LB770 from BERTHOLD and CANBERRA Genie PC  $\gamma$ -spectroscopy system with GeLi-detector. TXRF spectra were taken with ATOMIKA TXRF 8010 and in some special experiments ATOMIKA EXTRA IIA spectrometers.

### 3. RESULTS

Studies of exchange reactions performed with Fe showed that the reaction is very fast (a few seconds). The exchange is superposed by desorption of Fe from the surface (fig. 1 and 2). After longer immersion in the radionuclide solution (10-20 min) the Fe concentration reaches a level of  $10^{12}$  atoms/cm<sup>2</sup> which corresponds to an equilibrium between Fe on the Si-surface and in the solution.

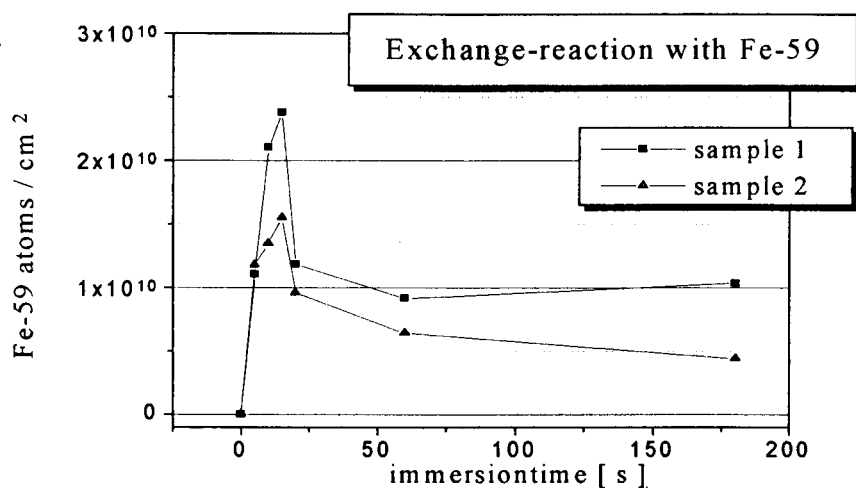


Figure 1  $\gamma$ -measurement of the exchange reaction

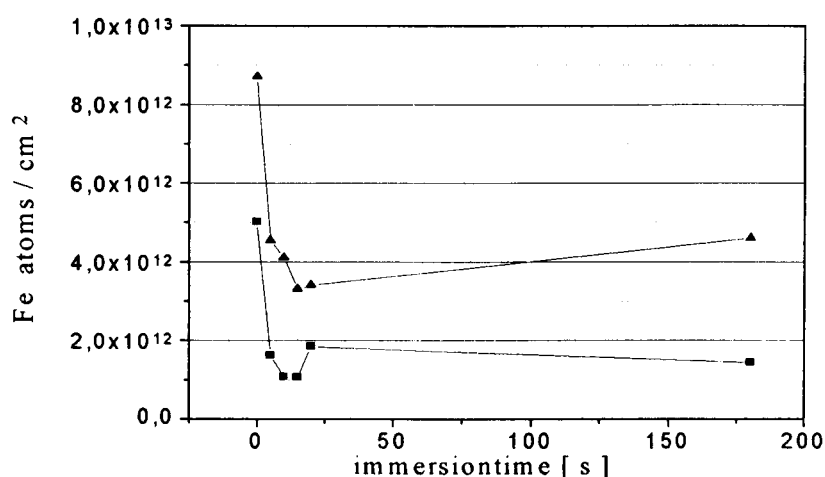


Figure 2 TXRF-measurement of the exchange reaction

Recently performed VPD experiments with Fe showed significant differences of the collecting efficiencies ( CE ) for TXRF and radiochemistry measurements of the DSE residues (fig 3a). The  $\gamma$ -measurements provided obviously CE values in the 80% range whereas by standard VPD-TXRF typical CE values around 50% were found. Since the VPD procedure in both cases was the same, the discrepancy was supposed to be caused by the different measurement principles of TXRF and  $\gamma$ -spectroscopy. Whereas thickness and shape of the DSE residue do not influence  $\gamma$ -spectroscopy, they show a strong effect on TXRF measurements.

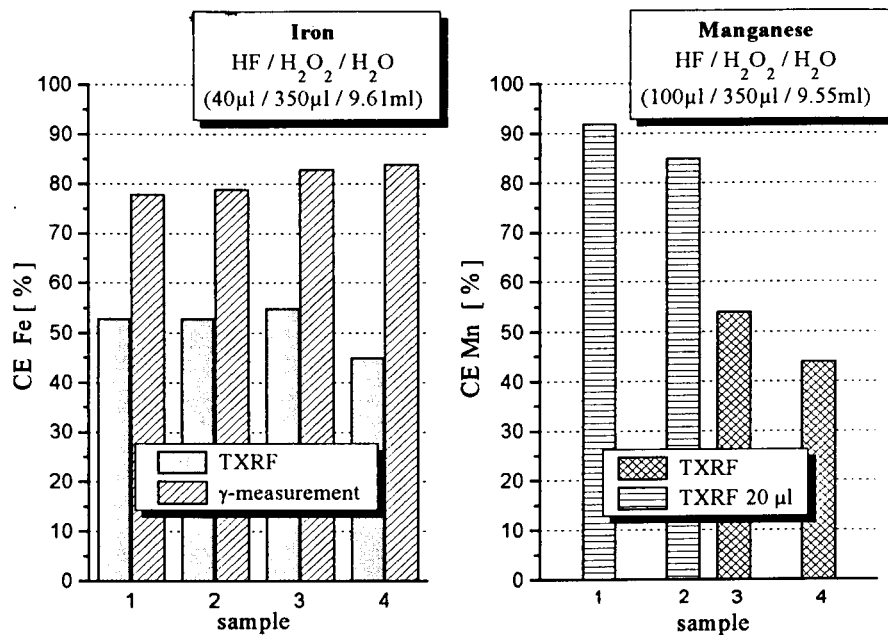


Figure 3a Collecting efficiencies for Fe

3b Collecting efficiencies for Mn

Therefore we examined the DSE droplet residues by scanning electron microscopy ( SEM ). Fig. 4 displays a DSE droplet residue of a manganese contaminated wafer. It shows a thick salt crust at the outer rim of the initial droplet, indicating that this residue does not meet satisfactorily the conditions for TXRF measurements and, hence, gives rise to too low CE values. Drying the DSE droplet in vacuum produces more uniform and smoother residues.

In some special experiments with Mn contaminated wafers the DSE droplet was transferred into a cap. 20 µl of this solution were deposited on a quartz carrier, dried and measured by TXRF EXTRA II. The same procedure was carried out with a Si wafer, the residue measured by TXRF 8010. The CE values obtained by TXRF EXTRA II and TXRF 8010 agreed very well, exceeded 80% ( Fig. 3b ) and showed good accordance to the  $\gamma$ -measurements. For comparison the low CE values of the standard VPD-TXRF procedure are plotted in Fig. 3b also.

This demonstrates that unsuitable DSE droplet residues result in too low CE values and, hence, significant errors and scattering data in the standard VPD-TXRF procedure.

Moreover in the case of Mn the VPD collecting efficiency depends strongly on the starting concentration ( $E12$  or  $E13$  atoms/cm<sup>2</sup>) and the contamination conditions (acidic or SC1). The fact that Mn out of SC1 solution deposits rather as MnO<sub>2</sub> on the silicon surface is the reason for observed poor collecting efficiencies. By performing standard VPD treatment it is difficult to get MnO<sub>2</sub> in solution.



Figure 4 SEM picture of the residue of a VPD-droplet (Mn, IR-lamp, 200 µl)

For U and Th a dependence of the surface contamination from the concentration of the contamination solution and the pH as well as the immersion time has been found. The highest U-238 concentration on the silicon surface was  $1E16$  atoms/cm<sup>2</sup> (contamination solution: 10ppm U-238, pH 9), for Th-232 the maximum surface contamination was  $3E15$  atoms/cm<sup>2</sup> (contamination solution: 100ppm Th-232, pH 1,5). A monolayer of U and Th corresponds to  $4E14$  atoms/cm<sup>2</sup>. U-238 deposits as film and particle in an inhomogenous way while Th-232 deposits as a relatively homogeneous film on the silicon surface. The RCA cleaning sequence (SC1, HF-Dip, SC2) removes U-238 and Th-232 completely from the silicon surface. A cleaning treatment with SC1- or SC2-solutions shows only a partial cleaning effect (50%) for Th-232. This behaviour can be explained by the different chemistry of U and Th in aqueous solutions ( $UO_2^{2+}$  and  $Th^{4+}$ ) with very complex hydrolysis reactions.

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## IMPACT OF THE WAFER PRE-TREATMENT ON THE COLLECTION EFFICIENCY AFTER VPD

I. Rink, R. Girisch - Philips Semiconductors, Gerstweg 2, 6534 AE Nijmegen, The Netherlands

### 1. INTRODUCTION

For some analytical methods it is necessary (AAS, ICP-MS) or supplementary (TXRF) to collect the contamination of a Si-wafer surface or of a SiO<sub>2</sub>-layer in a solution in order to evaluate contamination on the surface or at and in the SiO<sub>2</sub>-layer. By means of VPD (Vapour Phase Decomposition <sup>[1,2]</sup>) the native or otherwise formed oxide is dissolved and the contamination is collected by scanning the surface with a scanning solution (usually DI-water, DHF, DHF/H<sub>2</sub>O<sub>2</sub> or other solutions). Initially, the collection efficiency of this method was determined using Si-wafers intentionally contaminated with some elements by means of spin-coating <sup>[1,2,7]</sup>. Besides the scanning-chemistry <sup>[3,4,5]</sup>, the physico-chemical condition of contamination (due to the process the wafers were treated with before analysis) strongly influences the collection efficiency. This dependency of the collection efficiency on the technological process will be illustrated by means of some examples as found in practical routine measurements.

### 2. EXPERIMENTAL

Since we started to analyse contamination by means of TXRF and VPD-TXRF we have been confronted with the whole spectrum of technological processes as mentioned by R.S. Hockett <sup>[6]</sup>. We found that the different processes cause typical contamination as generally known and also we found that the collection efficiency is more or less typical of the sort of pre-treatment.

We used a horizontal VPD-reactor with 50% HF (ultra-pure). The VPD-procedure was as follows: the oxide was dissolved until the silicon surface became hydrophobic, subsequently 50µl ultra-pure DI-water was dropped on the wafer-surface and stayed for 5min in the VPD-reactor. Next, the wafer-surface was scanned by hand or automatically (PAD-SCAN) using an edge-exclusion of 3 or 5mm. Finally, the droplet with the collected contamination was dried on a hot-plate at about 50 °C. For the TXRF-analyses an Atomika TXRF 8010 was used with a sealed Mo-tube and an angle of incident of 1.3 mrad.

Out of a wide field of analyses only those example-processes were selected which supplied a measurable concentration for direct TXRF.

These processes are:

- A spin-coating of RCA-cleaned wafers with a cocktail of Fe, Cu, Zn, As
- B A + SC1 - process (NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O)
- C dipping in HF, spiked with contaminants

- D C + SC1 - process
- E dipping in the SC1- bath, spiked with contaminants
- F transport through a plasma-etch machine, which was obviously contaminated
- G simulation of a dry resist-strip (ozone) on Si
- H simulation of a dry resist strip (ozone) on SiO<sub>2</sub> (85nm)
- I sputter-etching before metal-deposition on SiO<sub>2</sub> (500nm)
- J Ar-implantation at 40 keV on SiO<sub>2</sub> (630 nm)
- K Ar-implantation at 40 keV on SiO<sub>2</sub> (27nm)

### 3. RESULTS AND DISCUSSION

The following abbreviations were introduced:

- $Q_D$  (at/cm<sup>2</sup>) - average value of contamination on the surface got from direct TXRF-analyses (TXRF-D) before VPD
- $Q_R$  (at/cm<sup>2</sup>) - concentration, determined from analysis of the droplet-residue (TXRF-R)
- $Q_{Si}$  (at/cm<sup>2</sup>) - average concentration on the Si-surface measured after VPD (TXRF-Si) exclusive of the contamination of the droplet-residue

Collection efficiency CE is defined as:

$$CE = \frac{Q_R}{Q_D} \times 100\%$$

Including the remaining part of contamination on the Si-surface  $Q_{Si}$  a “remnant ratio” RR has been defined as:

$$RR = \frac{Q_{Si}}{Q_D} \times 100\%$$

All direct TXRF measurements on scanned (TXRF-Si) as well as on non scanned surfaces (TXRF-D) were referred to a film-type Ni-standard achieved by means of spin-coating, whereas the droplet-residue measurements (TXRF-R) were referred to a droplet Ni-standard. This calibration procedure was followed because of a calibration difference that was observed between film-type and particle-type contamination. From other contaminants the elements Cu, Fe, Zn and As were taken as examples as shown in Figs 1 to 4.

Figure 1 shows the collection efficiency (CE) and the residual ratio (RR) for Cu. As generally known Cu can easily plate on the Si-surface because of its higher electronegativity (1.9eV) compared with Si (1.8eV). Therefore, it generally shows a poor collection efficiency. However, clear differences between the variants were found. For the spin-coated wafers (A) CE was about 30%, for the other wet processes (C, E) it was about 20%. In variant F, an environmental contamination of the silicon surface Cu was almost not to collect. The best CE by about 50% was found for the oxide layer contaminated at its surface (I). Such a high collection efficiency for Cu is generally observed by us in case of “thick” oxide layers. The

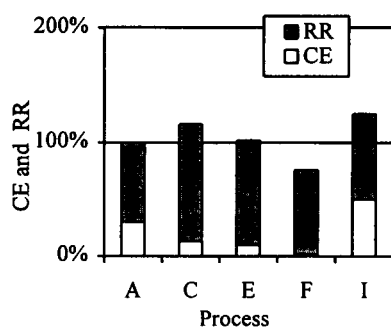


Figure 1. CE and RR for Cu.

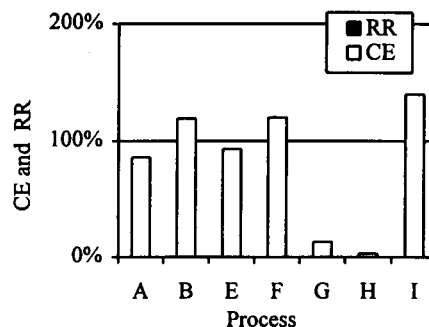


Figure 2. CE and RR for Fe.

non-collected part of Cu was detected on the scanned Si for all variants mostly resulting in (CE+RR)-values of approx.100%.

Fe (Figure 2) was almost completely collected for A, B, E and F. For the variants G and H a very poor CE was found and no Fe was found on the scanned surfaces either. We suppose, the ozone-strip process (G, H) formed Fe-compounds which either were volatile themselves or became volatile due to the subsequent VPD-scanning-drying process. For variant I more Fe was found after VPD ( $Q_R$ ) than before VPD ( $Q_D$ ). This can be explained by the depth-distribution of Fe in the 500nm thick oxide layer.

Zn (Figure 3) showed a good CE in all variants. Also no residual Zn was observed at the scanned surface ( $RR \approx 0$ ). The high CE-value for variant D is not yet understood.

Finally, the contaminant As is presented in Figure 4. In variant A the arsenic was spin-coated on the Si-surface as As-nitrate and a good CE of about 80% was determined. For variant F (contamination due to transport in a plasma-etcher) an apparently high CE was found (>100%). This effect could be explained by the before mentioned calibration inconsistency (film-type versus particle-type). This may result in  $Q_D$  lower than the actual value in case of particle-type contamination. The variants J and K refer to Ar ion-implantation in the oxide

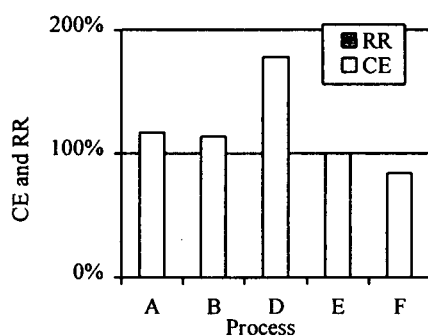


Figure 3. CE and RR for Zn.

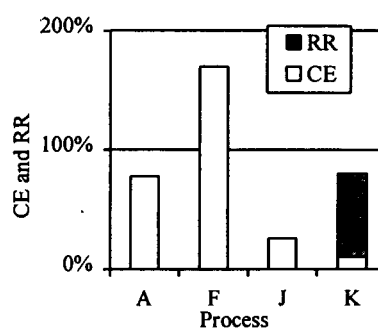


Figure 4. CE and RR for As.

layers which introduced As as cross-contamination. In case of J the As-contamination is completely located in the 630 nm thick oxide layer (Figure 3). The CE is considerably low with 26%, whereas no As was found on the scanned Si-surface after VPD. An explanation for the loss of As could be that As was present as  $\text{As}_2\text{O}_3$  in the oxide layer, which could partly react to form  $\text{AsH}_3$  or other volatile As compounds during the VPD-procedure. In case of K the As-contamination was partly located in the oxide and partly in Si,

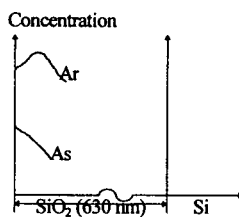


Figure 3 Ar and As distribution (sketch)

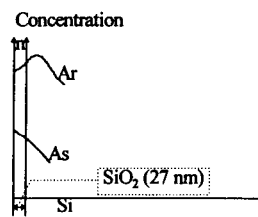


Figure 4 Ar and As distribution (sketch)

as sketched in Figure 4. Consequently, the collected amount for As (oxide layer) was smaller than in variant J while  $Q_{\text{Si}}$  was  $>0$ .

#### 4. CONCLUSIONS

From these examples it can be concluded that the "collection efficiency" as well as the "ramnent ratio" for contaminants depend considerably on the chemical condition of the element which is strongly influenced by the process performed before analysing the wafer surface. For instance, sometimes the volatility of formed compounds reduce considerably the collection efficiency. In other words, a general value for collection efficiency for a single element can not always be defined. The cause of the dependence of collection efficiency on wafer processing must be further investigated.

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# RECOMBINATION-LIFETIME CORRELATION METHOD FOR CHARACTERIZING METALLIC IMPURITIES IN Si OF VERY-LOW CONCENTRATION

Manabu Itsumi\*

## 1. INTRODUCTION

Rapidly determining the amount of metallic impurities with high space resolution is essential for future ultraclean technology. Recombination lifetime measurement is most suitable for this when impurity is known. When the impurity is not known, however, this method is not applicable. This paper shows that a correlation between p-type and n-type Si (p-Si & n-Si) lifetime can roughly lead to the isolation of iron(Fe), copper(Cu) and SUS components (Fig. 1)[1]. The ratio of p-Si and n-Si lifetime variations, which is not 1:1 but 0.67:1 for Fe and 1:0.67 for Cu (Fig. 1), is discussed in terms of precipitates. The advantages of this correlation method are quantitatively shown for cleaning, furnace and plasma processes. In addition, this method is highly sensitive ( $10^8 \text{ cm}^{-2}$  or less) as demonstrated with wafer scrubbing.

## 2. EXPERIMENT

The p-Si and n-Si wafers used were <100>, 14-16 ohm-cm CZ-Si, 150 mm in diameter. The wafers were subjected to contaminated processing (such as wafer cleaning with SC1 solutions, thermal oxidation with a contaminated jig, or plasma etching processes). Thin oxides (7 nm) were formed on the wafers for passivation. Recombination lifetime (LT) was measured by the photoconductivity decay method with microwave reflection (u-PCD). Total reflection X-ray fluorescence (TRXF) was also used to analyse the metallic impurities.

## 3. EXPERIMENTAL RESULTS

The lifetime dependence on the surface Fe concentration is shown in Fig. 2(a). Data reported elsewhere are also shown for comparison. The gradient index of lifetime to concentration is given in Fig. 2(b) & (c). The average of the gradient index for p-Si is about 0.69 and is smaller than that of n-Si, which is about 1. The ratio between the two is about 0.67:1. On the other hand, the lifetime vs. surface Cu concentration gives the reverse relation (the average of the gradient index for n-Si is about 0.60 and is smaller than that of p-Si). The behaviors of Fe in p-Si or those of Cu in n-Si are closely related to the value of 0.67.

Fe precipitation [8-10] is responsible. Henley et al [8] showed that the precipitate defect size is proportional to the square root of the iron concentration for a wide range [6]. The gradient index of lifetime to Fe concentration will be 0.5, if all the Fe atoms in Si form precipitate defects and lifetime depends on the density of the precipitate defects. In reality, precipitate defects and Fe atoms are both involved in

\* NTT System Electronics Laboratories, Morinosato, Atsugi-Shi, Kanagawa 243-01 Japan

the Si, and thus the gradient index is between 0.5 and 1, which agrees closely with the above value of 0.67. For Cu in n-Si, Cu-induced-complexes [11] are responsible.

p-Si and n-Si lifetimes were measured for various samples. At the same time, Fe, Cu and Ni concentration was measured by TRXF and the lifetime of each was estimated from the data (e.g. using Fig. 2). The total lifetime was then calculated from these three lifetimes. The total lifetime is compared with the measured lifetime. There is a good agreement for all the samples. This indicates that even when the impurity is not known, we can roughly estimate the type and quantity of impurities from the measured lifetimes for many cases.

An example of lifetime distribution across a wafer is shown in Fig. 3. This revealed that lifetime reduction in the center of the wafer is due to Ni contamination, and lifetime reduction at periphery is due to Fe contamination. This result was developed by plotting all the lifetime data in the graph in Fig. 1.

The p-Si lifetimes of some wafers with thin oxides were a little scattered. If the related contamination is Fe, which is most sensitive to the lifetime, the quantity of the contamination estimated from Fig. 1 is about  $10^8 \text{ cm}^{-2}$  or less, although the impurities could not be fully characterized with TRXF. Wafer scrubbing (Fig. 4)[12] was found to be effective for sharpening and increasing the scattered lifetimes (Fig. 5). This indicates that oxide-surface scrubbing is effective for passivating the contamination located near or at the Si-SiO<sub>2</sub> interface. This is different from the effect related with the removal of contamination from the oxide surfaces. Friction between the ionized water and oxide surface produces electrons, and the resulting passage of electrons across the Si-SiO<sub>2</sub> interface is assumed to have an important role in increasing in the lifetimes. This technique is useful for thinner-gate-oxide formation.

#### 4. SUMMARY

The advantages of the correlation method have been demonstrated. This method will be useful for rapidly estimating the wide range ( $10^8$ - $10^{12} \text{ cm}^{-2}$ ) of metallic contamination.

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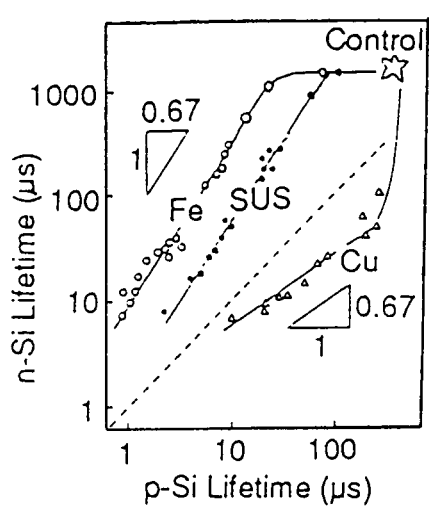


Fig. 1 n-Si lifetime vs p-Si lifetime.

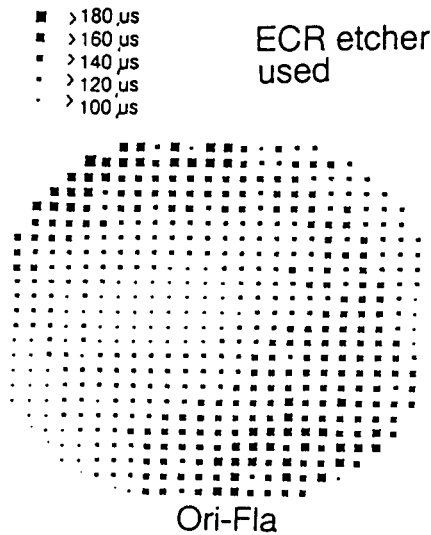


Fig. 3 Lifetime distribution across a wafer.

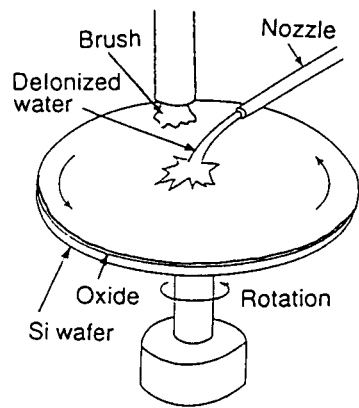


Fig. 4 Wafer scrubbing system.

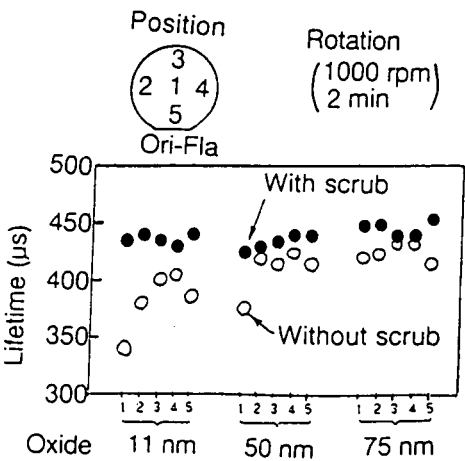
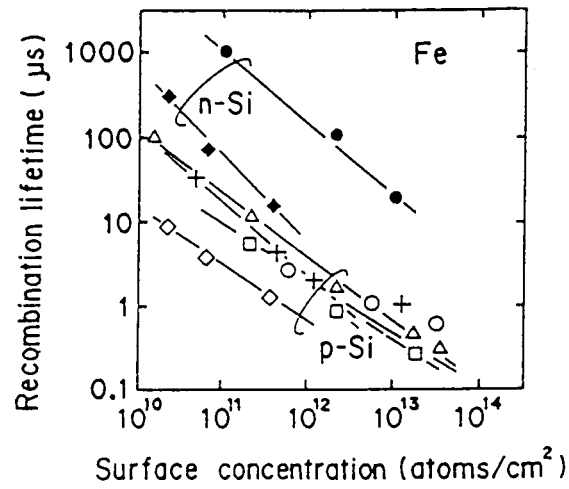


Fig. 5 Effect of wafer scrubbing.

a)



b)

| Fe<br>Ref     | Symbol      |                 | $k = -\log LT / \log N$ |      |        |
|---------------|-------------|-----------------|-------------------------|------|--------|
|               | p-Si        | n-Si            | p-Si                    | n-Si | Ratio  |
| Tsuji [3]     | $\triangle$ | —               | 0.75                    | —    | —      |
| Ishihama [4]  | $\square$   | —               | 0.67                    | —    | —      |
| Rotondaro [5] | +           | —               | 0.89                    | —    | —      |
| Sano [2]      | $\circ$     | $\bullet$       | 0.49                    | 0.85 | 0.57:1 |
| Itsumi [1]    | $\diamond$  | $\blacklozenge$ | 0.67                    | 1.02 | 0.66:1 |
| Average       |             |                 | 0.69                    |      |        |

c)

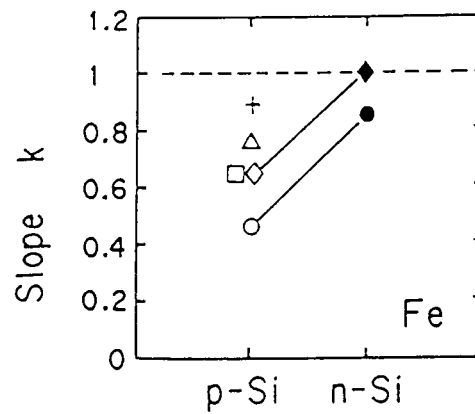


Fig. 2 lifetime(LT) vs surface Fe concentration (N) and slope (k)



## ADVANCES IN THE CHARACTERIZATION OF PARTICLE AND SURFACE METALLIC CONTAMINATION

Alain C. Diebold \*, Kenton Childs \*\*, and B.Y.H. Liu \*\*\*

Although there are many sources of particles/defects in process equipment, only contamination that deposits on a sensitive part of the wafer results in yield or reliability loss. Therefore, contamination control and prevention for particles ultimately depends on the ability to locate (defect/particle detection) and characterize (defect/particle review) particles, defects, and other contamination on patterned and unpatterned wafers. With this capability, one is able to source particles to the process tool and then to the origin inside the tool. As IC design rules decrease, the 1994 National Technology Roadmap for Semiconductors has predicted a 1/3 design rule requirement for particle detection and analysis.(1) This challenges traditional scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDS) defect review capabilities. In this paper, we compare Auger, Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and SEM/EDS for near term, sub 1 $\mu$ m particle analysis and discuss scanning near field optical microscopy and new x-ray detectors as longer term solutions. Contamination control for surface cleaning also depends on characterization of metallic species. We discuss the requirements that statistical process control of surface preparation processes places on total reflection x-ray fluorescence and static SIMS.

SEM/EDS and now Auger and ToF-SIMS are now available as patterned wafer defect review systems. Defect review tools are equipped with whole wafer stages capable of driving to the coordinates of defects/particles located in a "wafer level" defect map obtained by defect detection tools. Auger and ToF-SIMS based review can provide more chemical information than SEM/EDS. In addition, ToF-SIMS is capable of characterizing surface metallic contamination levels for the so-called light elements Na, Al, and K and for the transition elements Fe, Ni, Zn, etc.

Signal from particle vs background, the ability to determine chemical vs elemental composition, and the amount of sample destruction are all factors in selecting an analysis method.(2,3,4) We previously reported a study of particle analysis for a controlled set of particles, 0.5, 0.3, and 0.1  $\mu$ m Al and Al<sub>2</sub>O<sub>3</sub> particles which were deposited on 1 inch diameter Si wafers.(2) In Figure 1, the possible sources of signal (EDS or Auger) from a substrate background are shown. Preliminary modeling work indicated that for submicron particles, the effect of beam voltage on the ratio of particle to substrate signal depends on particle size.(2) In Figure 2, we show the variation of the Auger signal from Al<sub>2</sub>O<sub>3</sub> particles ratioed

\* SEMATECH, 2706 Montopolis Drive, Austin, TX

\*\* Physical Electronics, 6509 Flying Cloud Drive, Eden Prairie, MN

\*\*\* University of Minnesota, 111 Church Street SE, Minneapolis, MN

to that from the Si substrate as a function of electron beam voltage. This work shows that optimal conditions for analysis of Al and  $\text{Al}_2\text{O}_3$  particles depends on particle size. It is important to note that optimal conditions also depend on particle and substrate compositions. The EDS results for this particle set had a very large spread in values for each particle size. This is also shown in Figure 2. The present status of ion beam systems results in an apparently larger particle size than that observed by SEM imaging.

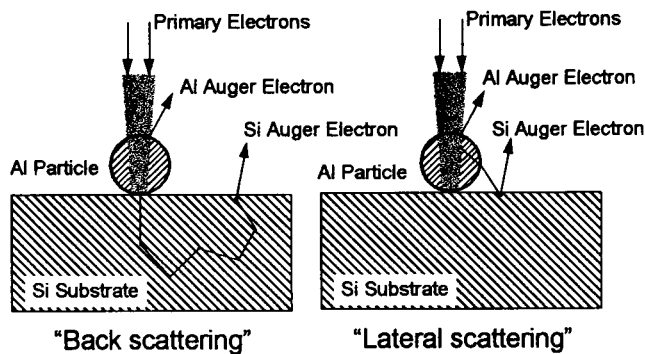


Figure 1. Auger electrons or x-rays can be created by backscattering and lateral scattering. Figure 1 appears in reference 2 and is used with the permission of the authors (© AIP).

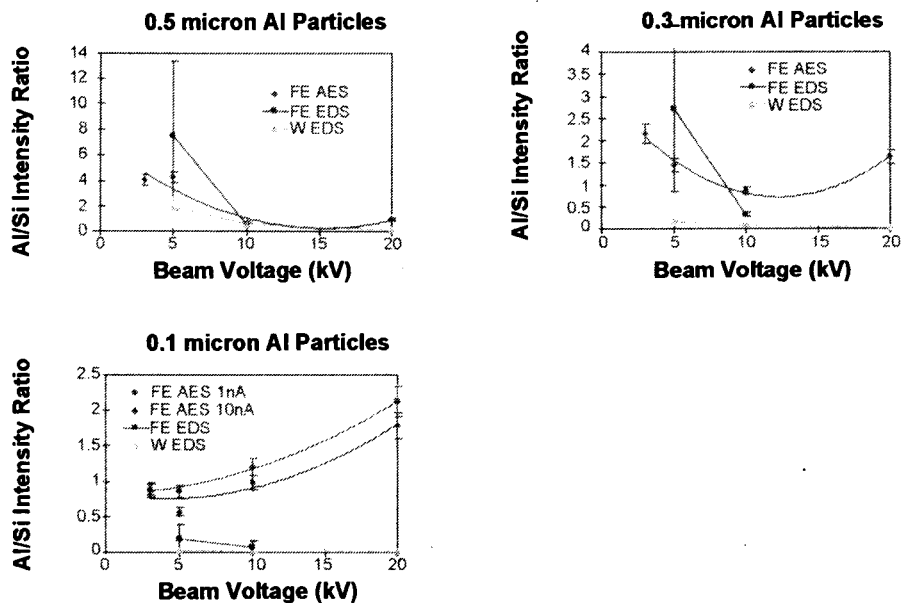


Figure 2. Ratio of Al/Si signal from  $\text{Al}_2\text{O}_3$  particles on Si. Both Auger and x-ray signals are plotted. Figure 1 appears in reference 2 and is used with the permission of the authors (© AIP).

Another complicating aspect of particle analysis is the effect of beam induced charging. Previous experience indicates that low voltage ( $> 5$  keV) Auger analysis

will be difficult at the surface of thick oxide layers. This work will use 200 mm wafers. 0.5, 0.3, and 0.1  $\mu\text{m}$  particles were deposited on 150 mm Si wafers having 1  $\mu\text{m}$  of thermal oxide. In Figure 3, we show the ratio of particle to substrate Auger signal vs beam voltage for 0.3  $\mu\text{m}$   $\text{TiO}_2$  and Al particles. It is interesting to note that while Auger spectra were obtained from the particles at 3 keV beam voltages, charging issues made substrate spectra difficult to obtain. Figure 3 illustrates the effect of particle composition on optimal analysis conditions. Previous work leads us to believe that the higher Z containing 0.3  $\mu\text{m}$   $\text{TiO}_2$  particles are more effective in containing the 3 keV electron beam scatter inside particles than the Al on 1  $\mu\text{m}$  of  $\text{SiO}_2$  or Al and  $\text{Al}_2\text{O}_3$  on Si. Therefore, lower beam voltages give enhanced particle to substrate signal ratios for 0.3  $\mu\text{m}$   $\text{TiO}_2$ . It is interesting to note that although the change in particle to substrate ratio is relatively small, the magnitude of the Al to Si ratio is larger for all beam voltages for Al on 1  $\mu\text{m}$  of  $\text{SiO}_2$  vs Al on Si.

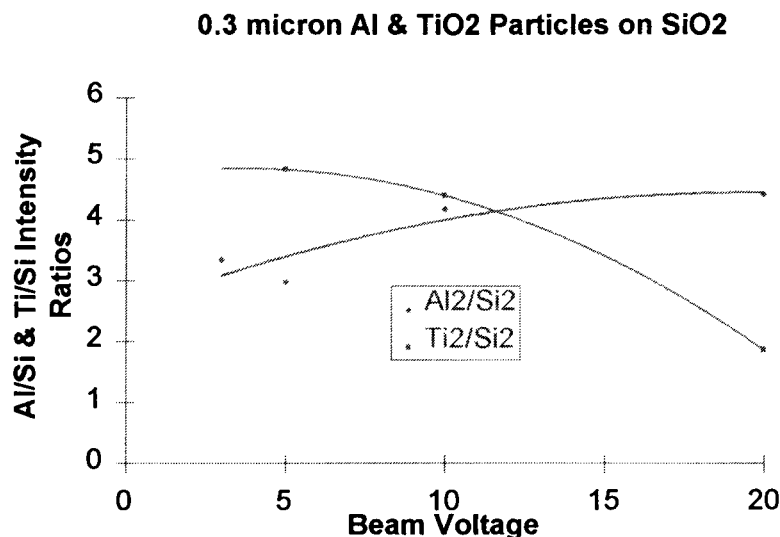


Figure 3. Al/Si and Ti/Si Auger intensity ratios for 0.3  $\mu\text{m}$  Al and  $\text{TiO}_2$  particles on 1  $\mu\text{m}$   $\text{SiO}_2$ . The Al and Si KLL and Ti LMM Auger lines were used.

Scanning Near Field Optical Microscopy (NFOM) and a new microcalorimeter based x-ray detector have been proposed as defect/particle analysis methods. Progress toward development of NFOM was discussed by both Duncan and Person at the recent NIST sponsored workshop on Industrial Applications of Scanned Probe Microscopy.(5) Duncan indicated that spectroscopy was made difficult by the blocking effect that the probe tip has on any fluorescent or Raman signal emitted by the particle. His initial results showed that even the strong Raman signal from diamond was greatly diminished when observed by NFOM.

Microcalorimeter x-ray detectors hold the promise of greatly improving energy resolution and low energy x-ray detection. Recently Martinis showed the first x-ray spectra obtained using a near transition edge microcalorimeter x-ray detector inside an SEM.(6) This was closely followed by Silver's results using a silicon thermometer based microcalorimeter in an SEM.(6) Microcalorimeter x-ray detectors are expected to extend the usefulness of SEM/EDS defect review tools to smaller particle sizes. The results shown in this and previous papers indicate that more study is required to understand the potential of SEM-microcalorimeter based defect review. Auger and ToF-SIMS provide chemical information today, while microcalorimeters with a few eV resolution required for observing x-ray chemical shifts may be possible.

Statistical process control is possible when the associated metrology meets a 30% value for the process to tolerance ratio  $P/T = 6\sigma/(UL-LL)$ .  $\sigma$  is the appropriately combined long term and short term measurement deviation, and UL and LL are the upper and lower process limits. For surface contamination,  $LL = 0$  and  $P/T = 3\sigma/UL$ . If you wish to control Fe surface contamination to  $1 \times 10^{10}$  atoms/cm<sup>2</sup>, then the measurement deviation must be 1/10 this value (ie.,  $1 \times 10^9$  atoms/cm<sup>2</sup>). Typically, measurement deviations increase near detection limits, and therefore statistical process control requirements drive low detection limits. Evidence of this from TXRF and SIMS round robins are presented. (7,8)

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## Use of Grazing Emission XRF Spectrometry for silicon wafer surface contamination measurements

S. De Gendt<sup>+</sup>, K. Kenis<sup>+</sup>, P.W. Mertens<sup>+</sup>, M.M. Heyns<sup>+</sup>, M. Claes<sup>#</sup>,  
R.E. Van Grieken<sup>#</sup>, A. Bailleul<sup>\*</sup>, M. Knotter<sup>\*</sup> and P.K. de Bokx<sup>\*</sup>

Grazing Emission X-Ray Fluorescence Spectrometry (GEXRF) is a new analytical X-ray fluorescence technique, which like TXRF takes advantage of the total reflection phenomenon. In GEXRF however, detection is performed using wavelength-dispersive techniques, which have better resolution and sensitivity for light elements (compared to energy-dispersive detectors used in TXRF). This paper describes initial analysis results for the detection of light element (magnesium, aluminum and calcium) silicon wafer surface contamination.

### **Introduction:**

Measurement of chemical contamination on silicon integrated circuit (IC) devices is not always possible due to the lack of 'on-line' analysis equipment. The latter is explicitly true for light element contamination. Semi-conductor industry routinely uses TXRF to monitor surface contamination given its multi-element detection capabilities and easy automation [1,2]. However, for commercially available instrumentation, this technique is insensitive for elements with  $Z < 20$ . Only synchrotron radiation as excitation source allows low  $Z$  detection [3], however, this is not routinely available. Also, other analytical techniques suffer from drawbacks, thus, a new method having the advantages of TXRF, with the added benefit of light element detection would be highly welcome.

The relative insensitivity of TXRF for detection of elements lighter than silicon on silicon wafers, is caused by the use of an energy-dispersive detection system, which suffers from poor resolution for elements lighter than chlorine, and also has a limited dynamic range. An obvious solution would be the use of wavelength-dispersive detection. However, in a laboratory TXRF using an X-ray tube source, so much of the source power is sacrificed in making a collimated (monochromatic) incident beam, that good detection limits (DL's) can only be attained by using large solid angle detectors.

In GEXRF however, the sample is irradiated with an uncollimated, polychromatic X-ray beam, without stringent requirements to the angle of incidence (i.e. perpendicular). The emitted fluorescence radiation is detected at grazing angles with wavelength-dispersive detection systems. The surface sensitivity of emitted radiation at grazing angles was discussed by Becker et al. [4]. Based on this work, a prototype GEXRF spectrometer was developed by the Philips Research Laboratories [5,6]. This work focuses on evaluating the capabilities of this prototype for the detection of light elements (magnesium, aluminum and calcium) on silicon wafers.

### **Experimental:**

A research version GEXRF spectrometer, based on a conventional Philips XRF spectrometer was used. It should be noted that for this prototype, no optimization for determination of trace metal amounts on silicon substrate has been done yet, neither with respect to the excitation nor to the detection part of the instrument.

Samples are excited using a sealed X-ray source with a Rh target, operated at 40kV and 70mA. Light element excitation mainly occurs by the characteristic L-lines of our source (Rh-La = 2.7 keV) and by the Brehmstrahlungs continuum close to the absorption edge of the respective element. The detection part consists of an adjustable double slit system for collimating the fluorescence radiation and the standard crystal changer of a conventional Philips PW 2400 spectrometer. For detection, a flow proportional counter detector is used. Specific analysis details for the elements under study are given in Table 1.

<sup>+</sup> IMEC vzw, Kapeldreef 75, B-3001 Leuven, Belgium.

<sup>#</sup> University of Antwerp (UIA), Universiteitsplein 1, B-2610 Wilrijk, Belgium.

<sup>\*</sup> Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

| element | crystal type | 2 $\theta$ angle (degrees) | q <sub>crit,theor.</sub><br>K $\alpha$ of El. X on Si(mrad) | counting time (seconds) | slit width (mm) |
|---------|--------------|----------------------------|-------------------------------------------------------------|-------------------------|-----------------|
| Mg      | TLAP         | 45.17                      | 23.52                                                       | 1000                    | 500             |
| Al      | PET          | 45.20                      | 19.46                                                       | 1000                    | 500             |
| Ca      | PET          | 145.12                     | 8.50                                                        | 1000                    | 500             |
| Si      | -            | -                          | 15.76                                                       | -                       | -               |

**Table 1:** Overview of analysis parameters.

For all elements, synthetic calibration samples were prepared, applying either spin-coat or immersion techniques. We used p-type CZ [100] 6" wafers which received a standard clean, consisting of SPM, HF, SC-1 and SC-2, prior to controlled contamination. Suitable blanks were included in the analysis procedure. Geometry requirements of the current prototype made it necessary to cut the wafers to squares of 4x4 cm. All prepared samples were cross calibrated with alternative analytical techniques such as VPD/AAS, VPD/ICP-OES, and RBS. Details on sample preparation can be found in Table 2.

| element | cont. technique | range (at/cm <sup>2</sup> ) | cross calib. tech. |
|---------|-----------------|-----------------------------|--------------------|
| Mg      | spin            | 5E12 - 5E14                 | VPD/AAS            |
| Al      | spin            | 1E14                        | VPD/ICP-OES + AAS  |
|         | SC-1 immersion  | 5E12 - 5E14                 | VPD/ICP-OES        |
| Ca      | spin            | 5E12 - 5E14                 | RBS + VPD/AAS      |

**Table 2:** Overview of sample preparation procedure.

### Results and Discussion:

It has been observed for TXRF that, owing to its shallow information depth, the measured fluorescence intensity in the total reflection mode depends strongly on parameters which are usually not of interest in X-ray fluorescence (XRF) analysis.

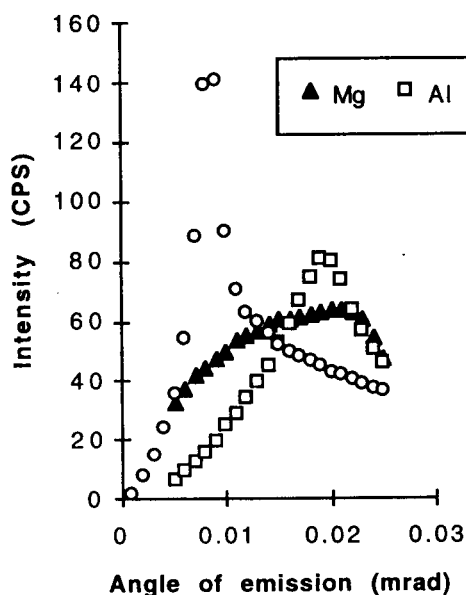


Fig. 1A: Analytical signal for Mg, Al, Ca vs angle of emission.

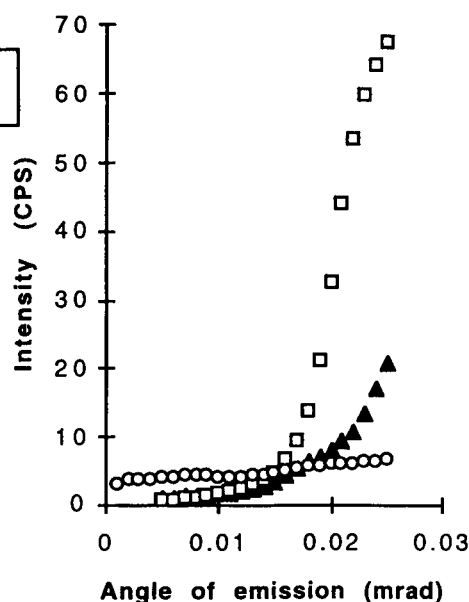


Fig. 1B: Background signal for Mg, Al, Ca vs angle of emission.

These factors include the position of the analyte atoms with respect to the interface and the incident angle of the exciting beam. The influence of both parameters on the measured signal can be exemplified by two boundary conditions, e.g. particle or film type, which can be distinguished depending on their response before the angle of incidence of the X-rays exceeds the critical angle [7,8].

Given the analogy between TXRF and GEXRF, a similar response can be expected. Therefore, it is of importance for our current evaluation of GEXRF to determine the fluorescence intensity as a function of the 'angle of emission' for the three elements under study. For this evaluation, we used one of the highest contaminated wafers (E14 at/cm<sup>2</sup> range) for each metal, and varied the angle of measurement (thus emission) between 0 and 25 mrad. The results are presented in Figure 1A for magnesium, aluminum and calcium, respectively.

Given the strong dependence between the angle of emission and the fluorescence intensity, it can be concluded that all metals under study behave according to a 'film type' response. Additionally, these curves also allow to determine the critical angle for either metal under study on silicon wafers. The critical angles as estimated from Figure 1A correspond well with the theoretical values for the critical angle, as listed in Table 1. The aluminum and magnesium value are slightly biased by the presence of a silicon background peak ( $q_{crit} = 16\text{mrad}$ ) as can be seen in Figure 1B, where the measured background is plotted as a function of the angle of emission for the magnesium, aluminum and calcium analysis conditions.

Both figures also allow to determine the optimum measurement angle for either element, with respect to the signal-to-noise ratio (and thus detection limits). These optimum measurement conditions were used to determine a calibration curve for all three elements (3 contam. levels and blank wafer). These calibration curves are given in Figure 2. The X-axis lists the concentration values as determined from cross calibration analysis, while the Y-axis contains the measured GEXRF intensity (CPS) for either analyzed wafer. Each measurement was repeated at least three times.

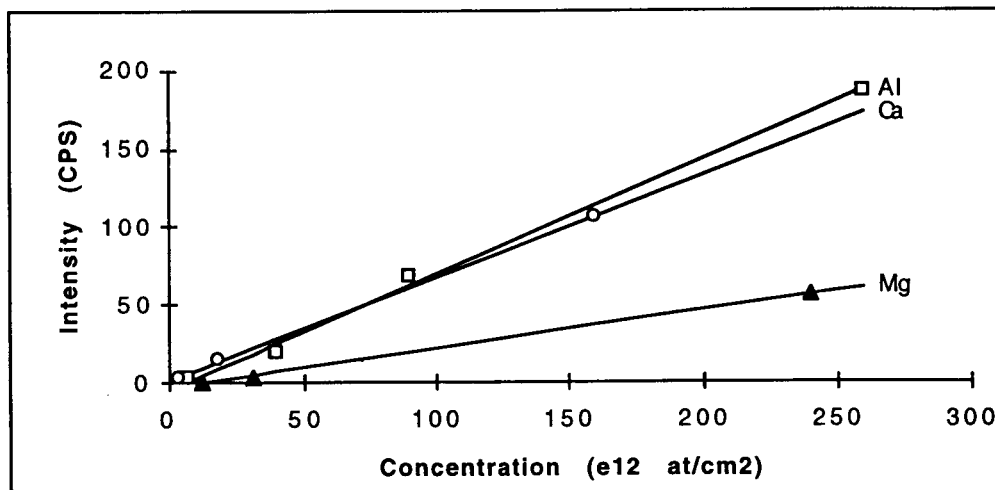


Fig.2: Calibration curves for Mg, Al, Ca on Si.

It can be observed that the sensitivity for Mg is lower than for Al and Ca, which can be attributed in part to the different monochromating crystals used for either analysis (TLAP for Mg, and PET for Al and Ca). Also, the fluorescence yield decreases for lower Z elements. Nevertheless, linear calibration curves are obtained for all three elements with a wafer-to-wafer reproducibility in the order of 10% maximum (between 1 and 10%RSD). These calibration curves can also be used to determine limits of detection for magnesium, aluminum and calcium respectively.

| Element | slope    | Correlation coefficient | DL1000sec<br>( $\text{e}^{11} \text{at/cm}^2$ ) |
|---------|----------|-------------------------|-------------------------------------------------|
| Mg      | 2.45E-11 | 0.9996                  | 5.6                                             |
| Al      | 7.35E-11 | 0.9982                  | 3.2                                             |
| Ca      | 6.58E-11 | 0.9999                  | 2.6                                             |

**Table 3:** GEXRF detection limits for Mg, Al and Ca.

The calculated limits of detection for a 1000 seconds integration time are reported in Table 3. Limits of detection of the order of a few  $\text{E}11 \text{at/cm}^2$  are obtained for all elements under study. Given the prototype status of the GEXRF technique, it is anticipated that these values will be improved in a more mature version of the instrumentation, which is currently under development. However, it should be noted that the Ca value compares well with TXRF results obtained on a commercial TXRF instrument in our lab, where a limit of detection of  $7\text{E}11 \text{at/cm}^2$  has been found [9].

Also, as with TXRF, the use of Vapor Phase Decomposition - Droplet Surface Etching (VPD - DSE) preconcentration, is likely to bring the limits of detection further down (scaling factor depending on the wafersize). Currently, this procedure is under study, and the first results indicate an improvement in DL, although not yet to the expected height. This is likely due to inefficient collection efficiency of the DSE mixture, poor performance of the VPD treatment, ... Current investigations are under way to study this more thoroughly.

#### **Conclusion:**

The promising capabilities of GEXRF for light element contamination measurements on silicon wafers have been demonstrated. Direct measurements yield detection limits in the low  $\text{E}11 \text{at/cm}^2$  range, values which are anticipated to be improved with the further instrumental development of the technique. Also, use of preconcentration steps such as (VPD - DSE) are likely to improve these values.

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## ANALYSIS OF ORGANIC CONTAMINANTS IN GASES USING NON-VOLATILE RESIDUE (NVR) MONITORS AND TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY (TOF-SIMS)

P.M. Lindley\*, J.J. Lee\*, W.D. Bowers\*\*, G.S. Strossman\* and R.S. Hockett\*

### 1. INTRODUCTION

Increasing capabilities in semiconductor and hard disk technologies are often tied to more stringent requirements for surface cleanliness, particularly in the processing environment. As cleanliness requirements become more important, organic/molecular contamination has become the focus of renewed interest in the evaluation of existing processing problems and in new process development.

One area of concern as a source for organic contaminants is the chemicals supplied for various processing steps. In particular, a need has been identified to measure low levels of non-volatile residue (NVR) contaminants in process gases used in the microelectronics industry.

Current techniques for evaluating contamination in these gases are limited in that they: (1) require relatively large volumes of gas to be used for the testing process, and (2) provide information only about specific types of contamination (e.g., hydrocarbons). More useful methods to evaluate gas contaminants are required to have good sensitivity to low (sub-monolayer) levels of contamination, to provide specific chemical information that will allow a compound to be traced to its source, and to operate under conditions that will permit the analysis of a wide range of materials.

This work describes a technique for gas contaminant analysis that combines a sensitive Non-volatile Residue (NVR) monitor to *quantify* levels of contamination with Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) to *identify* the detected contaminants. The NVR monitors are based on SAW (surface acoustic wave) devices, sensitive piezoelectric microbalances that can detect submonolayer levels of airborne molecular contamination.<sup>1</sup> TOF-SIMS, with its excellent sensitivity and ability to provide fingerprint spectra that can be compared to reference materials, has proven to be valuable in providing specific chemical identification of many types of contaminants. However, because it is a high vacuum ( $10^{-8}$ - $10^{-10}$  torr) technique, it has primarily been useful for less volatile contaminants. This work has been performed on a TOF-SIMS system equipped with a cold stage to permit evaluation of more volatile organic species.

For these analyses, a set of SAW devices has been exposed to cylinders of

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\* Charles Evans & Associates, 301 Chesapeake Drive, Redwood City, CA 94063, USA

\*\* Femtometrics, 1001 W. 17th St., Suite R, Costa Mesa, CA 92627, USA

a common gas used in microelectronics applications. The cylinders, provided by two different suppliers, are to be evaluated for contamination.

## 2. EXPERIMENTAL

The SAW-based NVR monitor used in this work was a modified version of a commercial instrument designed by Femtometrics to measure ambient contamination in aerospace and microelectronic cleanroom facilities. A series of SAW sensors was cleaned by plasma treatment, then exposed to small quantities (approximately 50 g) of gas from various cylinders (Table 1). The deposition of material on each SAW was monitored, and then TOF-SIMS analyses were performed within 24 hours.

TOF-SIMS data were obtained on a Physical Electronics TFS I instrument<sup>2</sup> equipped with a temperature-controlled sample stage. For these experiments, the stage was pre-cooled with liquid nitrogen to provide a sample temperature of approximately -50C. . Each SAW device was mounted in a modified holder that was designed to permit re-use of the sensor after the analysis. The sample and holder were placed in a dry nitrogen atmosphere and cooled to approx. -70C using liquid N<sub>2</sub>. The sample was introduced into the instrument under dry N<sub>2</sub>. Positive and negative ion spectra were acquired using a bunched <sup>69</sup>Ga<sup>+</sup> Liquid Metal Ion Gun (LMIG) primary ion beam operated at 15 kV.

*Table 1.* SAW devices analyzed by TOF-SIMS

| SAW Sample           | Description                            |
|----------------------|----------------------------------------|
| control              | plasma-cleaned only (no gas exposure)  |
| N <sub>2</sub> blank | exposed to dry nitrogen gas            |
| supplier #1, "dirty" | semiconductor gas, known contamination |
| supplier #1, "clean" | semiconductor gas, "clean" cylinder    |
| supplier #2, "clean" | semiconductor gas, "clean" cylinder    |

## 3. RESULTS AND DISCUSSION

SAW data from the four cylinder-exposed samples described in Table 1 indicates that only the N<sub>2</sub> cylinder (N<sub>2</sub> blank) did not deposit significant levels of contamination on the sensor. SAW traces from the three samples treated with cylinders of the microelectronics gas all reveal significant levels of contaminant deposition.

TOF-SIMS analysis results are consistent with the SAW data and also serve to identify specific contaminants on each of the samples. Spectra from the N<sub>2</sub> blank, where no significant deposition was observed on the SAW, are quite similar to spectra from the control sample (Figure 1).

Positive ion spectra from the SAW device exposed to a microelectronics gas cylinder known to be contaminated with hydrocarbons (supplier #1, "dirty")

clearly show a series of  $C_{25}$ - $C_{35}$  hydrocarbon peaks in the mass range from 300-500 Da. This sample also highlights the importance of the cold stage in the TOF-SIMS work, since spectra of the SAW acquired under room temperature conditions do not contain this series of peaks (Figure 2).

While results from the “dirty” cylinder are generally as predicted, the more interesting data from an applications perspective are those from the two cylinders described as “clean.” Spectra from the gas supplier #1 “clean” sample contain a series of peaks typical of chlorotrifluoroethylene (CTFE), a material used as a sealant in many applications. Figure 3 shows a region of a positive ion spectrum from this sample. In Figure 4, a positive ion spectrum from gas supplier #2’s “clean” sample contains significant peaks for dioctyl phthalate (DOP).

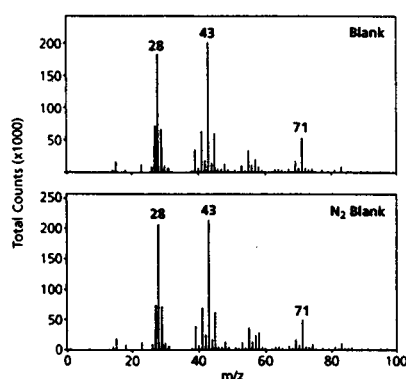


Figure 1. Comparison of positive ion spectra from control (top) and  $N_2$  blank (bottom) SAW samples.

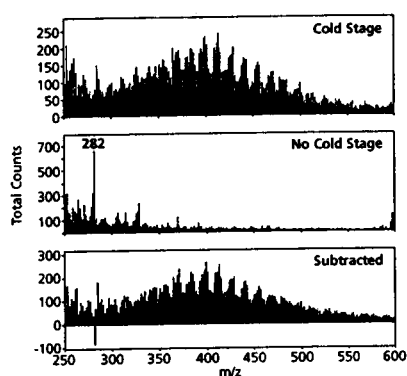


Figure 2. Comparison of positive ion spectra obtained with (top) and without (center) cold stage from the gas supplier #1 “dirty” SAW.

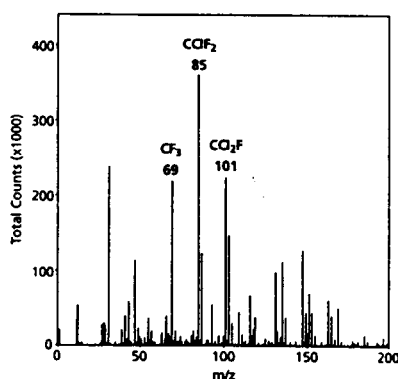


Figure 3. Positive ion spectrum from the gas manufacturer #1 “clean” SAW.

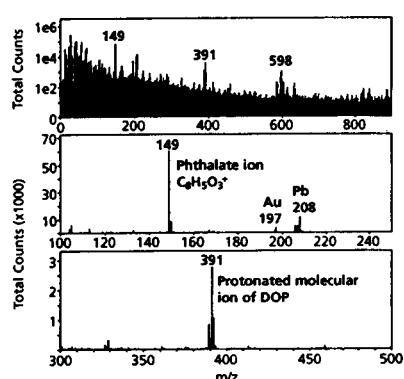


Figure 4. Positive ion spectrum from the gas manufacturer #2 “clean” SAW.

#### 4. SUMMARY

The chemical specificity of TOF-SIMS can be a valuable tool for the identification of contaminants in many types of processing steps. With a cold stage, the increased range of contaminants that can be observed makes the technique more useful for the analysis of organic/molecular contamination. Combining TOF-SIMS' sensitivity and chemical identification capabilities with the quantification possible with SAW-based NVR monitors provides a very powerful contamination analysis tool.

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## PPB-LEVEL MEASUREMENTS IN NITROGEN AND ESG's USING A DIODE LASER HYGROMETER

**J.-M. Girard and P. Mauvais**

**Air Liquide Research and Development / Electronics**

Among the volatile impurities that are likely to be found in Electronic Speciality Gases, moisture is one of the most critical for several reasons : It affects the process yield, by directly polluting the deposited material or through particle generation in the reactor chamber. Moisture also enhances the corrosion of the piping and the components, leading to regulator failures and the generation of metallic impurities. It is also the most difficult to remove from metallic surfaces, and therefore would be the best tracer of the distribution system quality and integrity in the scope of piping commissioning using the process gas itself.

An instrument based on Near IR Tunable Diode Laser Spectroscopy has been developed in order to match the sensitivity requirements (low ppb level detection limit of H<sub>2</sub>O), as well as the stringent constraints on footprint reduction, ruggedness, and compatibility with corrosive gases, for point of use analysis purposes.

The sensitivity of the instrument has been first evaluated with nitrogen, and then with a set of Electronics Speciality Gases (ESG's), including NF<sub>3</sub> and NH<sub>3</sub>, which are known to be difficult to analyse using FTIR technology.

### 1- EXPERIMENTAL

The principle of the instrument is based on the detection of the absorbance due to the trace moisture contained in the gas (Figure 1) [1-4]. Using a diode laser as an IR source allows a precise tuning of the wavelength, by adjusting the temperature of the diode, and a high spectral resolution ( $10^{-4}$  cm<sup>-1</sup>).

Once centred over a moisture absorption peak (7294 cm<sup>-1</sup>), the wavelength is quickly swept across this peak by modulating the input current of the diode with a sawtooth ramp, which amplitude is adjusted to the peak width. After collimation, the laser beam is split into a probing beam and a reference beam by mean of a membrane type beam splitter. The probing beam is focused on a InGaAs IR detector after a 10 meter pathlength in the gas cell, whereas the reference beam is directly focused on another detector. The pathlength of the reference beam is adjustable in order to account for the absorption caused by residual moisture in the housing containing the optics, despite a permanent dry nitrogen purge. The signals from the detectors are amplified, subtracted and filtered before digitalisation by a fast data acquisition and averaging system. Typical operating conditions involve a modulation frequency of several kHz, leading to a averaging of 8192 scans in less

than 5 seconds. This high speed acquisition allows to strongly improve the signal to noise ratio by lowering the instrument  $1/f$  noise [5]. The intensity of the recorded absorption peak is then correlated to the moisture concentration in the gas cell.

In order to avoid the cumbersome cryogenic cooling of lead salt diodes, we chose to operate in the near infrared region ( $1.368\ \mu\text{m}$ ) using custom made InGaAsP/InP DFB diodes. These diodes are monomode and operate from  $5^\circ\text{C}$  to  $45^\circ\text{C}$  and from 10 mA to 100 mA input current without any mode hops, and with an emitted power of a few milliwatts.

The system described here utilises a Herriot-type multipass cell [6], whose parameters have been optimised to permit the smallest volume for a selected pathlength and after considering the acceptable tolerances on the beam misalignment. The cell has a 10 meter pathlength, and a total volume of 1 litre. The compatibility with ESG's, such as HBr or HCl, which are known to be extremely corrosive, places very stringent constraints on the material. Consequently, the cell and all the wetted parts are made of polished Hastelloy C22. The mirrors and nickel O-rings are gold plated in order both to enhance the chemical resistance of the metal and to limit the moisture outgassing from the surface.

The final instrument footprint ( $L560 \times W227 \times H182\ \text{mm}^3$ ), including the optical housing and the cell itself, is small enough to fit into a standard 19" rack.

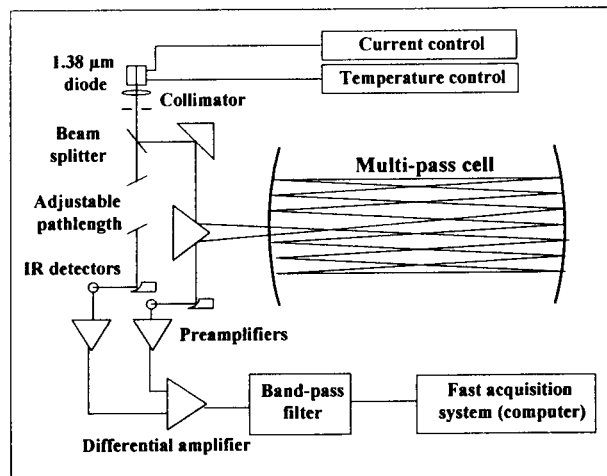


Figure 1 : Schematic diagram of the Diode Laser Hygrometer

## 2- PERFORMANCES EVALUATION IN NITROGEN

The system was operated at atmospheric pressure. From the peak heights (or peak area) recorded at various concentrations, a calibration curve can be extracted, as shown in figure 2.

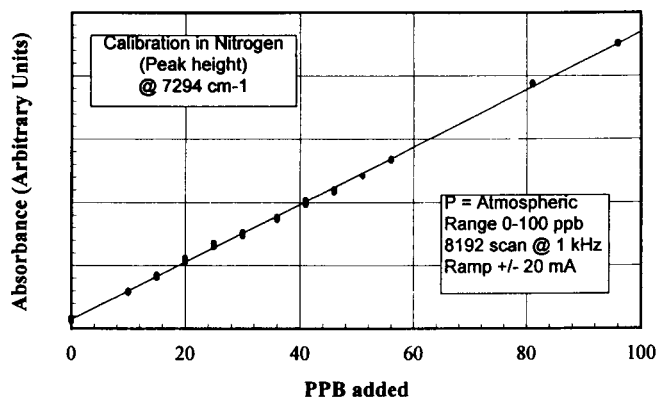


Figure 2 : Calibration curve in nitrogen

The detection limit of the instrument can be calculated using the usual  $3\sigma$  criterion, where  $\sigma$  refers to the standard deviation of a set of at least 10 points successively measured in the gas in the lower concentration range [7]. It is interesting to point out that this  $3\sigma$  value remains basically constant over the calibration range. As a result, the precision of a measured concentration will be below 3 ppb in the 0-100 ppb range, and the detection limit can be estimated to be ca. 5 ppb.

In order to handle higher concentration measurements, the linearity of the calibration curve has been experimentally verified and is very satisfactory up to the maximum achievable  $\text{H}_2\text{O}$  concentration with our calibration system (10 ppm).

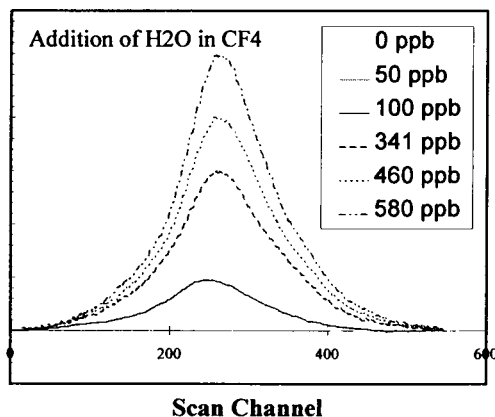
Another important factor for practical field implementation of an instrument is the stability in time, i.e. the stability of the reading when the concentration is kept constant. This experiment has been carried out by flowing nitrogen containing 35 ppb  $\text{H}_2\text{O}$  at 2 SLM during one day. After stabilisation of the concentration (20 min), the fluctuations remained within  $\pm 9\%$  of the average value over 8 hours and 50 measurements.

### 3- MEASUREMENTS IN PFCs

The gases selected for this study ( $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{NF}_3$ ) are inert ESG's, but  $\text{NF}_3$  is especially known to present spectral interference problems by FTIR.

As an example, the  $\text{H}_2\text{O}$  peaks measured in moist  $\text{CF}_4$  are shown in figure 3, and exhibit a perfect Lorentzian profile, typical of collisional broadening at high

pressure. For all these gases, the detection limit, related to the background fluctuations, and the sensitivity are basically similar as in nitrogen.



#### 4- MEASUREMENTS IN $\text{NH}_3$

The absorption peak at  $7294\text{ cm}^{-1}$  is unfortunately located close to a small ammonia peak, leading to a difficult straightforward determination of the absorbance. This interference problem could be lowered by operating at lower pressure (50 mbar), thus reducing the peak width and the overlapping. Still, the absorption peak was obtained by subtracting a dry  $\text{NH}_3$  spectrum to the moist  $\text{NH}_3$  one. The resulting calibration curve is shown in figure 5. The detection limit of the instrument is  $\sim 50$  ppb, corresponding to an improvement of a factor 20 compared to FTIR technology.

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## GENERATION AND TRANSPORT OF CORROSION PRODUCTS IN HCL GAS LINES

G. Vereecke, N. Anderson\*, C. Elsmore\*\*, P. Espitalier-Noel\*\* and M.M. Heyns

IMEC, Kapeldreef 75, B-3001, Belgium

\* BOC Gases @ IMEC.

\*\* BOC Ltd., 10 Priestley Rd., Surrey Research Park, Guildford, Surrey, GU2 5XY, UK

### 1. INTRODUCTION

Over the last few years increasing attention has been focused on the purity of gas supply, particularly gas distribution systems. It is no longer sufficient to guarantee gas purity at the storage medium; gas suppliers are increasingly being asked to guarantee purity at point of use (POU). This trend necessitates a more thorough understanding of the influence of the gas distribution system on both the generation and transport of contaminants. A reasonable understanding already exists of the behaviour of moisture in inert gas ambients [1-2]. A more challenging and complex area for examination is the behaviour of moisture in corrosive gases [3-5]. Moreover, with corrosive gases, the POU purity is also affected by the corrosion products generated by the chemical reactions taking place at the wetted surfaces. With the common use of POU filters, the concern is more with volatile corrosion products as they could enter the semiconductor process tools [5].

### 2. EXPERIMENTALS

An experimental rig has been constructed to investigate the variables of most concern in dynamic conditions, simulating those encountered during gas lines service. It allows mixtures of purified HCl and N<sub>2</sub> containing high calibrated H<sub>2</sub>O concentrations [6] to flow through a test tube maintained at a controlled temperature. All peripheral tubing consists of EP-SS up to the point where the two flows meet. All parts wetted by moist HCl are made of Ni 200 or PFA to minimize the system contribution to the measurements. The gas flow exiting the test tube is scrubbed in small quartz bubblers. Data on the metallic content of the gas flow is collected by analysing by TXRF microsamples of the bubblers' solutions dried on Si wafers. The TXRF limit of detection is  $\sim 10^{11}$  atoms/cm<sup>2</sup>, giving a  $\sim 10$  ppt detection limit for metals in the HCl gas with the present setup. The use of two bubblers in parallel, one of which is equipped with a particle filter (PC membrane filter, 0.2  $\mu$ m pore size), allows discrimination between large particles on one hand, and small particles and/or volatiles on the other hand. The influence of HCl exposure on the dry-down characteristics of the tube is determined periodically by APIMS. To this end, the HCl flow is interrupted and the tube is equilibrated with a N<sub>2</sub> flow containing 200 ppb H<sub>2</sub>O before switching to purified N<sub>2</sub>.

In this paper, results are presented for the corrosion of both 316L EP-SS and Ni-200 1/4" tubes. Unless otherwise stated, the tubes are 6 m long, coiled to a diameter of 10". The test tubes have VCR connectors of the same material welded on both ends. Before exposure to HCl, the tubes are first cleaned with acetone and DIW and then baked for 24 hours at 150 °C under a 2 SLM flow of purified N<sub>2</sub>. The corrosion experiments are run at 30 °C and a pressure slightly above 1 atm under a total flow of 0.2 SLM. This flow is made either of purified HCl or 'moist' HCl, a 50/50 mixture of purified HCl and moist N<sub>2</sub> giving 10 ppm moisture in HCl.

### 3. RESULTS AND DISCUSSION

#### 3.1. Ni-200

The main metallic contaminant detected under both purified and moist HCl flows are Ti particles larger than 0.2  $\mu$ m (Fig. 1). The average molecular concentrations in the gas phase are larger during the first two days of flow. Thereafter, the generation drops down, particularly under the purified HCl flow, indicating some stabilisation of the tube inner surface. No Ti contaminants smaller than 0.2  $\mu$ m are detected. Other contaminants are detected in the sub-ppb range: Zn  $\sim$  Fe  $>$  Ni  $\sim$  Cu. They show different behaviors than Ti. For example, Zn contaminants (Fig. 1) are significantly generated only under the wet HCl flow, as both large and small contaminants, and do not show the same decrease in concentration after the first two days of exposure.

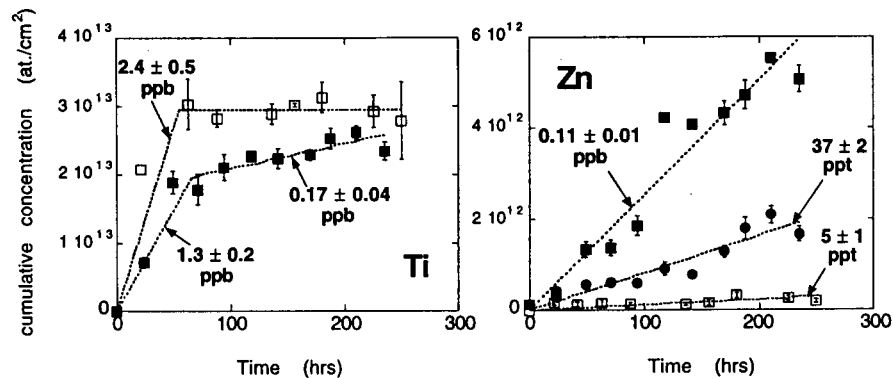


Figure 1. Results from the TXRF analysis of the dried microdroplets sampled from the bubblers for Ni-200 tubings exposed to purified ( $\square$ ) and moist ( $\blacksquare$ ,  $\bullet$ ) HCl.  $\square$ ,  $\blacksquare$ : total metal concentrations (particles + volatiles), measured from the non-filtered half of the flow.  $\bullet$ : concentrations of contaminants  $< 0.2 \mu\text{m}$ , measured from the filtered half of the flow. The derived average gaseous concentrations are given as inserts. Error bars:  $\pm 1$  stdev.

The results from the moisture dry-down tests are presented in Fig. 2. The curves have been shifted to allow a better comparison of their slopes. They show an increased affinity of  $\text{H}_2\text{O}$  for the corroded tube surface, particularly for the tube exposed to moist HCl. In both cases, this effect seems to have stabilised after a few days.

The stabilisation of the Ni-200 surface after a few days of exposure seems to preclude large interferences from the Ni parts of the setup in the study of the corrosion of other materials.

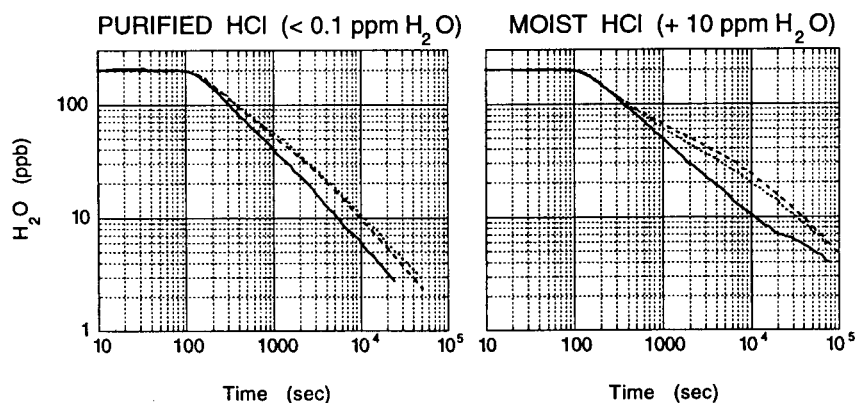


Figure 2. Influence of the HCl flow time on the dry-down properties of a Ni-200 tube.  
 — : before exposure, - - - : after 5 days of flow, ..... : after 10 days of flow.

### 3.2. 316L EP-SS

Metallic contaminants from EP-SS tubings exposed to purified HCl are detected by TXRF only during the first day of flow. The results from two experiments are summarized in Table 1. Fe, Cr and Ni are the three main elements of 316L stainless steel. The differences observed for Cr and Ni between the two runs may point to weld variations. Run #1 is one of the first experiments performed with this setup. The Ti observed during this run is likely to come from the Ni-200 parts

of the setup. The absence of detection of Ti during Run #2 would indicate that the setup had reached stability at that time. Zn and Cu could be trace elements from the EP-SS.

*Table 1.* Molecular concentrations of metallic contaminants in purified HCl flowing through 1 m EP-SS tubings, detected by TXRF analysis. The concentrations are averages over the first day of exposure, given in ppb ( $\pm 1$  stdev).

| Metal | Run #1           | Run #2            |
|-------|------------------|-------------------|
| Fe    | $0.85 \pm 0.32$  | $0.78 \pm 0.11$   |
| Cr    | $0.47 \pm 0.03$  | < DL              |
| Ni    | $0.16 \pm 0.01$  | $0.020 \pm 0.005$ |
| Zn    | < DL             | $0.086 \pm 0.005$ |
| Cu    | $0.035 \pm .008$ | $0.038 \pm 0.005$ |
| Ti    | $0.28 \pm 0.01$  | < DL              |

The size distribution of the contaminants vary from metal to metal. For example, most of the detected Fe is made of contaminants smaller than  $0.2 \mu\text{m}$ . The occurrence of direct reactions between EP-SS surface oxides and halogen gases has already been shown to happen with dry HBr [5,7]. The following reaction between HCl and iron oxide is also thermodynamically possible:



Volatiles could contaminate the gas flow as a result of the relatively high vapor pressure of the corresponding corrosion product [8]. They are expected to be particularly harmful to process tools as they would not be stopped by POU filters.

The results from the moisture dry-down tests are presented in Fig. 3. The curves have been shifted to allow a better comparison of their slopes. They show a slight increase of the affinity of  $\text{H}_2\text{O}$  for the corroded tube surface under purified HCl. However this effect is quite large for the tube exposed to moist HCl. In both cases, the tube surfaces seem to have stabilised after a few days.

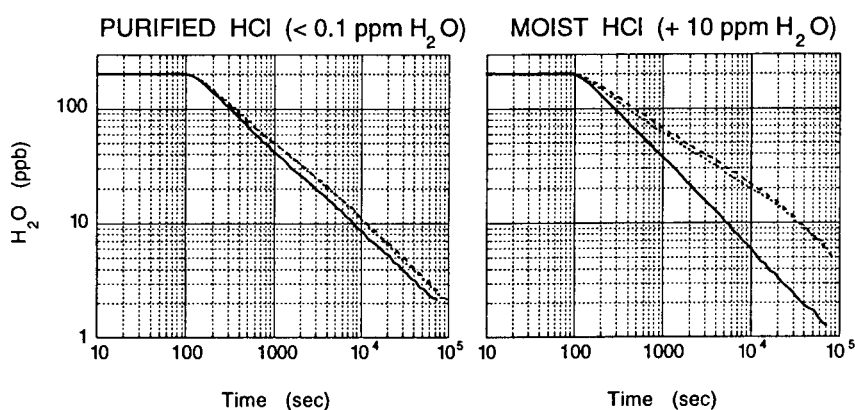


*Figure 3.* Influence of the HCl flow time on the dry-down properties of an EP-SS tube.  
 — : before exposure, ---- : after 5 days of flow, ..... : after 10 days of flow.

The stabilisation under purified HCl flow is not a real passivation, as shown by the results of the successive exposure of EP-SS to purified and moist HCl (Fig. 4). A second generation of metallic contaminants is observed upon moisture addition to the purified HCl flow. However, in this case, no contaminants smaller than  $0.2 \mu\text{m}$  have been detected.

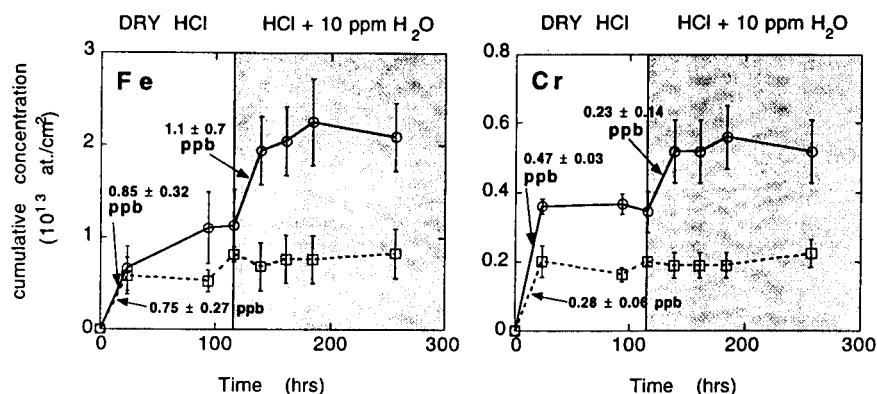


Figure 4. As at Fig. 1 but for a 1 m long EP-SS tubing exposed successively to purified and moist HCl.  $\circ$ : total metal concentrations (particles + volatiles), measured from the non-filtered half of the flow.  $\square$ : concentrations of contaminants  $< 0.2 \mu\text{m}$ , measured from the filtered half of the flow.

#### 4. CONCLUSIONS

The present study has shown that the corrosion of 316L EP-SS and Ni-200 tubings occurs equally under purified and moist HCl flows. The metallic corrosion products can be generated as both large particles ( $> 0.2 \mu\text{m}$ ) or small contaminants ( $< 0.2 \mu\text{m}$ ), depending on the metal and the moisture concentration. Under constant moisture conditions, the generation of metallic contaminants generally drops down to sub-ppb levels after one to two days of HCl flow. However, in the case of EP-SS exposed to purified HCl, this surface stabilization is not a real passivation, as evidenced by the further generation of metallic contaminants upon the addition of moisture to the HCl flow.

Moisture dry-down tests show an increased affinity of  $\text{H}_2\text{O}$  for the corroded surfaces. This effect is enhanced under moist HCl flow. Under constant moisture conditions, the surface modifications seem to stabilize within a few days of flow.

#### ACKNOWLEDGEMENTS

The authors thank Millipore for providing the filters and purifiers used in this study. The support by H. Berger, A. Athalye and N. Verma of the BOC Group is gratefully acknowledged. G. Doumen and N. Wuestenberg of IMEC are thanked for their help with the building of the experimental setup.

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## Fluoride gas distribution system

Taiji Hashimoto, Yasuyuki Shirai, Masaki Narazaki, and Tadahiro Ohmi  
Tohoku University  
Sendai, Japan

### 1. Introduction

Recently in semiconductor manufacturing, the vapor phase reaction have developed. And the purity of gases and cleanness of the gas distribution systems have been important. In semiconductor manufacturing, many kinds of gases are used. In those gases, high corrosive specialty gases including halogen are difficult to handle. For example, HF, Cl<sub>2</sub>, HCl and HBr are essentially reactive and lead corrosion to equipment. And BF<sub>3</sub>, BCl<sub>3</sub>, SiF<sub>4</sub>, SiH<sub>2</sub>Cl<sub>2</sub>, ClF<sub>3</sub> and WF<sub>6</sub> can react and generate HF when moisture exist. In many kinds of processes, for example RIE (Reactive Ion Etching), CVD (Chemical Vapor Deposition), Ion Implantation, Chamber Cleaning and Metallization, those gases are used for.

Those gases are used in the process chambers, valves, flow controllers and tubes made of stainless steel. Those are weak for corrosion. As a result, it decrease purity, worsen process environment and lead outgas from surface.

The surface of wafer is patterned with lithography. And the accuracy of pattern by a lithography effects all micro processes, yield and performance after that.

An excimer laser can image fine pattern. Using F and Kr, high power 248nm UV can be obtain. F<sub>2</sub> gas is a source of F, and Kr is gas too. In a gas distribution system for excimer laser, gas purity is important. Impurities degrade beam profile, reduce output power, and shorten laser lifetime. Air contaminants effect excimer performance and can reduce power output by such as 17% per 100ppm of impurity<sup>1)</sup>. In lithography, gas handling system to use excimer laser is started to necessary.

In future semiconductor manufacturing, ultra high pure gas and passivation technology for piping system technology to make 100% are important more and more for gas delivery system. We developed the passivation Cr<sub>2</sub>O<sub>3</sub> films on stainless steel surface<sup>2)</sup>.

But F<sub>2</sub> gas has a high oxidation potential. An analysis with XPS cleared that F atom invade to Cr<sub>2</sub>O<sub>3</sub> passivation film when film is exposed to F<sub>2</sub> gas.

Then we developed the fluorine passivated (FD) technology for stainless steel 316L-EP. Using this surface treatment, fluoride gases distribution can be stable.

In this paper, we describe about evaluations about fluorine consumption, corrosion, dyrdown property and, welding technology of passivated tube.

### 2. Passivation process of metal surface

Fluorine passivation technology is composed of three processes. 1) etching to remove native oxide of 316L-EP stainless steel surface, 2) fluoridation to form fluoride film, 3) heat treatment to improve the fluoride film called thermal modification.

#### 1) Etching

Stainless steel has a native oxide at the surface with about 2nm thickness. In the case of without etching, oxide and fluoride consist in a passivation film surface. The native oxide can be etched easy with HF solution. Removal condition is examined 0.5% HF solution.

#### 2) Fluoridation

Fluoridation need a high pure F<sub>2</sub> gas. If moisture exists in process system, F<sub>2</sub> react with moisture and generate corrosive HF. So baking is important process to eliminate moisture. After Baking at 250°C, F<sub>2</sub> gas is introduced and fluoridation is carried out at 220°C.

#### 3) Thermal modification

After fluoridation, F<sub>2</sub> gas is completely purged off from the chamber by N<sub>2</sub>, and then the fluoridated stainless steel surface is heat treated at 350°C in N<sub>2</sub> for 10hours to improve the film quality.

Figure 1 shows the depth profiles analyzed with XPS. Top result shows a nonstoichiometric structure without thermal modify, and bottom result shows a stoichiometric structure with thermal modify. The direct fluoridated film contains excessive amount of fluorine, FeF<sub>3</sub> and FeF<sub>2</sub> before the process of thermal modification.

Figure 2 shows that a sealed  $F_2$  pressure decrease in tube having nonstoichiometric and stoichiometric structure. It shows metal is fluoridated, and  $F_2$  gas is continuously consumed in a nonstoichiometric structure.

### 3. Exposure to $F_2$ gas

Figure 3 shows XPS depth profile of 316L-EP stainless steel after exposure to  $F_2$  gas. The experimental processes are 1) baking at  $200^\circ\text{C}$  to eliminate adsorbed moisture 2) 1%  $F_2$  in Ne flows 20cc/min for 48 hours. Fluorine changes metal to fluoride, and invade to about 3.5nm deep. This means consumption of fluorine gas by tube surface.

### 4. Corrosion test with fluoride gases

We evaluate corrosion resistance for  $ClF_3$  and  $WF_6$ . Cut samples of tubes are sealed with gas having  $1.0\text{kg}/\text{cm}^2$  pressure at  $100^\circ\text{C}$  for 24hours.

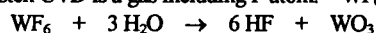
Figure 4 shows SEM (Scanning Electron Microscope) observation of 316L-EP stainless steel and fluorine passivated 316L before and after corrosion test.

The corrosion by  $ClF_3$  is remarkable when moisture exist with.  $ClF_3$  and moisture react and generate corrosive HF, HCl and oxifluorides.

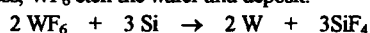
In SEM observation of each samples after corrosion test with  $ClF_3$ , the surface of 316L-EP can be seen black spots as corrosion. And the grains at the surface can not be seen clearly.

On the other hand, a SEM images of a fluorine passivated tube shows no corrosion products and looks similar to background.

$WF_6$  used in tungsten CVD is a gas including F atom.  $WF_6$  react with moisture.



In the CVD process,  $WF_6$  etch the wafer and deposit.



In SEM observation after corrosion test with  $WF_6$  about 316L-EP and fluorine passivated 316L, there is no significant difference between before and after the test. There is no corrosion by  $WF_6$ .

### 5. Drydown property of fluorine passivated tube

For manufacturing process, the purity of gas is important parameter. Delivered clean gas can be contaminated by outgassing and particle generation from the tube. Tubing system must have excellent cleanness and drydown property. Especially, moisture is easy to adsorb and hard to desorb. So drydown property effects the impurities concentration just after construction.

In addition, for corrosive gas handling, moisture is a cause of corrosion. So drydown property is very important.

Figure 5 shows drydown property of 316L-EP stainless steel and fluorine passivated 316L. The result of fluorine passivated tube is similar to 316L-EP stainless steel. Fluorine passivated tubing system can start up in short time.

### 6. The welding technology for fluorine passivated tube

Gas distribution system is constructed by welding and fitting. The inner surface of the welded fluorine passivated tube is evaluated with optical microscope observation. Figure 6 shows welded point with passivation film.

By melting and solidify of metal fluorides, surface looks having roughness at wide area. The particles can be measured when tube receive a shock. It is clear that welded point is a source of particles.

Passivated film can be removed with hot ultra pure water at  $80^\circ\text{C}$ . Figure 7 shows the depth profile of film removed surface.

Figure 8 shows optical microscope images of welded point with removing film. The surface looks clean. We confirm the possibility of clean welding.

In addition, re-fluoridation of welded point is formed using 1%  $F_2$  at  $200^\circ\text{C}$  for 30minutes, and its depth profile shows figure 9.

## 7. Conclusion

Fluorine passivation technology for 316L stainless steel has been investigated.

Many kinds of inert and specialty gases are used in semiconductor manufacturing. And a lot of these gases are reactive, corrosive and poisonous. This fluorine passivation technology is surface treatment for gas distribution having high corrosion resistance against corrosive fluoride gas. In near future, 256MDRAM made with quarter micron is coming soon to semiconductor manufacturing. Using application of this technology to gas distribution for excimer laser, decrease impurities, extend gas lifetime and decrease lens exchange will be available.

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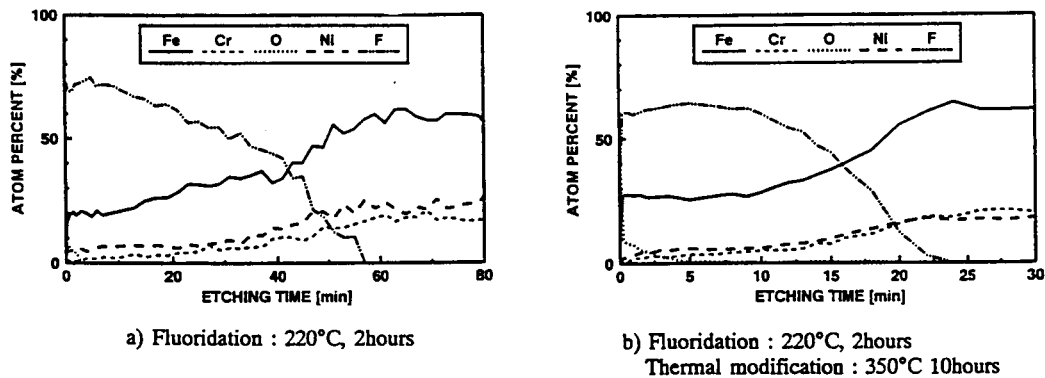


Fig. 1 Depth profiles of XPS Spectra a) a direct fluorine passivated surface b) a thermal modified surface of 316L stainless steel.

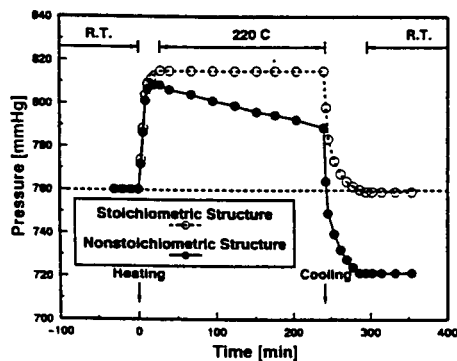


Fig. 2 Time variation of fluorine pressure due to heat cycle for nonstoichiometric and stoichiometric structure.

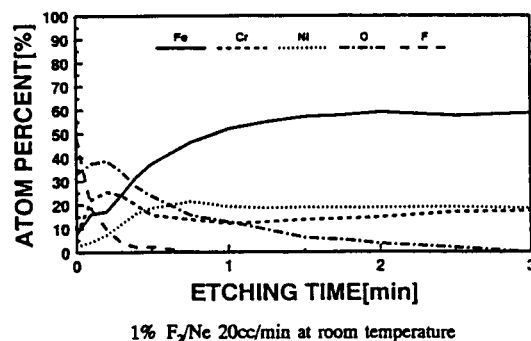


Fig. 3 The depth profile of 316L-EP stainless steel after  $F_2$  gas flow for 48hours.

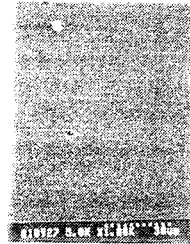
Table 1 Properties of various fluoride gases

|                    | CF <sub>4</sub> | CClF <sub>3</sub> | C <sub>2</sub> F <sub>6</sub> | SF <sub>6</sub> | NF <sub>3</sub> | CF <sub>3</sub> | WF <sub>6</sub> | BF <sub>3</sub> | F <sub>2</sub> | HF     |
|--------------------|-----------------|-------------------|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|--------|
| *Process           | 1               | 1                 | 1                             | 1               | 1, 2            | 2               | 3               | 4               | 5              |        |
| Boiling Point (°C) | -127.9          | -81.4             | -78.2                         | -68.3           | -129.0          | 12              | 17.5            | -99.9           | -188           | 19.5   |
| Corrosion          | x               | x                 | x                             | x               | x               | ○               | ○               | x               | ○              | ○      |
| Reaction           |                 |                   |                               |                 |                 |                 |                 |                 |                |        |
| moisture           | stable          | stable            | stable                        | stable          | stable          | react           | react           | react           | react          | stable |
| Metal              | stable          | stable            | stable                        | stable          | stable          | react           | react           | stable          | react          | react  |
| Poisonous          | Low             | Low               | Low                           | Low             | High            | High            | High            | High            | High           | High   |

\*Process    1 : RIE (Reactive Ion Etching)  
               2 : Chamber Cleaning  
               3 : Metallization  
               4 : Ion Implantation  
               5 : Excimer Laser

316L-EP stainless steel

Fluorine passivated 316L



Before corrosion test

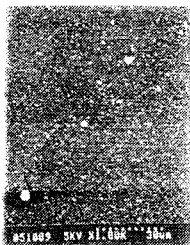
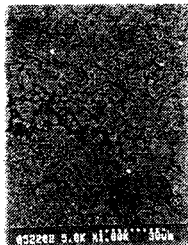
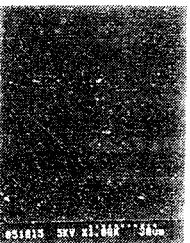
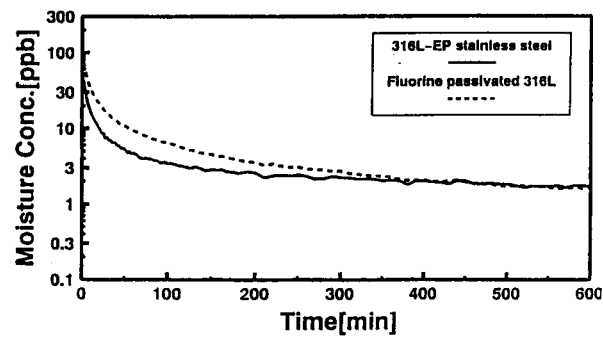
After ClF<sub>3</sub> corrosion testAfter WF<sub>6</sub> corrosion test

Fig. 4 The SEM images of 316L-EP stainless steel and fluorine passivated 316L after ClF<sub>3</sub> and WF<sub>6</sub> corrosion test.

Corrosion conditions : 100% ClF<sub>3</sub> or WF<sub>6</sub>

1.0kg/cm<sup>2</sup> at 100°C for 24hours





1/4" x 2m Ar 1.2 l/min at room temperature

Fig. 5 Drydown Properties of fluorine passivated and unpassivated 316L stainless steel.

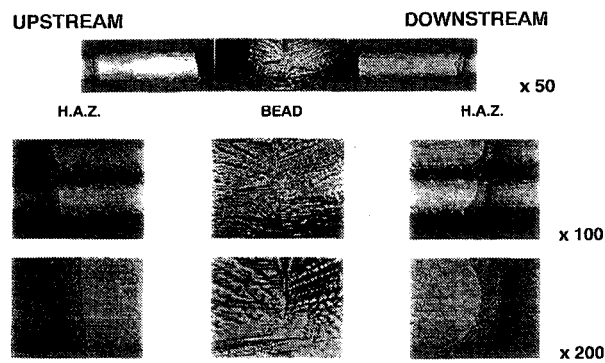
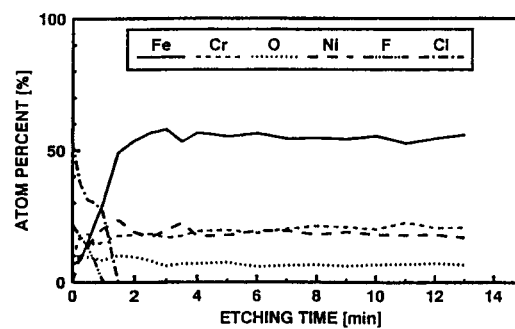


Fig. 6 Optical microscope images of welded point and HAZ (Heat Affected Zone) on fluorine passivated tube.



Dipping in UPW for 5min at 80°C

Fig. 7 The depth profile of film removed surface.

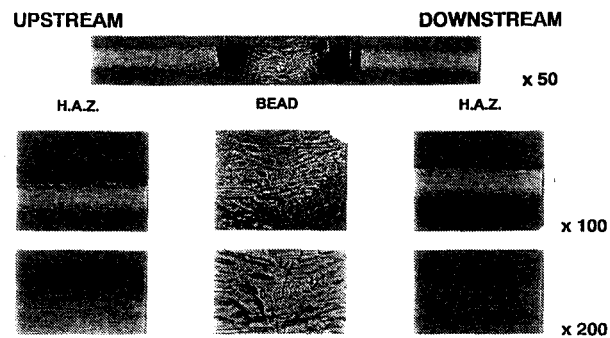


Fig. 8 Optical microscope images of welded point and HAZ on film removed tube.

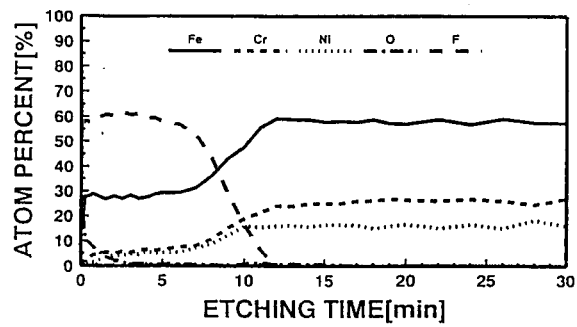


Fig. 9 The depth profile of re-fluorine passivated surface on welded point.

# Carbon and oxygen contamination free silicon surface cleaning for gas-source MBE

H.Okumura, T.Akane, Y.Tsubo and S.Matsumoto

Department of Electrical Engineering, Keio University,  
3-14-1 Hiyoshi, Yokohama 223, Japan

The following five wet cleaning methods have been investigated as substrate preparation for MBE: (1)modified Shiraki, (2) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  treatment, (3) $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{HF}$  treatment, (4)RCA, and (5)RCA + HF dipping. The surface micro roughness of the samples treated with each method was measured with atomic force microscopy. Residual carbon and oxygen were evaluated with secondary ion mass spectroscopy after capping layer growth by MBE using  $\text{Si}_2\text{H}_6$ .

The experimental results showed that  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{HF}$  treatment was superior to any other method in terms of removal efficiency of carbon and oxygen as well as surface flatness.

## 1 Introduction

Silicon molecular beam epitaxy (Si-MBE) has a great deal of attractiveness because of its controllability of epitaxial layer thickness and doping profile. To obtain high quality film, cleaning of substrate surface is one of the most essential factors. Consequently various cleaning methods have been proposed.

In general, the main parts in the methods consist of two processes : formation of clean chemical oxide and removal of the oxide.

In respect of wet processing, there are a lot of way to form the oxide such as Ishizaka-Shiraki method[1], RCA method[2] and SPM(Sulfuric acid hydrogen Peroxide Mixture) treatment. Recently, *Ohnishi* et al.[3] proposed a  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{HF}$  mixture (they call as SPFM) as an advanced treatment of SPM in terms of particle removal efficiency. However, there is no detailed description about the difference of carbon and oxygen removal efficiency between SPM and SPFM treatment.

Concerning the oxide removal, either thermal annealing process in UHV(Ultra High Vacuum) or HF dipping process is commonly employed.

In this paper, we study the following five cleaning methods as substrate preparation for MBE: (1) modified Shiraki method + annealing in UHV, (2) SPM treatment + annealing in UHV, (3) SPFM treatment + annealing in UHV, (4) RCA method + annealing in UHV, and (5) RCA method + HF dipping. From the point of surface flatness and residual carbon and oxygen, we discuss which method is the most suitable for MBE.

Table 1: Cleaning procedures

|                      |                                                                                                                                                                                                      |
|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (1) modified Shiraki | $\text{HNO}_3 \rightarrow \text{HF} \rightarrow 3\text{HCl} + 1\text{H}_2\text{O}_2 + 1\text{H}_2\text{O}$ (100 °C, 10min)                                                                           |
| (2) SPM              | $4\text{H}_2\text{SO}_4 + 1\text{H}_2\text{O}_2$ (80-100 °C, 10min)                                                                                                                                  |
| (3) SPFM             | $4\text{H}_2\text{SO}_4 + 1\text{H}_2\text{O}_2 + 0.01\% \text{ HF}$ (80-100 °C, 10min)                                                                                                              |
| (4) RCA              | $1\text{NH}_4\text{OH} + 1\text{H}_2\text{O}_2 + 6\text{H}_2\text{O}$ (80 °C, 10min)<br>$\rightarrow \text{HF} \rightarrow 1\text{HCl} + 1\text{H}_2\text{O}_2 + 5\text{H}_2\text{O}$ (80 °C, 10min) |
| (5) RCA+HF           | (4) $\rightarrow \text{HF}$ (0.5% 1min)                                                                                                                                                              |

## 2 Experimental

The substrates used were n-type CZ-Si(001) with the resistivity of 10  $\Omega\text{cm}$ . The cleaning procedures are summarized in table 1. Micro roughness of the samples were measured with AFM (Atomic Force Microscopy) after each cleaning procedure. Before AFM measurement, the chemical oxide was removed by dipping in 0.5% HF solution. We have also evaluated residual carbon and oxygen with SIMS (Secondary Ion Mass Spectroscopy) after capping layer growth by MBE using  $\text{Si}_2\text{H}_6$ .

## 3 Results and discussion

Figure 1 shows the relationship between micro roughness and cleaning methods. As shown in this figure, each sample has similar average roughness of about 0.2 nm except RCA treated one.

Figure 2 shows the amount of residual carbon and oxygen existing at the interface between the substrate and the epitaxial layer. The result indicates the following two important things : First, HF dipping process for removal of the oxide causes carbon and oxygen piling up as many researchers reported [4][5]. To suppress the piling up, particular methods must be utilized [6][7]. Second, the most effective treatment to eliminate carbon and oxygen is SPFM treatment.

As for the substrate preparation for MBE, lowering the temperature and shortening the time to remove the oxide is also a crucial issue. Figure 3 shows the relationship between the annealing temperature and annealing time to evaporate the oxide formed with each treatment. We confirmed the evaporation of the oxide by using RHEED (Reflection High Energy Electron Diffraction). This result indicates that the oxide formed with SPFM treatment can be removed at lower substrate temperature and for shorter time than the oxide formed with any other method.

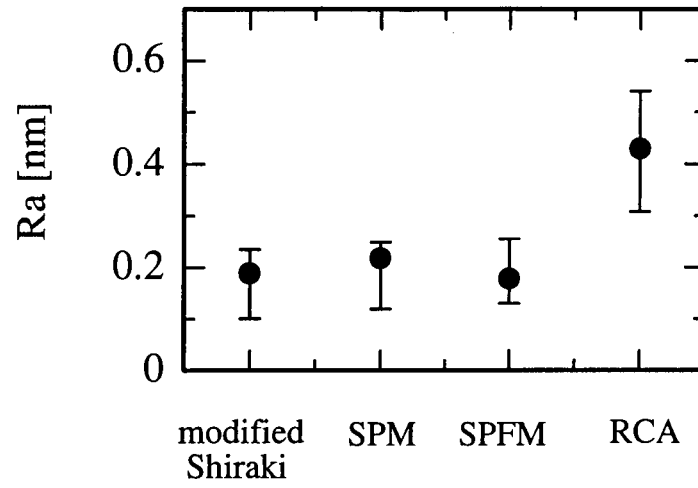


Figure 1: The relationship between micro roughness and cleaning methods.

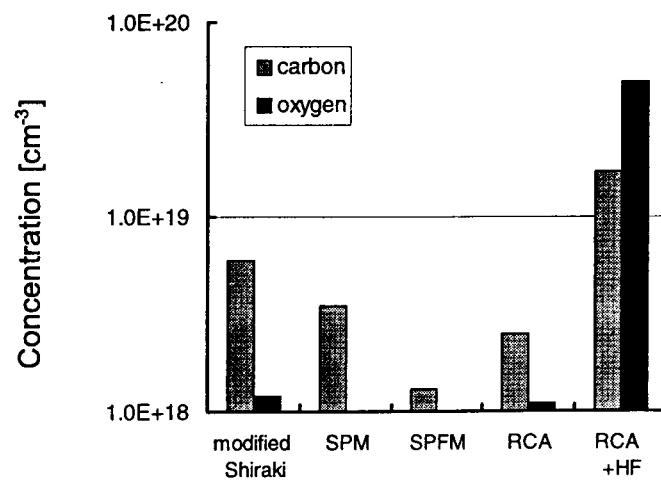


Figure 2: Residual contamination between the substrate and the epi-layer.

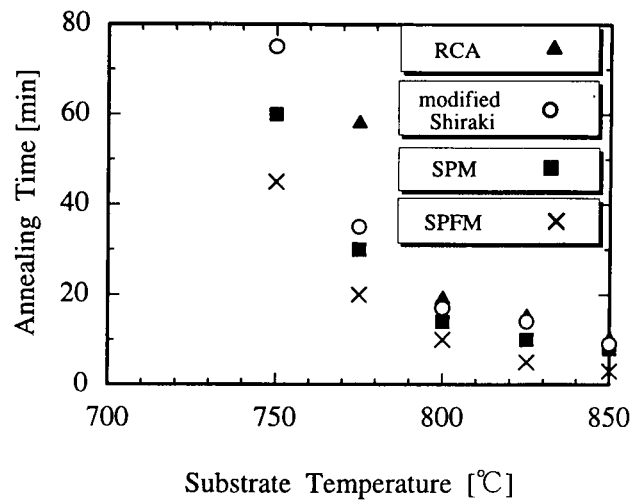


Figure 3: The relationship between annealing time and substrate temperature to remove the chemical oxide.

## 4 Summary

We have investigated several cleaning methods as substrate preparation for MBE. The results of the experiment were as follows: (1) micro roughness of the SPFM treated sample could be suppressed as the same level of the conventionally treated one, (2) SPFM treatment showed superior ability of carbon and oxygen removal, and (3) the chemical oxide formed with SPFM treatment could be removed at lower substrate temperature.

It is concluded that the most suitable method of substrate preparation for MBE is SPFM treatment followed by annealing in UHV.

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## LOW THERMAL BUDGET SI EPITAXY : AN OVERVIEW STUDY OF THE SUBSTRATE/EPI INTERFACE IN A NUMBER OF COMMON EPITAXIAL GROWTH SYSTEMS

M. Caymax<sup>1</sup>, L. Vescan<sup>2</sup>, K. Werner<sup>3</sup>, D. Bensahel<sup>4</sup>, D. Gravesteijn<sup>5</sup> and I. Szendro<sup>6</sup>

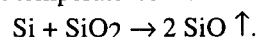
1. IMEC, Leuven, Belgium ; 2. ISI-KFA Juelich, Germany ; 3. DIMES TUDelft, The Netherlands ; 4. CNET Meylan, France ; 5. Philips Research labs, Eindhoven, The Netherlands ; 6. MicroVacuum, Budapest, Hungary

### 1. INTRODUCTION

Since the mid-eighties, several types of epitaxial Chemical Vapour Deposition (CVD) reactors have been developed to cope with the ever increasing demand for lower thermal budget Si epitaxy. Lower thermal budget epi is important for creating/maintaining sharper impurity profiles, for not damaging existing possibly sensitive structures on the wafer, and for SiGe epitaxy where one wants to prevent thermally driven relaxation processes. Whereas most research attention so far has gone to the epi layer itself and its applications, here we present a comparative study of the interface between the epilayer and the substrate. This is especially relevant for processes where the standard high-temperature H<sub>2</sub>-bake for native oxide removal is not allowed, and/or where the use of a Si buffer layer grown at high temperature is not desirable.

### 2. EXPERIMENTAL TECHNIQUES

Successful epi growth requires removal of the native oxide before the layer growth is started. In standard high-temperature epi, this is accomplished in-situ by a short bake at temperatures well over 1000 °C, invoking the reaction



By applying an HF dip before loading the wafers into the reactor, this temperature can be lowered to 900 °C. In systems with very low background partial pressures of water and O<sub>2</sub> such as Ultra High Vacuum (UHV) systems, it is even possible to grow epi after an ex-situ HF dip without any bake at all. It is known, however, that in such cases one always finds back traces of O and/or C at the interface. In this work, we have applied both these methods of O removal including small variants.

For this work, many different epi systems have been used, covering most of the available reactor types used worldwide : an AMT Centura (Rapid Thermal CVD-type) and a Riber Epineat (UHV-CVD single wafer) at CNET, a Solid Source Molecular Beam Epitaxy (SSMBE) system and a Gas Source (GSMBE) MBE at DIMES, a Low Pressure CVD at ISI-KFA, an SSMBE at Philips, and a home-build UHV-CVD batch reactor at IMEC. For reference purposes a single Si layer sample was grown after a standard high temperature (1150 °C) H<sub>2</sub> prebake in an Atmospheric Pressure CVD (APCVD) ASM Epsilon-One reactor at IMEC. The growth temperatures varied between 560 and 850 °C except for the high-temperature APCVD reference sample.

Two different sample structures have been grown. A first one had a Si "buffer" layer of 10 nm, followed by a 200 nm  $\text{Si}_{1-x}\text{Ge}_x$  layer with  $x = 0.07-0.10$  in order to trace back the real epi/substrate interface if not readily visible. On the other hand, the Si buffer prevented any interfering reaction between the starting substrate surface and the Ge-source gas. A second structure had a 10 nm Si buffer, 20 nm of  $\text{Si}_{1-x}\text{Ge}_x$  with  $x = 0.15$ , and on top, a Si cap of 100 nm. The samples with a Si cap were destined for Photo-Luminescence (PL) measurements, in which the Si cap serves to prevent excitons from radiationless recombination at the surface.

After growth, samples of all wafers were sent to ISI-KFA Juelich for TEM, RBS and PL, to DIMES Delft for SIMS and PL, and to MicroVacuum Budapest for SIMS. In this way, our measurements are completely internally comparable because carried out in the same measurement set-up, so avoiding definite problems with system calibration. At the same time cross check measurements from different set-ups could rule out eventual systematic errors.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

Two examples of SIMS profiles of C, O and Ge are given in Fig. 1

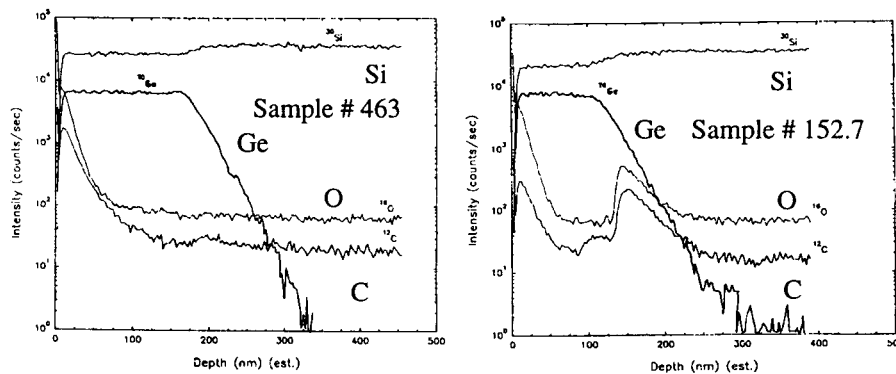


Fig. 1 SIMS profiles of C, O, Ge and Si of Samples # 463 and # 152.7

Table 1 summarises the type of cleaning per sample and the SIMS results of interfacial contamination. The interfacial C and O contents are given as a percentage of a monolayer ( $6.78 \times 10^{14}$  atoms/cm<sup>2</sup>) with detection limits for C and O of  $1 \times 10^{11}$  and  $1 \times 10^{12}$  atoms/cm<sup>2</sup> resp. Furtheron, a short description of the interface structure as observed in TEM is added. Fig. 2 shows TEM cross-sectional images of a number of samples.

For the cases with in-situ native oxide removal at really high temperature ( $> 1000$  °C, samples CNET 25 and IMEC b), a very clean interface not detectable at all in SIMS or TEM is observed. A bake at slightly lower temperature (900 °C in UHV or low H<sub>2</sub> pressure) still does its job, although a minor contamination becomes visible. The MBE systems seem to have a slight problem with C, which probably is due to i) in-situ contamination and ii) too low bake temperatures to drive the C into the substrate. A trial at CNET to lower this temperature by introducing a



Table 1. Overview of samples, cleaning and SIMS results

| Partner                                    | Sample | System | Cleaning                                   | C*    | O*   | TEM interface             |
|--------------------------------------------|--------|--------|--------------------------------------------|-------|------|---------------------------|
| <i>In-situ removal of the native oxide</i> |        |        |                                            |       |      |                           |
| CNET                                       | 24     | RTCVD  | 850 °C 1' H <sub>2</sub> +GeH <sub>4</sub> | 1.6   | 550  | thick line                |
| CNET                                       | 25     | RTCVD  | 1100 °C 20 torr H <sub>2</sub>             | 0.0   | 0.0  | no TEM                    |
| CNET                                       | 463    | UHVCVD | 900 °C 1' H <sub>2</sub>                   | 0.1   | 0.0  | not visible               |
| DIMES                                      | 152.10 | SSMBE  | 900 °C 10' UHV                             | 0.7   | 0.0  | no TEM                    |
| DIMES                                      | 150.7  | SSMBE  | 700 10', 900 10' UHV                       | 7.4   | 0.7  | no TEM                    |
| DIMES                                      | 152.9  | GSMBE  | 900 °C 10' UHV                             | 4.4   | 0.0  | line                      |
| DIMES                                      | 198.5  | GSMBE  | 900 °C 10' UHV                             | 0.1   | 0.0  | no TEM                    |
| DIMES                                      | 198.6  | GSMBE  | 900 °C 10' UHV                             | 0.6   | 0.0  | no TEM                    |
| DIMES                                      | 198.7  | GSMBE  | 900 °C 10' UHV                             | 1.5   | 0.0  | no TEM                    |
| ISI-KFA                                    | 832-o  | LPCVD  | 900 °C 10' H <sub>2</sub>                  | 29.5  | 1.5  | interrupted, precipitates |
| Philips                                    | a      | SSMBE  | 900 °C 5' UHV                              | 7.4   | 29.5 | weak line                 |
| IMEC                                       | b      | APCVD  | 1150 °C 90" 1 bar H <sub>2</sub>           | 0.0   | 0.0  | not visible               |
| <i>RCA + HF dip before loading</i>         |        |        |                                            |       |      |                           |
| DIMES                                      | 152.7  | GSMBE  |                                            | 7.4   | 4.4  | line                      |
| DIMES                                      | 152.8  | SSMBE  | 300 °C 60' UHV                             | 14.8  | 59.0 |                           |
| DIMES                                      | 197.3  |        |                                            | 88.5  | 103  |                           |
| IMEC                                       | 675    | UHVCVD | 2% HF 30" no rinse                         | 5.9   | 4.4  | interrupted               |
| IMEC                                       | 568    | UHVCVD | 2% HF 30" no rinse                         | 0.7   | 7.4  | interrupted               |
| IMEC                                       | 773    | UHVCVD | 2% HF 30" no rinse                         | 1.5   | 1.5  | weak line                 |
| IMEC                                       | 774    | UHVCVD | 2% HF 30" no rinse                         | 0.6   | 3.7  | weak line                 |
| ISI-KFA                                    | 832-m  | LPCVD  |                                            | 175.0 | 29.5 | line                      |
| ISI-KFA                                    | 928    | LPCVD  | no heating                                 | 19.2  | 14.8 | no TEM                    |

\* in percent of a monolayer

small flow of GeH<sub>4</sub> in order to reduce the SiO<sub>2</sub> into more volatile GeO didn't result in the expected clean interface. Alternatively, the pre-epi HF dip not followed by an in-situ high T bake results in slightly higher C and O levels, visible for TEM as a line at the interface. It should be realised that this line, although continuous on the cross-sectional image, probably is the result of a superposition of separate islands in the (rather thick) TEM sample on the image plane. There is a clear correlation between the intensity of this line and the contamination level as measured by SIMS. A remarkable observation on the TEM images is the absence of any extended crystalline defect in connection with that interfacial line.

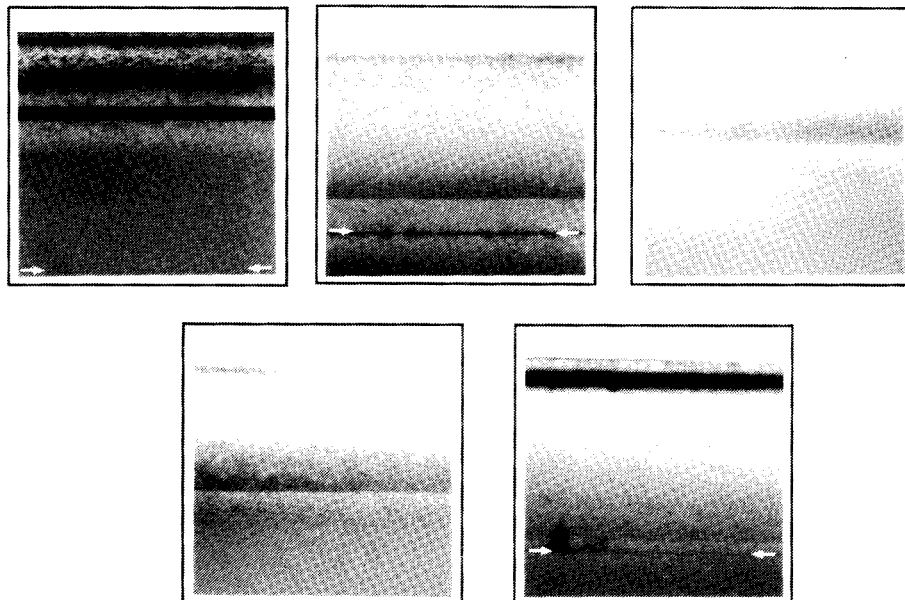


Fig. 2 x-TEM of Samples IMEC 774, ISI-KFA 832.m, DIMES 152.7, CNET 463, Philips a (the arrows indicate the interface)

About the ISI-KFA samples, it has to be mentioned that the more important interface contamination found in these LPCVD layers is likely due to the loadlock : the transport stick is only sealed by means of O-rings, such that during transport, the sliding movement creates a leak allowing air to enter into the system (the pressure rises from  $10^{-5}$  to  $10^{-2}$  torr during loading). An interface, created by growing a second epi-layer on a previous one without taking the sample out of the reactor (even after many hours without growth), is not detectable by SIMS.

According to RBS channeling experiments, there are no real problems with the crystalline structure : all samples show less than 4 % back scattering minimum yield, in accordance with the X-TEM observations.

Photoluminescence measurements have been carried out on all samples. Although many features were observed, no systematic correlation between interface contamination and PL could be established.

In conclusion, we can say that with both cleaning methods, high quality epitaxial Si can be grown. Still, a perfectly clean interface can be produced only by methods using high bake temperatures. On the other hand, when one has to avoid high temperatures, an ex-situ HF dip before epi combined with very clean working conditions (chemicals, environment, reactor background,...) is the method of choice. A general conclusion seems to be that the combination of low temperature and perfect cleanliness appears very difficult.

#### ACKNOWLEDGEMENTS

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## Dry Cleaning of Cu, Ni and Fe from Silicon and Oxide Surfaces at Room Temperature

Jane P. Chang<sup>\*</sup>, Zhe Zhang<sup>\*</sup>, Han Xu<sup>†</sup>, Herbert H. Sawin<sup>\*</sup>  
and Jeffery W. Butterbaugh<sup>\*\*</sup>

### 1. INTRODUCTION

Copper, nickel and iron contamination of silicon surfaces before furnace processes can affect device yield and/or performance. Dry cleaning processes are being developed to remove these contaminants and possibly to replace the conventional wet etching process as the feature sizes shrink down to quarter-micron range. Dry cleaning methods such as the thermal beams described here, can be incorporated into an integrated cluster system and also reduce the chemical consumption. Thermal beams have previously been demonstrated to achieve highly selective, anisotropic and almost damage-free etching<sup>1</sup>. A mixture of dichlorosilane (DCS) and F<sub>2</sub> beam at 1000°C was shown to remove monolayer metallic contamination to below the detection limit of the X-ray Photoelectron Spectroscopy (XPS) and left the surface terminated with fluorine after process.

### 2. EXPERIMENTAL SETUP

The apparatus used in this work has been described previously<sup>2</sup> and is shown in Fig. 1. In the UHV analytical chamber, XPS was used to analyze and determine sample surface compositions. The analytical chamber is also equipped with an ion gun for sputter cleaning samples and metal targets (1 cm square metal foils of Cu, Ni, Fe, and other materials) for controlled contamination of the sample surface. Atomic Force Microscopy (AFM) is available *ex situ* for surface roughness studies.

The multiple beam chamber is connected to the analytical chamber by vacuum corridors through which samples can be transferred while maintaining base pressures in the 10<sup>-8</sup> Torr range. The thermal beam source generates neutral radicals pyrolytically. The gas flow through the beam tube is rarefied during operation making the pyrolysis a surface mediated process. Beam tube temperatures up to 1200°C can be achieved to dissociate or excite gas molecules such as fluorine and dichlorosilane. In this work, the ClF<sub>3</sub> was used at room temperature. The specialty gases used in this work are: 99.0% ClF<sub>3</sub>, 99.99% SiH<sub>2</sub>Cl<sub>2</sub>, 98% F<sub>2</sub> and 99.5% Cl<sub>2</sub>. The surface flux level produced by the beam is approximately 1-5×10<sup>16</sup> cm<sup>-2</sup> s<sup>-1</sup>. Etching and deposition rates were measured by laser interferometry.

Both n-type and intrinsic polysilicon samples were studied in this work. A pristine silicon surface was generally yielded by *in situ* argon ion sputtering to

<sup>\*</sup> Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

<sup>†</sup> ULVAC Technologies Inc., Andover, MA 01810

<sup>\*\*</sup> FSI International, Chaska, MN 55318

remove the native oxide. Silicon samples with native oxide were pre-cleaned with ethanol before insertion into the chamber.

Metal contamination was sputter deposited on the sample surface using a 3 kV Ar ion beam. The amount of metal deposited on the sample surface was controlled by deposition time and detailed calibration can be found in the work of Lawing<sup>3</sup>.

### 3. RESULTS AND DISCUSSION

The focus of this paper is on copper removal from both Si and SiO<sub>2</sub> surfaces. The additive of silicon bearing species such as DCS is inspired by the previous study of metal removal with a chlorotrifluoride (ClF<sub>3</sub>) beam<sup>4</sup>. ClF<sub>3</sub> removed metal contaminant in conjunction with the etching of the underlying substrate. It removed dispersed copper, but failed to remove the copper island at room temperature. The results suggest that a volatile silicon bearing species (e.g. a copper-fluoro-silyl compound) was formed in order to achieve the copper removal.

#### 3.1 Sequential SiCl<sub>2</sub> and ClF<sub>3</sub> Studies

Sequential exposure of DCS and ClF<sub>3</sub> was studied as a way to simultaneously etch the deposited silicon film and remove copper remaining on the surface. Copper contamination on the order of a monolayer was used. All the measurable copper was removed using this sequential DCS deposition and ClF<sub>3</sub> etching process, as shown in Fig. 2. The surface was highly terminated by fluorine after this process. The AFM scan of the etched sample showed no copper island feature after this process and no surface roughening by this process.

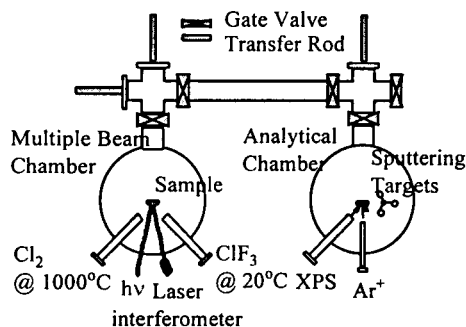


Fig.1: Experimental Setup

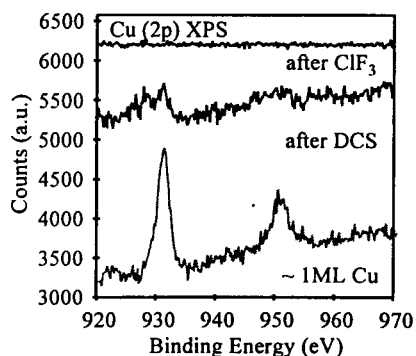


Fig. 2: XPS signals for the Cu (2p) emission

The most important aspect of this DCS/ClF<sub>3</sub> process is its ability to achieve complete metal removal with the sample at room temperature. Lower sample temperature is preferred in semiconductor fabrication due to the fact that higher temperature can induce diffusion which in turn significantly influences the quality and performance of devices.

To better understand whether fluorine or chlorine dominates the copper removal process,  $\text{Cl}_2$  and  $\text{F}_2$  are then used in conjunction with DCS. The inhibition of DCS deposition is expected since both fluorine and chlorine atoms have been shown to etch heavily doped n-type polysilicon spontaneously<sup>5</sup>.

### 3.2 Simultaneous $\text{SiCl}_2$ and Cl Beam Studies

A combined beam of DCS and  $\text{Cl}_2$  was used to make a non-depositing source to remove copper. Copper contamination on the order of half a monolayer was used. Zero deposition was not achieved at a  $\text{Cl}_2$  to DCS ratio of six. Approximately 8-15 Å deposition was always observed. Appreciably copper remained on the surface, suggesting that the copper was embedded by the deposited  $\text{SiCl}_2$  film.

In the attempt to use  $\text{SiCl}_4$  as a dry cleaning gas in a UV/ $\text{Cl}_2$  reactor, Sugino<sup>6</sup> reported 90% removal efficiency of Fe from both Si (with native oxide) and  $\text{SiO}_2$  surfaces at above 350°C. By adding  $\text{Cl}_2$  to  $\text{SiCl}_4$ , complete removal of Fe is observed from silicon surface but not  $\text{SiO}_2$  surface. They suggested that chlorine radicals penetrates the native oxide (but not thermal oxide) to react with silicon and form incomplete silicon chloride ( $\text{SiCl}_{1.3}$ ), which in turn diffuses out, reacts with residual Fe and vaporizes.

### 3.3 Simultaneous $\text{SiCl}_2$ and F Beam Studies

A combined beam of DCS and  $\text{F}_2$  were then studied based on the distinct difference in copper removal efficiency between DCS/ $\text{ClF}_3$  and DCS/ $\text{Cl}_2$ . No measurable amount of copper was observed after processing, as shown in Fig. 3. Deposition of DCS was prevented by increasing the  $\text{F}_2$  flowrate with respect to DCS and reducing the exposure time. The sample surface was highly terminated with fluorine.

Comparing the results of copper removal using sequential DCS/ $\text{ClF}_3$ , with mixtures of DCS/ $\text{Cl}_2$  and DCS/ $\text{F}_2$ , we conclude that the fluorine atom plays an important role in copper removal by forming a copper-fluoro-silyl complex.

### 3.4 Removal of other metals: Ni and Fe

Since nickel, iron and copper are all transition metals with the similar electronic configuration, the mechanism proposed for copper removal has a great potential to be applied to the removal of nickel and iron contamination. The calibration of Ni and Fe contamination can be found elsewhere<sup>2</sup>.

Approximately one monolayer of nickel contamination was sputter deposited and exposed to a DCS/ $\text{F}_2$  mixture at a ratio of 1:4. No measurable nickel was detected after the cleaning process, as shown in Fig. 4. The result again suggests the formation of the volatile nickel-fluoro-silyl compound since nickel halides are not even as volatile as copper chloride. Repeat experiments have been performed to verify the reproducibility.

This DCS/F<sub>2</sub> process was also applied to remove iron. Approximately one to two monolayer of iron contamination was sputter deposited on an oxide sample surface and exposed to a DCS/F<sub>2</sub> mixture at a ratio of 1:4. Shown in Fig. 5 is the XPS spectra for Fe(2p) before and after the cleaning process. Since iron is more easily oxidized than copper or nickel, it is partially oxidized after deposition on the wafer surface. The peaks at 707, 709, 713 eV represent the Fe(0), Fe(II), Fe(III). All the measurable iron has been removed after 5 seconds of DCS/F<sub>2</sub> processing. Obviously, DCS/F<sub>2</sub> beam processing has the same effect on removing metal regardless the oxidation state.

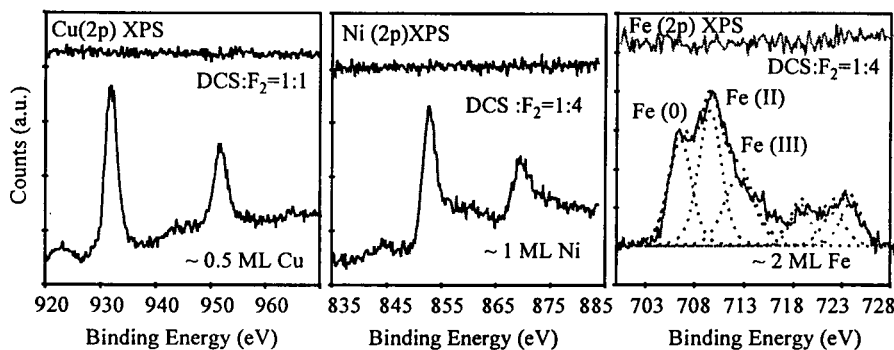


Fig. 3: Cu (2p) XPS spectra

Fig. 4: Ni (2p) XPS spectra

Fig. 5: Fe (2p) XPS spectra

#### 4. CONCLUSION

Removal of copper contamination at room temperature has been demonstrated. Sequential DCS and ClF<sub>3</sub> processing demonstrates copper removal to below the detection limit of the XPS by etching the deposited silicon layer. AFM scans show no surface roughening by this process. Utilizing DCS/Cl<sub>2</sub> and DCS/F<sub>2</sub> mixtures indicates that the fluorine atom plays an important role in copper removal. DCS/F<sub>2</sub> achieves complete copper removal at room temperature and suppresses the silicon deposition rate. DCS/F<sub>2</sub> also removes Ni and Fe from a native oxide surface at room temperature.

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## OXIDE REGROWTH BY SHORT APM EXPOSURES - FLASH™ APM

K. K. Christenson\* and B. Carlson\*

### 1. INTRODUCTION

It has been demonstrated recently that the DHF, and not the APM, is primarily responsible for particle removal in the B Clean chemistry sequence in a spray processor.[1] The typical 1.5 to 3 minute, warm APM dispense serves primarily to regrow a chemical oxide on the silicon. (Hot, 5 minute APM dispenses are effective; removing over 99% of Si<sub>3</sub>N<sub>4</sub> particles larger than 0.15 microns.[2] Since the oxide regrowth process occurs very quickly, the APM exposure time can be reduced which reduces the chemical usage. Further, the surface roughening and the metals deposited on the wafer scale with the APM exposure time.[3] Short, cold APM exposures result in smoother surfaces with lower metals levels. This study investigates the use of short, cold and dilute APM solutions for oxide regrowth.

### 2. EXPERIMENTAL

*Beaker Tests:* 150 mm, 0-100  $\Omega$ -cm, p type, (100) wafers were precleaned in a B Clean chemistry sequence in a MERCURY® MP Spray Acid Processor (Table 1). The chemical oxide was removed by dipping the wafers for 30 seconds in HF diluted 10:1 by volume followed by a DI water rinse. Any remaining water drops on the hydrophobic surface were blown off with N<sub>2</sub>. Wafers were then dipped for various lengths of time in a standard or dilute solution of APM at 20° C.

*Spray Processor Tests:* The chemical oxide was removed from precleaned wafers as a group with the SPM/HF portion of the S/2HF/FLASH/H process sequence in the spray processor. Wafers were then individually exposed to the APM/HPM portion of the S/2HF/FLASH/H process with APM exposure times ranging from 10 to 600 seconds at 20° C. Ashland "SEMI" grade chemicals were used throughout the experiment. All oxide thickness measurements were made with a Gaertner L104B ellipsometer.

### 3. RESULTS

Figure 1 shows the oxide thickness for a range of APM blend ratios and exposure times in a beaker and a spray processor. Blend ratio and exposure method have little effect. The oxide is near full thickness after 20 seconds.

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\* FSI International, 322 Lake Hazeltine Dr., Chaska, Minnesota 55318

| RECIPE TIME             | SPM Sec. Blend | DHF Sec. Blend | APM Sec. Blend       | HPM Sec. Blend   | H <sub>2</sub> SO <sub>4</sub> Use cc | HF Use cc | H <sub>2</sub> O <sub>2</sub> Use cc | NH <sub>4</sub> OH Use cc | HCl Use cc | Total Use cc |
|-------------------------|----------------|----------------|----------------------|------------------|---------------------------------------|-----------|--------------------------------------|---------------------------|------------|--------------|
| B Clean 33:50           | 70<br>4:1      | 90<br>100:1    | 190<br>0.5:1:6       | 90<br>1:1:6      | 900                                   | 30        | 1,660                                | 410                       | 460        | 3,460        |
| B Clean (w/o HPM)       | 70<br>4:1      | 90<br>100:1    | 190<br>0.5:1:6       | ---              | 900                                   | 30        | 1285                                 | 410                       | ---        | 2,625        |
| Beaker Tests - Standard | ---            | 30<br>10:1     | 0 - 600<br>0.5:0.5:6 | ---              |                                       |           |                                      |                           |            |              |
| Beaker Tests - Dilute   | ---            | 30<br>10:1     | 0 - 600<br>0.1:0.1:6 | ---              |                                       |           |                                      |                           |            |              |
| Flash B 30:05           | 70<br>4:1      | 90<br>100:1    | 30<br>0.13:0.2:6     | 70<br>0.2:0.2:6  | 900                                   | 30        | 725                                  | 50                        | 290        | 1,995        |
| Flash B (w/o HPM)       | 70<br>4:1      | 90<br>100:1    | 30<br>0.13:0.2:6     | ---              | 900                                   | 30        | 400                                  | 50                        | ---        | 1,380        |
| S/2HF/FLASH/H 29:25     | 90<br>4:1      | 140<br>100:1   | 20 sec<br>0.1:0.1:6  | 150<br>0.5:0.5:6 | 750                                   | 45        | 480                                  | 65                        | 210        | 1,550        |
| S/2HF/3A/H 31:50        | 90<br>4:1      | 140<br>100:1   | 190<br>0.5:0.5:6     | 100<br>0.5:0.5:6 | 750                                   | 45        | 690                                  | 410                       | 250        | 2,145        |

Table 1: Exposure Times, Blend Ratios and Chemical Consumption for Process Sequences



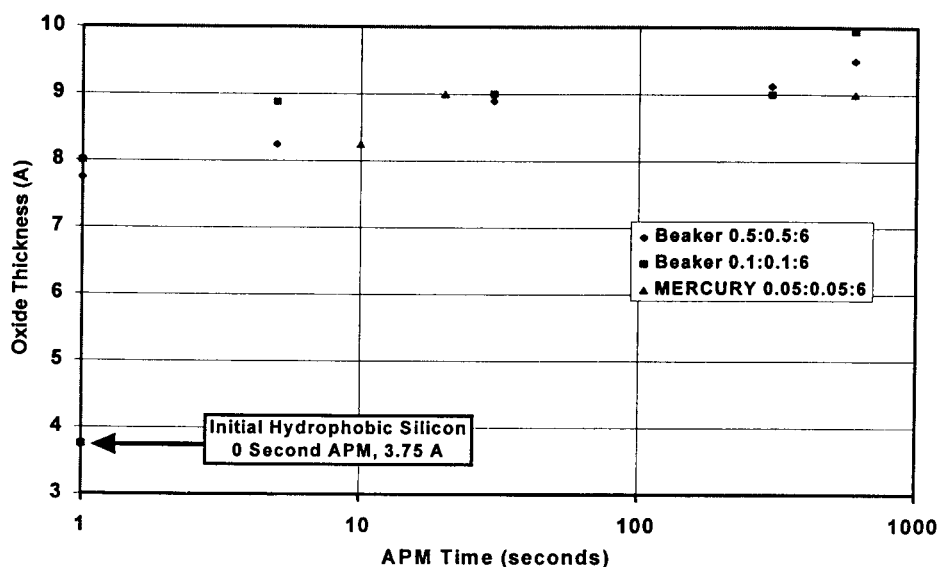


**Figure 1: Oxide Thickness vs APM Exposure Time**

Table 2 shows the metals results for B Clean chemistry sequences with short (flash) and normal APM times and with and without an HPM treatment (w/o HPM) after the APM exposure. With the exception of calcium, the metals levels after the FLASH™ APM exposure are significantly lower than those after the standard APM. In both cases, the final HPM treatment reduced the Al and Ca to near the 0.25 micron device requirements and the Fe, Ni, Cu and Zn to the 0.18 micron device requirements.

| Recipe                     | Al<br>V/I | Ca<br>V/T | Fe<br>V/T | Ni<br>V/T | Cu<br>V/T | Zn<br>V/T |
|----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| B Clean                    | 7.9       | 0.5       | 0.02      | 0.2       | 0.005     | 0.09      |
| B Clean (w/o HPM)          | 260       | 4         | 8         | 0.90      | 0.2       | 30        |
| Flash B                    | 6.7       | 3         | 0.9       | 0.30      | 0.04      | 0.20      |
| Flash B (w/o HPM)          | 18        | 7         | 0.9       | 0.40      | 0.04      | 9.0       |
| S/2HF/3A/H                 | <2        | 1         | 0.04      | 0.09      | 0.009     | 0.3       |
| SIA Roadmap<br>0.25 micron | 5         | 5         | 2.5       | 2.5       | 2.5       | 2.5       |

**Table 2: Metal Levels** Surface concentration of metals in units of  $10^{10}/\text{cm}^2$  using Ashland “SEMI” grade chemicals. “V/I”: VPD-ICP-MS measurements at Balazs Laboratory. “V/T”: VPD-TXRF measurements at Charles Evans and Assoc.

The abnormally high Ca levels may be due to a problem with the DI water system during the experiment. The higher post HPM metals levels in the FLASH B process vs the B Clean process may be due to the shorter, more dilute HPM used in the FLASH B. Higher grade chemicals should reduce the final metals levels substantially.

Table 1 shows the total chemical consumption and process times for the recipes. Compared to the standard B Clean, the S/2HF/FLASH/H process sequence reduces total chemical consumption from 3,460 cc to 1,550 cc and the process time from 33:50 to 29:25.

#### 4. CONCLUSIONS

Incorporating a FLASH APM exposure into the B Clean chemistry sequence can result in a 55% reduction in chemical usage along with a 4:25 reduction in cycle time while still meeting the 0.25 micron device requirements for both particle removal and metals with SEMI grade chemicals.[1] Introducing a FLASH APM in the S/2HF/FLASH/H should improve the present 0.18 micron metals performance to 0.13 micron levels. The FLASH process requires no equipment modifications and can be implemented on any generation of spray processor.

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<sup>3</sup> metals dep

## COMPARISON OF $\text{Si}_3\text{N}_4$ DEPOSITION TECHNIQUES FOR USE IN PARTICLE REMOVAL EXPERIMENTS\*

P.J. Clews\*\*, L.C. Petersen\*\*, K.K. Christenson\*\*\*, C.A. Matlock\*\*

### 1. INTRODUCTION

As device critical dimensions decrease in size it becomes increasingly important to remove particles from the wafer surface so they do not impact device yield. A typical method to evaluate various cleaning techniques is to deposit silicon nitride ( $\text{Si}_3\text{N}_4$ ) particles on the wafer surface and then process the wafers through the desired cleaning processes. The National Technology Roadmap for Semiconductors specifies the standard challenge for percent particle removal from silicon wafers to be based on "> 1000 nitride particles" added to the wafers [1]. However, it does not specify the deposition technique to be used for the  $\text{Si}_3\text{N}_4$  particles. Two common methods used to deposit  $\text{Si}_3\text{N}_4$  on silicon test wafers are the aerosol deposition technique [2-3] or the wet dip deposition technique [4-5]. A comparison between these two  $\text{Si}_3\text{N}_4$  deposition methods to determine if these methods create an equivalent particle removal challenge has not been reported in the literature to date. In this paper we compare these two deposition techniques. We found advantages and disadvantages for both deposition methods. The preferred method for particle deposition is dependent on the specific application.

### 2. EXPERIMENTAL DETAILS

Six-inch n-type silicon wafers (resistivity 2.0 to 20.0 ohms) were pre-cleaned using a 1:4:65 SC-1 ( $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) at 45°C to establish the same initial starting conditions on all wafers. This SC-1 clean was performed in a Verateq chain drive focus beam megasonic tank using 250 watts of power.  $\text{Si}_3\text{N}_4$  particles were deposited on the wafers using either a wet dip deposition technique or an aerosol deposition technique. In the aerosol deposition technique,  $\text{Si}_3\text{N}_4$  particles are added to the wafer surface by aerosolizing a 0.005 wt.% suspension of AESAR  $\text{Si}_3\text{N}_4$  particles in a constant output atomizer. The  $\text{Si}_3\text{N}_4$  particle suspension is agitated in a Branson 2200 ultrasonic bath for 5 minutes before it is aerosolized. This aerosolized particle stream is passed through a cascade impactor to remove the larger particles. Deposition is performed by exposing one wafer at a time to this particle stream in front of a nozzle. In the wet dip deposition technique, a 0.02 wt.% suspension of  $\text{Si}_3\text{N}_4$  particles is agitated in the ultrasonic bath for 5 minutes to break up the large agglomerates. The large particles in this solution are removed by allowing this suspension to settle for 1 hour before decanting the top half of the liquid into another bottle. This top liquid is agitated ultrasonically for 5 minutes immediately before diluting a few milliliters of this suspension with 16 liters of

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\*\* Sandia National Laboratories, Albuquerque, NM USA

\*\*\* FSI International, Chaska, MN USA

deionized water. A full boat of 25 wafers is then agitated in this extremely dilute  $\text{Si}_3\text{N}_4$  suspension for the amount of time required to deposit the desired number of particles and then rinsed in a quick dump rinse (5 cycles) followed by a spin dry step. A test wafer is used to determine the required deposition time. The deposition rate during the wet dip technique decays over time, therefore some practice is needed to achieve the desired number of particle counts. Both deposition techniques were performed on the same day to eliminate differences in aging effects. All depositions were performed within two hours after the SC-1 pre-clean was completed to make particle removal more difficult [4].

In order to determine if the two deposition techniques create an equivalent particle removal challenge, the wafers of each deposition type were processed through a deionized water rinse step at the times specified in Table 1. This rinse step was performed in a standard quick dump rinse tank using 5 dump cycles to remove the loosely adhered particles. One week after the particles were deposited, all wafer splits, shown in Table 1, were cleaned in a moderate 1:4:30 SC-1 at 60°C with no megasonic power applied during the clean. This non-optimized clean is a more aggressive clean than the water rinse step but was not designed to remove all of the particles. The SC-1 clean was used to determine if there is any difference in how tightly bound the particles are to the silicon surface for all splits shown in Table 1. The particle removal efficiencies for the water rinse and moderate SC-1 steps were calculated to compare particle adhesion forces. Particle counts (>0.13 microns) were measured using a Tencor Surfscan® 6200.

**Table 1.** Description of wafer splits used in experiment.

| Description of Split | Deposition Method | Elapsed time between particle deposition and water rinse step. |
|----------------------|-------------------|----------------------------------------------------------------|
| Aerosol (no rinse)   | Aerosol           | No rinse performed                                             |
| Aerosol (ASAP)       | Aerosol           | As soon as possible after deposition (< 1 hour)                |
| Aerosol (3 day)      | Aerosol           | 3 days after deposition                                        |
| Wet (no rinse)       | Wet               | No additional rinse following deposition                       |
| Wet (3 day)          | Wet               | 3 days after deposition                                        |

### 3. EXPERIMENTAL RESULTS

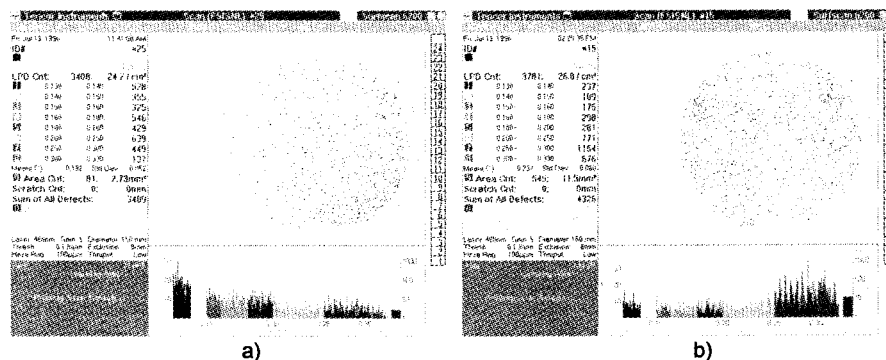


**Figure 1.** Representative Surfscan® 6200 wafer maps for a) aerosol & b) wet deposition techniques.

The wafer maps in Figure 1a and 1b illustrate that the wet deposition technique produces a more uniform particle distribution across the entire wafer surface. The histograms, also shown in Figure 1a and 1b, indicate that the wet deposition technique adds significantly more larger size  $\text{Si}_3\text{N}_4$  particles than the aerosol deposition technique. A full boat of wafers can be coated using the wet deposition technique so the particle counts on all wafers in the boat are more consistent than the aerosol deposition technique, which coats one wafer at a time. See box plot shown in Figure 2.

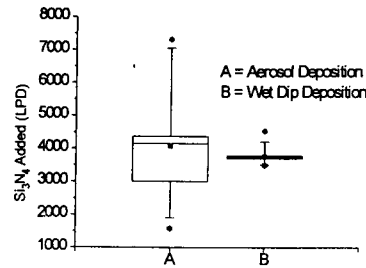


**Figure 2.** Box plot of the number of  $\text{Si}_3\text{N}_4$  particles added vs. particle deposition technique.

Percent particle removal efficiencies for the water rinse ( $E_{\text{rinse}}$ ) and SC-1 clean ( $E_{\text{SC1}}$ ) are calculated by using Equations 1 and 2.  $C_0$  is the background particle count on the wafers before  $\text{Si}_3\text{N}_4$  was deposited,  $C_1$  is the post  $\text{Si}_3\text{N}_4$  deposition count,  $C_2$  is the post water rinse particle count and  $C_3$  is the post SC-1 clean particle count. If all particles are removed the removal efficiency is 100 %.

$$E_{\text{rinse}} = [(C_1 - C_2) \div (C_1 - C_0)] \times 100 \quad (1)$$

$$E_{\text{SC1}} = [(C_2 - C_3) \div (C_2 - C_0)] \times 100 \quad (2)$$

The box plot in Figure 3 shows the aerosol (3 day) wafer split has a lower particle removal efficiency during the water rinse step than the aerosol (ASAP) wafer split. This indicates that the aerosol deposited particles become more tightly bound to the wafer surface over time. None of the wet deposited particles were removed during the water rinse step. A box plot of the particle removal efficiencies obtained during the SC-1 clean step is shown in Figure 4. Aerosol deposited wafers which were cleaned in SC-1 without a prior deionized rinse exhibited a particle removal efficiency of 94%. When a rinse was introduced immediately after the aerosol particle deposition, the particle removal efficiency dropped to 29%. Wafers which received a rinse three days after deposition achieved an intermediate removal efficiency of 57%. Apparently the water rinse step selectively removes the loosely bound aerosol deposited particles so that the particles remaining are the more difficult to remove particles. When the rinse step is delayed, fewer of the loosely bound particles are removed during the water rinse step because they become more tightly bound to the wafer surface over time. However, these intermediate particles can still be removed by the more aggressive SC-1 clean. The average particle removal efficiency in the SC-1 clean for the wet deposition wafers is 34% which is only slightly higher than the Aerosol (ASAP) wafers. The variability in the particle

removal efficiency data for the wet deposited particles is smaller than with the aerosol deposited particles and the removal efficiency is not dependent on the timing of a water rinse step.

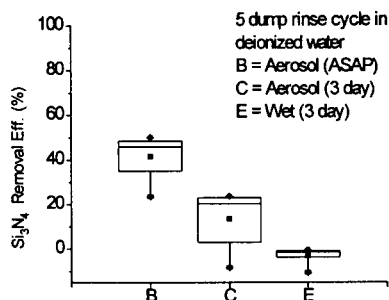


Figure 3. Box plot of particle removal efficiency following the water rinse step.

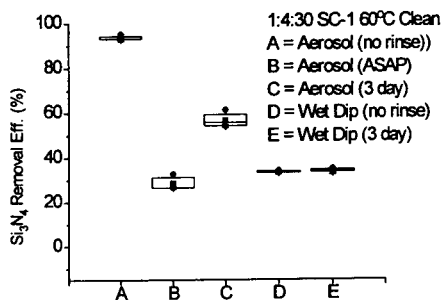


Figure 4. Box plot of the particle removal efficiency following the 1:4:30 SC-1 clean at 60°C.

#### 4. CONCLUSIONS

Adhesion of  $\text{Si}_3\text{N}_4$  particles to silicon wafers are similar for both wet deposited and aerosol deposited particles provided the wafers prepared by the aerosol deposition method are rinsed in deionized water immediately after particle deposition. Each deposition technique has advantages and disadvantages. The aerosol technique is very quick to perform if only a few wafers are required. This method also deposits smaller size  $\text{Si}_3\text{N}_4$  particles on the wafer surface. A water rinse step is required on the aerosol deposited wafers if a more difficult particle removal challenge is required. However, the time between aerosol deposition and water rinse step must be controlled to obtain a consistent particle removal challenge. The wet deposition technique provides a method to coat a large number of wafers with approximately the same number of particles added to each wafer and a very uniform distribution of the particles on the wafer surface. There are significantly more larger size particles added to the wet dip wafers than in an aerosol deposition. Variation in the particle removal efficiency for wet deposited particles is smaller than that for the aerosol deposited particles. The cost for deposition equipment is also lower for the wet deposition method. These advantages and disadvantages must be considered when selecting the  $\text{Si}_3\text{N}_4$  deposition method to be used.

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## ROUGHNESS IN HYDROPHOBIC OR HYDROPHILIC (100) SILICON SURFACES INDUCED BY HF(1%) SOLUTION DURING RCA CLEANING

G. Franco<sup>\*</sup>, C.M. Camalleri<sup>\*</sup>, V. Raineri<sup>\*\*</sup>

Different surface morphologies were obtained on (100) silicon wafers by modified RCA cleaning. In hydrophobic surfaces a high frequency roughness component was measured while only low frequency components were obtained for hydrophilic surface. These surfaces originate different characteristics in thin gate oxide tunneling behaviour demonstrating the importance of surface morphology.

### 1. INTRODUCTION

Recently, the importance of silicon surface roughness has been demonstrated to affect the properties of materials (thin oxide, grown layers) or devices (surface scattering in CMOS, tunneling current in flash EEPROM), and many efforts have been produced to reduce its value [1,2]. In particular, the cleaning procedure is indicated as one of the main processes to control surface roughness, due either to the silicon surface itself or to particles present on it [3]. Previous analyses demonstrated that surface roughness at values less than 6 nm does not influence the tunneling characteristics of thin gate oxide [4]. Aim of our work is to demonstrate that the surface morphology is a quite important aspect with respect to the roughness absolute value, and, at low RMS, it becomes predominant influencing the gate oxide characteristics.

### 2. EXPERIMENTAL PROCEDURE AND RESULTS

Different surface morphologies were obtained by using several cleaning processes, as shown in the tapping mode atomic force microscope images of Fig. 1. In the standard RCA cleaning an HF(1%) dip was added after the SPM step. This cleaning process, referred as RCA, is compared with a cleaning procedure where extra HF(1%) treatments were introduced during a modified RCA cleaning (SC1 and SC2 steps are inverted) to produce a hydrophilic surface (clean C) or with a RCA cleaning with a final step in HF(1%) to obtain a hydrophobic silicon surface

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<sup>\*</sup>SGS-Thomson microelectronics - Stradale Primosole, 50 - I95121 Catania, Italy.

<sup>\*\*</sup>CNR-IMETEM - Stradale Primosole, 50 - I95121 Catania, Italy.

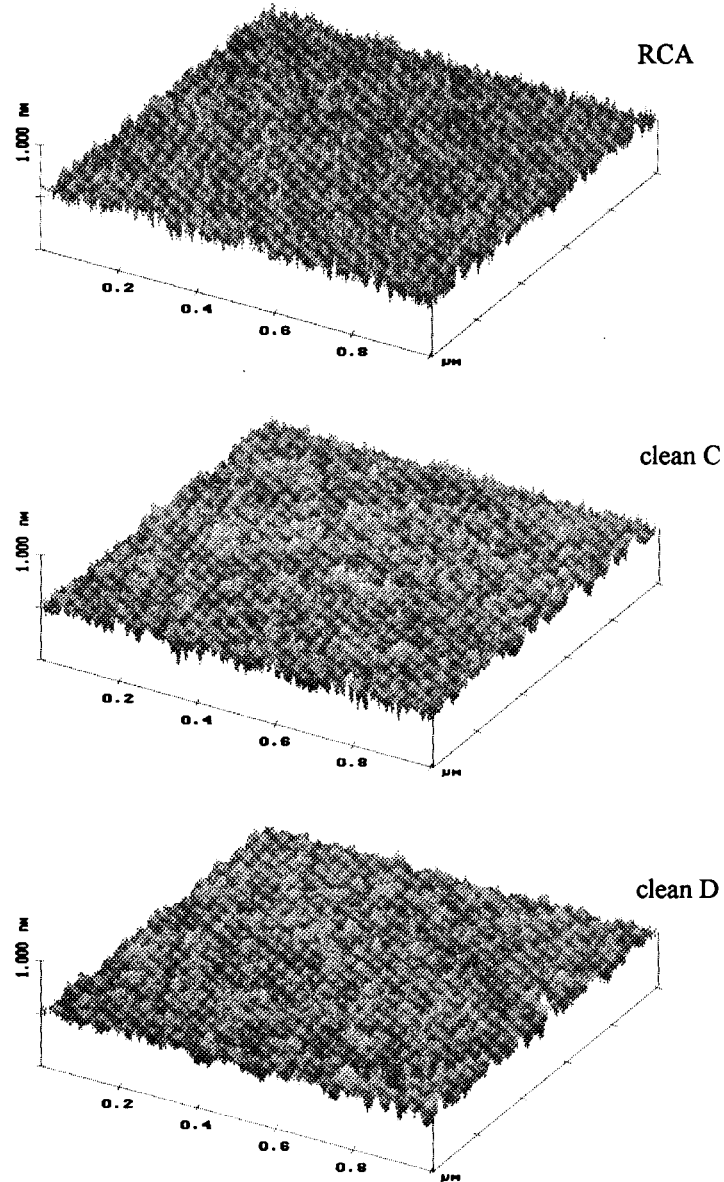


**Fig. 1 - AFM on Si (100) surface after different cleaning procedures.**

(D). The total time of immersion in HF(1%) diluted solution was maintained the same in all cleaning procedures.

In all cases the roughness value ( $\text{RMS}=0.031 \text{ nm}$ ), measured by atomic force microscopy in tapping mode configuration, is the same. However, the surface morphology is clearly different (see Fig.1) as can be quantitatively obtained by the depth distribution (Fig. 2) and by the power spectral density (see Fig. 3) analyses of the images. In the case of clean C and D a narrow depth distribution is obtained. In the power spectral density the high frequency component refer to real atomic



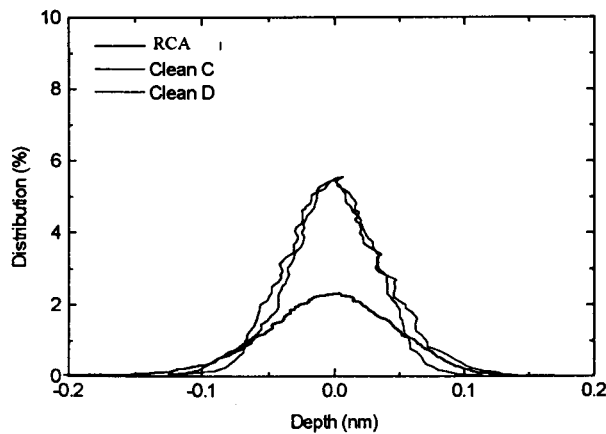


Fig. 2 - Depth distribution of images high for the different cleaning procedures

particles ( $>0.24 \mu\text{m}^2$ ) was obtained in the case of clean D. A comparable number of particles was found in the case of clean C and standard RCA. Particles can be organic materials or metallic aggregates. Metals have a high diffusivity and, after thermal processes they move through the silicon wafer influencing the leakage of the wafer devices while organic contaminants remain confined at the surface. By measuring the leakage current in large area diodes ( $4 \times 36 \text{ cm}^2$ ), very sensitive to metal contaminants present in the junction region, we could identify the particles on the surface as metal contaminants stuck on the hydrophobic surface (see Fig.4).

Surface properties were investigated by grown very thin gate oxide (10-30 nm) and measuring their electrical characteristics. Fowler-Nordheim measurements versus the injected current on thin oxides (10, 20, 35 nm) suggested the relation of the

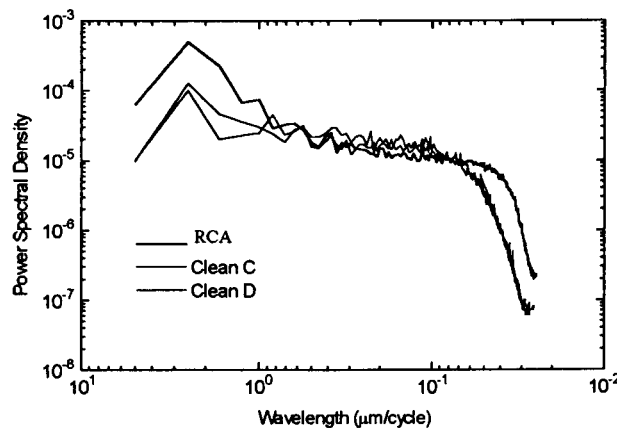


Fig. 3 -The power spectral density calculated for the different cleaning procedures.

dimensions, so that the decrease in high frequency component indicates a more stable surface chemical condition. Unstable surfaces can be charged due to the presence of dangling bonds, and the surface can attract particles. To separate the contribution of surface morphology from the particles present on it, we measured the number of particles by a surface scan light scattering equipment and a higher number of

oxide characteristics to surface morphology (see Fig.5). In fact, the same number of particles was measured for RCA and clean C, being the surface hydrophilic in both cases, while the only measured difference was in the surface morphology. The measurements clearly indicate a better behavior in the case of clean C (see Fig. 5). Being all the other surface characteristics

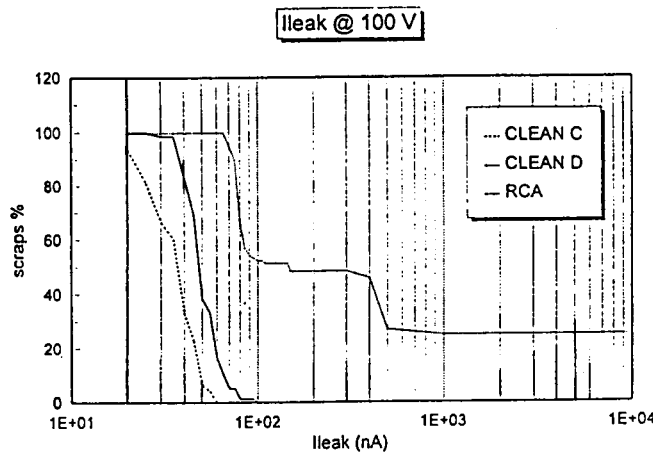


Fig. 4 - Leakage current in large area diodes.

measured on hydrophobic surfaces and it was related to the less chemical stability of them. The presence of hydrophilic surfaces with different morphologies does not influence leakage current of devices after thermal processes while tunnel characteristics of thin oxides grown on them.

the same we assume that the main reason of the oxide degradation is due to the different morphology.

### 3. CONCLUSION

Different surface morphologies were obtained on (100) silicon wafer by modified RCA cleaning procedures. An higher number of particles was

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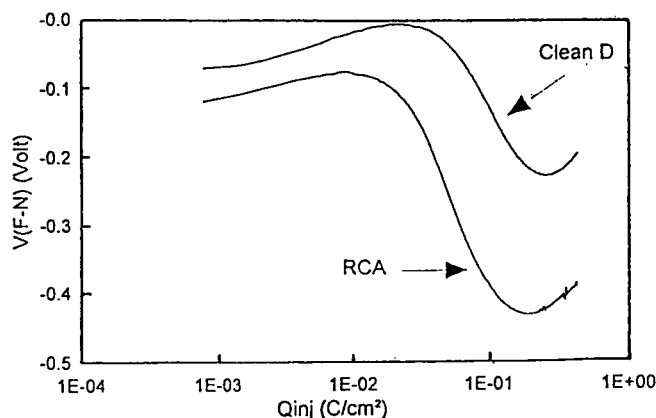


Fig. 5 - Fowler - Nordheim measurements versus injected current.

## Silicon Surface Roughening in an Iron Contaminated SC1 Bath

D. Martin Knotter,<sup>a\*</sup> Laurent Mouche,<sup>b,c</sup> Marc Meuris,<sup>b</sup> and Marc M. Heyns.<sup>b</sup>

### Introduction

The standard clean 1 (SC1) is an element of the RCA clean which is a procedure for the cleaning of silicon wafers during IC-manufacturing.<sup>1</sup> The SC1 solution consists of an Ammonium hydroxide and hydrogen Peroxide Mixture (APM) in water in a ratio of 1/1/5 (based on volumes of commercial available concentrations; ammonium hydroxide = 25% and hydrogen peroxide = 30%). The hydrogen peroxide oxidizes the silicon followed by the dissolution of the silicon dioxide by the hydroxyl anions. However, the concentration peroxide is that high that the silicon oxidation is anodically passivated.<sup>2</sup> Consequently, the SC1 solution etches the silicon slowly and homogeneously. A thin layer of a chemical oxide remains on the cleaned silicon surface.

A relation between the amount of metal ions present in the SC1 bath and the silicon surfaces roughening, which is said to have a negative influence on the gate oxide integrity, has been found.<sup>3,4</sup> Metals are incorporated in the chemical grown oxide and they catalyze the decomposition of the peroxide.<sup>5,6</sup> This latter can be observed by the oxygen evolving as bubbles. It has been found that hydrophobic wafers of which the surfaces were terminated with silicon hydride are more sensitive for metal-related surface roughening than hydrophilic silicon surfaces.<sup>3</sup> All these observation resulted in the conclusion that the surface roughening of hydrophobic wafers is due to the bubbles: The bubbles adhere to hydrophobic surfaces and mask it locally from the etching process.<sup>3</sup>

In this article results are presented to prove that the formation of bubbles and the surface roughening are caused by the same phenomena and that bubbles do not cause the observed surface roughness. A mechanism by which the roughening occurs is presented.

### Experimental

All chemicals and solvents used were with metal impurities lower than 0.1 ppb. Monitor wafers (n-type, [100] orientation, 150 mm diameter) were cleaned by immersion in a sulfuric acid/ hydrogen peroxide (5:1) mixture at 90°C for ten minutes. Subsequently, the wafers were rinsed in DI-water (10 minutes) and spin-dried in a spin-rinse drier. The oxide layer on the wafers was removed by a dip (10 minutes) in a 0.5% HF(aq) solution prior to the experiments. The SC1 solution was a mixture of ammonium hydroxide and hydrogen peroxide in water (1:1:5 ratio, respectively) at 70°C. Fe<sup>3+</sup> contaminated solvents were obtained by diluting a 1 ppm Fe(NO<sub>3</sub>)<sub>3</sub> stock solution.

\* Author to whom corresponds should be addressed

<sup>a</sup>Philips Research, Prof. Holstlaan 4 (WAG01), 5656AA Eindhoven, the Netherlands.

<sup>b</sup>IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>c</sup>On leave to Motorola, Toulouse, France

Surface morphologies were analyzed with a Censor ANS-100 and are denoted as Light Point defects (LPD). Total X-Ray Fluorescence (TXRF) measurements were done on an Atomica 8010 and the detection limits were lowered to  $10^9$  atoms  $\text{cm}^{-2}$  by the use of Vapor Phase Decomposition-Droplet Surface Etching (VPD-DSE).

## Results

Hydrophobic and hydrophilic wafers were dipped (within 1 second in and out) in a SC1 bath containing 1 w-bbp of  $\text{Fe}^{3+}$ . A part of the hydrophobic wafers was subsequently rinsed in DI-water (5 minutes). All wafers were hydrophilic after this dip and were dried with a nitrogen blow dry. The LPD's before and after dip were measured. It was found that the amount of LPD's only significantly increased on the formerly hydrophobic wafers. After a subsequent DI water rinse most of these LPD's are removed. The LPD's are typically clustered as stripes (see Figure 1). Since no LPD increase was observed on identically treated wafers from an unspiked SC1 bath, it can be concluded that these LPD's solely relate to the Fe-contamination. These results suggest that particles can selectively precipitate on hydrophobic wafers during their immersion into a Fe-spiked SC1 bath and these particles re-dissolve in DI-water.

In figure 2 the results are summarized of VPD-DSE-TXRF measurements of these wafers. After a dip in the Fe-spiked SC1 all wafers contained a basic amount of iron, i.e.,  $\pm 13 \cdot 10^{10}$  Fe at  $\text{cm}^{-2}$ , which is probably incorporated into the oxide layer.<sup>4</sup> On top of this, the formerly hydrophobic wafer (a) which had no subsequent water rinse, contained an amount of iron that strongly varied. If these wafers were subsequently rinsed (c), the extra amount of iron disappears which corresponds with the disappearance of the clustered LPD's. On the formerly

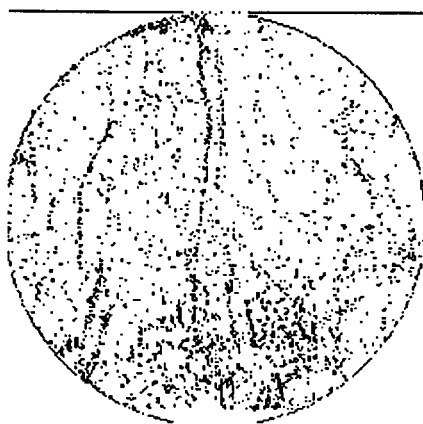


**Figure 1.** LPD plot of hydrophobic wafer dipped (1 s) in a decomposing, Fe-spiked SC1 solution.

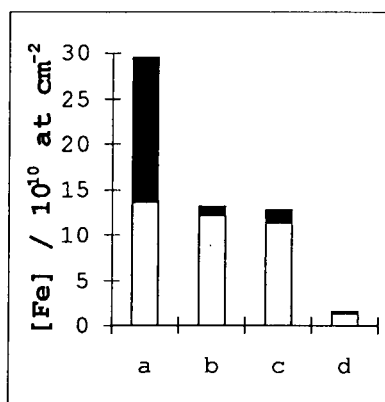


**Figure 2.** VPD-DSE-TXRF results where the measured data fall in the black area: a. hydrophobic wafer was dipped in spiked (1 w-ppb  $\text{Fe}^{3+}$ ) SC1 and blown dry (4 wafers measured); b. hydrophilic wafer was dipped in spiked SC1 and blown dry (3 wafers measured); c. as a. but after dip in SC1 5 minutes rinse in DI-water and dry (4 wafers measured); d. clean SC1 last (10 min. + 5 min. DI-water rinse) on one wafer of each previous series (3 wafers measured).

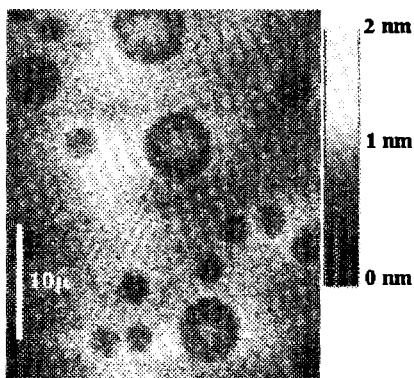


**Figure 3.** AFM picture of LPD's caused by selective etching.

hydrophilic wafers (b) no such clusters were deposited and no extra amount of iron was found. Furthermore, the amount of iron on all these wafers drops to a very low level after a clean in ultra-pure SC1. This was anticipated, because the amount of iron incorporated in the oxide layer linearly corresponds to the amount of iron in the solution.<sup>4</sup> The VPD-DSE-TXRF is an analytical method which gives the average amount of metal on the whole wafer surface. With direct TXRF local area's with or without clustered LPD's can be measured of wafers dipped in 3 w-ppb Fe-spiked SC1. Areas with clustered LPD's showed significantly higher and variable amounts of Fe (4 points:  $65(\pm 4)$ - $76(\pm 4)$   $10^{10}$  at  $\text{cm}^{-2}$ ) than area's where no LPD's were present (3 points:  $54(\pm 3)$   $10^{10}$  at  $\text{cm}^{-2}$ ). This suggest that the initial LPD's from a Fe-spiked SC1 are particles containing Fe.

If wafers are immersed for a longer period in a Fe-spiked SC1 the LPD's do not disappear after a subsequent DI-water rinse. A SC1 solution was spiked with 10 w-ppb of  $\text{Fe}^{3+}$  and heated at  $70^\circ\text{C}$  for 15 minutes. The decomposition of the peroxide was by that time significant. Hydrophobic silicon wafers were immersed for 10 minutes. With AFM measurements the profile of the roughened area was investigated (see Figure 3). Circular holes with a diameter of 2-5.5  $\mu\text{m}$  were observed. The silicon on the edge of the hole is etched a few nm, while closer to the center of the hole the amount etched is almost zero. This results in a plateau in the center of the hole.

### Discussion and Conclusion

There is a relation between the amount of iron in the SC1 bath and the decomposition rate of the peroxide. From mechanistic studies it was shown that the catalytic active species contains at least 5 Fe-ions and that these species decompose 34000  $\text{H}_2\text{O}_2$  molecules each second.<sup>7</sup> This fast decomposition results in a local depletion of  $\text{H}_2\text{O}_2$  and built-up of oxygen gas. When the oxygen concentration exceeds the solubility of oxygen, gas bubbles will be formed. On the gas/liquid interface of these gas bubbles the catalytic active species will remain active (figure 4a) and blow-up the bubble. If the gas bubbles have a critical size it emerges at the surface (see figure 4b) and the Fe species will be left on the air/liquid interface as a cluster of particles (figure 4c). When a hydrophobic wafer is immersed in a SC1 bath full of oxygen bubbles and these Fe-particles, deposition of particles will occur at the gas/liquid/solid interface. Particle deposition will be enhanced by the convection of the solvent which is perpendicular to and in the direction of the substrate surface (see figure 4d).<sup>8</sup> Since the iron aggregates cluster together they will be smeared out over the silicon surface resulting in lines of clustered LPD's parallel to the immersion direction as can be seen in figure 1.

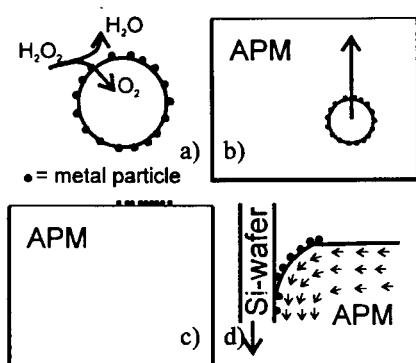


Figure 4. Schematic representation of the Fe-particle deposition in a Fe-spiked SC1.

Due to anodical passivation the etch process stops if the  $[H_2O_2]$  exceeds the  $10^{-3}$  M. The etch impression will be as the one depicted in figure 5b and corresponds to the patterns observed with AFM (figure 3).

Homogeneous precipitation of metals in a chemical oxide seems not problematic, because a subsequent step (SC2, dHCl, or dHF) can remove these metals. However, local high concentration of metal can cause irreparable damage to the silicon substrate. While surface roughening is held responsible for poor gate oxides, these local high concentrations of metal can induce defects in the gate oxide as well.

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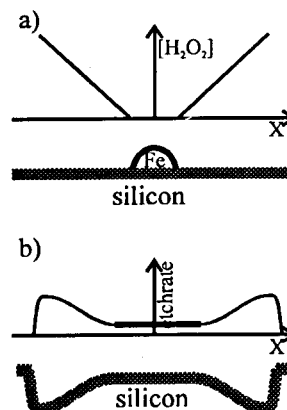


Figure 5. Selective surface etching.

## REMOVAL OF ORGANIC CONTAMINATION FROM SILICON SURFACES

C. Kenens\*, W. Storm<sup>a</sup>, D.M. Knotter\*\*, S. De Gendt\*, W. Vandervorst\* and M.M. Heyns\*

### 1. INTRODUCTION

In semiconductor cleaning technology most effort has been spent on the removal of particles and metals. This is due to their strong impact on yield and device performance. Organic contaminants appear to be less problematic. As device dimensions continue to shrink contamination problems associated with organics become more critical. Budde et al.<sup>1</sup> recently summarised published results showing the impact of organic contamination on semiconductor technology.

In this study we report on the removal efficiency of some cleaning solutions for organic contaminants on silicon surfaces under different conditions. Initially *SC1* and *SPM* were investigated, afterwards *SOM* (Sulfuric Ozonized Mixture) and *Ozonized DI-water* were also taken into account (non optimised conditions). Organic surface coverage has been monitored by TOF-SIMS<sup>2</sup>, which is especially suited for the detection of trace amounts of complex organic materials on surfaces<sup>3</sup>. This analysis technique generates mass-spectra with a high mass range, a high sensitivity (submonolayer-level) and a good mass resolution. Contact angles measurements were employed to indicate changes in the surface state.

### 2. EXPERIMENTAL SETUP

For the experiments a set of p-type monitor wafers was cleaned by *SPM*. Afterwards the wafers were intentionally contaminated with selected organic species. One subset of wafers was primed with HMDS (HexaMethylDiSiloxane) on a SVG track 8838VP. On the other subset a diluted solution (solvent : ethyl-lactate / concentration : 1%) of photoresist (IX500EL-30cP) was deposited in a spin coater and subsequently hardened with deep UV light (Fusion flash UV : 21min. 110°C and 70min. 180°C). This procedure yielded a layer thickness of 4 nm, determined by means of spectroscopic ellipsometric measurements ( $n_{625\text{ nm}} = 1.5867$ ).

Four different *SC1* solutions (see table 1) and one *SPM* solution [ $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ; (5/1/1) at 30°C] have been tested. The immersion time of each wafer was 1 minute. To prepare the *SOM* and  $\text{O}_3/\text{DI}$  mixtures the ozon bubbling (under non-optimised conditions) lasted 30 minutes. The *SOM* solution was brought to a temperature of 90°C while the  $\text{O}_3/\text{DI}$  mixture was kept at room temperature. Afterwards the wafers were immersed for 1 minute.

Contact angles were measured on a drop (5µl) of water on the surface.

Afterwards the TOF-SIMS analysis was performed on a TRIFT I spectrometer (Charles Evans & Ass., California, USA).

\* IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>a</sup> present : Wacker Siltronic AG, P.O. Box 1140, D-84479 Burghausen, Germany

\*\* Philips Research, Prof. Holstlaan 4 (WAG01), 5656 AA Eindhoven, The Netherlands

Table 1 . Parameter variation of SC1 clean (different volume ratios per solution)

| solution | H <sub>2</sub> O | H <sub>2</sub> O <sub>2</sub><br>(30%) | NH <sub>4</sub> OH<br>(29%) | T (°C) |
|----------|------------------|----------------------------------------|-----------------------------|--------|
| 1        | 5                | 1.0                                    | 1.0                         | 70     |
| 2        | 5                | 0.1                                    | 0.1                         | 70     |
| 3        | 5                | 0.1                                    | 1.0                         | 20     |
| 4        | 5                | 1.0                                    | 0.1                         | 20     |

### 3. RESULTS AND DISCUSSION

The surface coverage of TMS (TriMethylSilane) groups on the primed wafers, is well monitored by the  $\text{Si}(\text{CH}_3)_3^+$  signal at mass 73 in the SIMS-spectra. Similar to the observation in UCPSS'94<sup>4</sup>, a correlation of this signal versus the intensity of the  $\text{Si}^+$  peak and the measured contact angles was found, though with a much stronger dependency. The latter could be due to differences in experimental conditions (e.g. type of SSIMS-instrument). Figure 1 shows the positive spectra of a primed reference sample and the one, which was subsequently cleaned by SPM. The decrease of the characteristic signal shows the efficiency of the SPM-clean for removing the TMS groups.

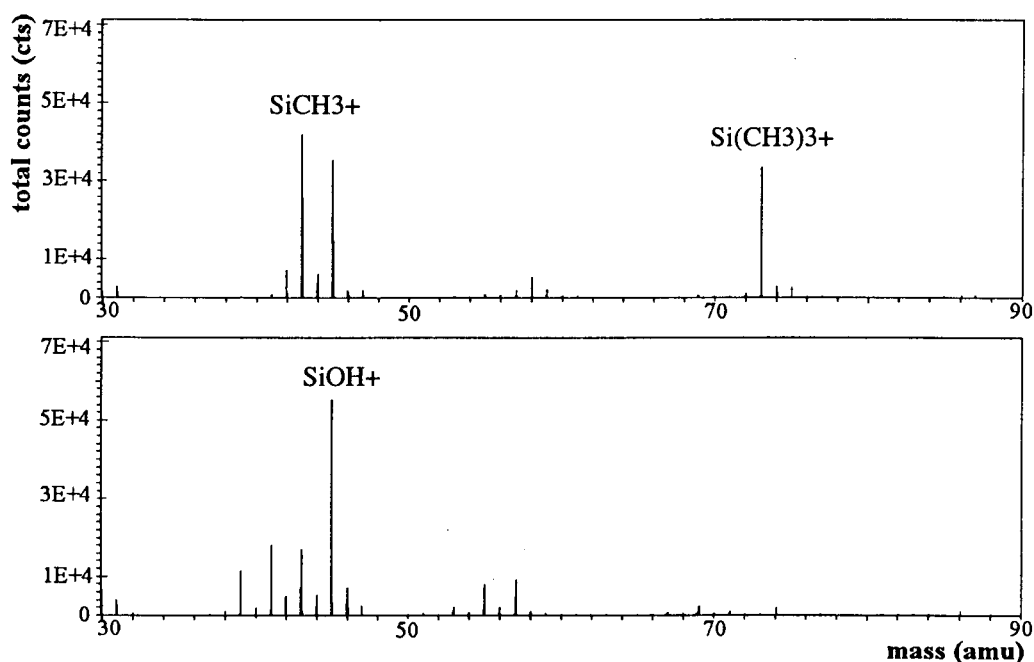


Figure 1 . Positive SIMS spectra of primed (upper part) and subsequently SPM cleaned sample (lower part)

In contrast to SPM, an effective removal of  $\text{Si}(\text{CH}_3)_3$  groups from the surface is only achieved by *hot* SC1, as can be seen in figure 2. At a temperature of 70°C there is much less residue left on the surface than at lower temperatures. Additionally *higher concentrated solutions* (in terms of a higher volume part) of either peroxide or ammonia, are more effective than diluted ones. The influence of



a high  $\text{H}_2\text{O}_2$  concentration seems to be more important than the amount of  $\text{NH}_4\text{OH}$ .

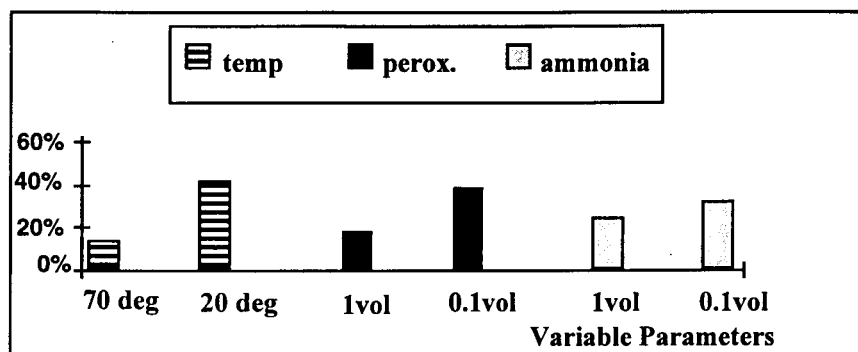


Figure 2 . Parameter comparison on the removal of HMDS in a SC1 solution : percentage of the mean residual  $\text{Si}(\text{CH}_3)_3^+$  signal versus  $\text{Si}^+$  signal\*

In contrast to the spectra of primed surfaces, one is not able to interpret the spectra of surfaces coated with photoresist in an accurate way because of the lack of understanding of the fragmentation pattern of this contaminant. In comparison with a positive spectrum of a non-contaminated sample, some peaks are assumed to be characteristic for the photoresist, more specifically at masses 103, 115, 131, 139, 163, 165, 189 and 239. These signals represent in general aromatic compounds with or without oxygen-containing groups.

The low intensities of these peaks compared to the height of the characteristic peaks of HMDS, are another problem concerning the interpretation. Therefore, the evaluation of SIMS data of HMDS is much more easier to perform than for photoresist. To discuss the cleaning efficiency of photoresist the intensity of mass 115 was examined.

As can be seen in figure 3, the removal efficiency of the resist with SC1 is

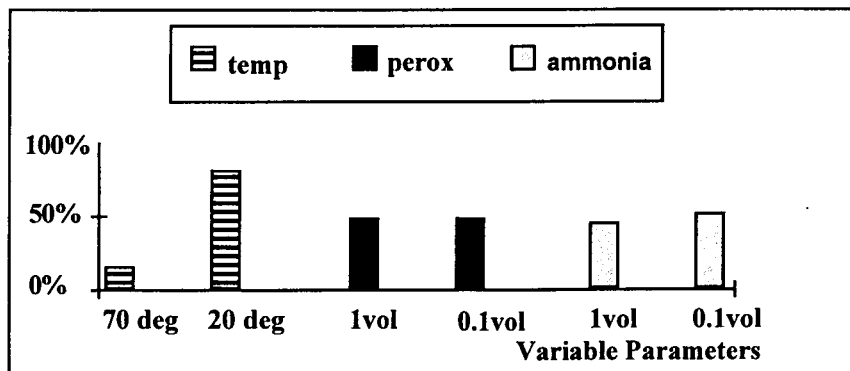


Figure 3 . Parameter comparison on the removal of photoresist in a SC1 solution : percentage of mean residual  $115^+$  signal\*\*

\*  $[\sum (I_{73} / I_{28}) / x] / [I_{73} / I_{28}]_{\text{contaminated}}$

\*\*  $[\sum (I_{115} / x)] / [I_{115}]_{\text{contaminated}}$

quite similar to the HMDS-cleaning. The main difference to the removal of  $\text{Si}(\text{CH}_3)_3$  is the *independence of the concentration*. The temperature seems to be the only determining factor : a *hot* SC1 solution cleans better irrespective of its mixing ratio. The different behaviour of low versus high temperature is even more pronounced than with the previous contaminant. Again SPM is more effective than SC1.

Additionally SOM and  $\text{O}_3/\text{DI}$ -water were used as a cleaning recipe. Wafers contaminated with HMDS and others with photoresist were cleaned under non-optimised conditions. To obtain an estimate of the removal efficiency only one spectrum per solution was taken into account. SOM seems to be the most effective cleaning tool for both contaminants (see figure 4). A *high*  $\text{O}_3$ -concentration has a positive influence on the HMDS-removal. For photoresist there is *no spectacular difference* in cleaning efficiency with varying  $\text{O}_3$ -concentration. In fact, ozonized DI-water seems to fail in removing the resist from the surface. Although further research concerning the influence of different parameters (concentration, pH, ...) is still needed.

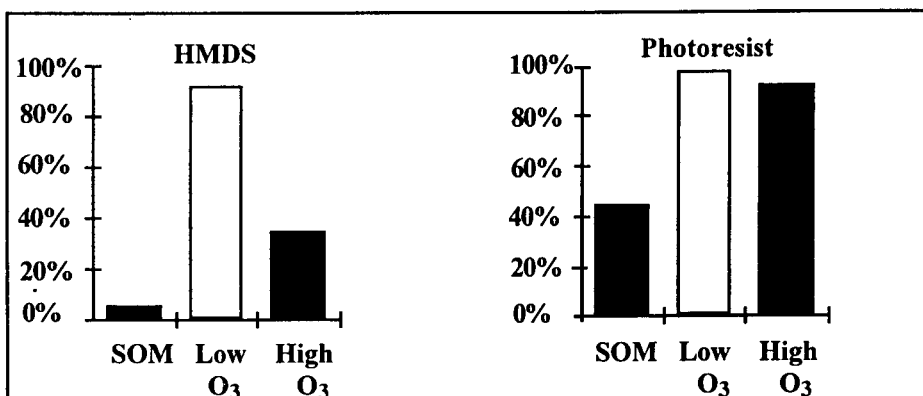


Figure 4. Cleaning efficiency for SOM and ozonized DI-water (low : order of 0.5 ppm / high : order of 10 ppm) : calculations are based on the  $\text{Si}(\text{CH}_3)_3^+$  signal versus  $\text{Si}^+$  signal (HMDS) and the  $115^+$  signal (Photoresist).\*

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\* Formulas used are identical to previous ones except the summation for the mean because only one value per condition is used.

## Integrated Dry Cleaning of Contamination Resulting from Reactive Ion Etching of Silicon Dioxide

A. Scott Lawing\*, Anthony J. Muscat\*\*, Herbert H. Sawin\* and Ty Fayfield\*\*\*

### 1. Introduction

We demonstrate in this work that an integrated dry cleaning sequence is capable of removing blanket polymer and oxide films that are produced by Reactive Ion Etching (RIE) and RIE/oxygen ashing processes. In our integrated sequence, the majority of the polymer contamination was first removed with ultraviolet excited chlorine (UV/Cl<sub>2</sub>) exposure. The thin silicon oxide film exposed by removing the polymer was then stripped using an HF/vapor mixture. Finally, a second UV/Cl<sub>2</sub> process was used to remove fluorocarbon polymer which could not be removed before stripping the oxide film. The dry cleaning sequence is compared to a typical wet sequence consisting of an H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (Piranha) clean followed by an SC1 clean and an aqueous HF dip.

The reader is referred to other sources for discussions of the UV/Cl<sub>2</sub> [1,2] and HF/vapor [3,4] processes.

### 2. Experimental

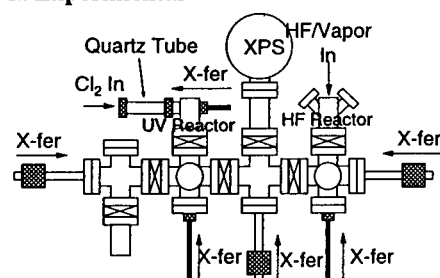


Figure 1 - Schematic diagram of the integrated dry cleaning apparatus.

The experimental apparatus in which these experiments were performed is schematically illustrated in Figure 1. As shown, the samples are transported via magnetically coupled transfer rods between reaction and analytical chambers without air exposure.

The UV reactor consists of a 1 " OD quartz tube mounted to a stainless steel chamber. The sample is mounted to the end of a stainless steel rod and transferred

axially into the tube along the center line. The UV/Cl<sub>2</sub> cleaning processes were performed at 10 Torr Cl<sub>2</sub> and nominally 90°C for 30 seconds.

The HF/vapor reactor is constructed from stainless steel. Metered amounts of anhydrous HF, isopropyl alcohol (IPA) vapor using a nitrogen carrier, and dry nitrogen were introduced into the reactor via a temperature controlled gas handling system. The reactor pressure was maintained at 250 Torr total pressure and 40°C with an HF partial pressure of 43.5 Torr and an IPA partial pressure of 23.6 Torr for 30 seconds.

Contaminant levels were monitored before and after processing using X-ray Photoelectron Spectroscopy (XPS). Mg K $\alpha$  radiation and a VG model 100 AX hemispherical electron energy analyzer were used in these experiments. The analyzer was set for a pass energy of 20 eV. Surface roughness measurements were performed

\* Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

\*\* Department of Chemical Engineering, San Jose State University, San Jose, CA, USA

\*\*\* FSI International, Chaska, MN, USA

with a Topometrix TMX 2000 Atomic Force Microscope (AFM). Film thickness was estimated from a combination of the XPS data and ellipsometric measurements.

The samples were plasma etched and ashed in the Materials Technology Laboratory at MIT. The wafers were etched with a  $\text{CF}_4/\text{CHF}_3$  chemistry in a Lam 590 auto etch, and  $\text{O}_2$  ashed in a barrel reactor. After processing, each wafer was cleaved into 1 x 1 cm square samples which were mounted on holders made of alumina for insertion into the load lock and processing.

A wet cleaning sequence consisting of 1) hot  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  at a ratio of 3:1 for 15 minutes (Piranha) 2)  $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$  at a ratio of 5:1:1 for 15 minutes (SC1) and 3)  $\text{H}_2\text{O}/\text{HF}$  at a ratio of 100:1 for 1 minute (HF Dip) was applied to samples which had been etched and ashed as described above.

### 3. Results and Discussion

#### 3.1 Analysis of Polymer Residue and Silicon Oxide Films after RIE and Ashing

XPS spectra of the polysilicon wafers after the etching process and after the etching and ashing processes are shown in Figure 2. The chemistry of these films has been investigated extensively and our results agree qualitatively with what has been reported in the literature. The peak assignments shown in Figures 2, 4 and 5 are adapted from a variety of sources [5,6] including the database of XPS spectra from our own laboratory. Based on our analysis, a representative cross-section of the contaminating films is given in Figure 3. After RIE, the contaminating film consists of a layer of bulk fluorocarbon polymer approaching 40 Å in thickness, atop a layer of relatively "clean"  $\text{SiO}_2$  approximately 10 Å thick. At the interface between the polymer and oxide is a transition region of mixed composition, 5-10 Å in thickness. Ashing removes virtually all of the bulk fluorocarbon film, such that most of the remaining polymer is in a mixed fluorocarbon polymer/oxide environment. This is evident by the shift to mostly  $\text{Si-O}/\text{CF}_x$  bonding in the oxygen and silicon (not shown) spectra. Ashing also reduces the total contaminating film thickness to about 30 Å although the amount of oxide in the layer has increased, indicating that some of the polysilicon substrate was consumed by the ashing process.

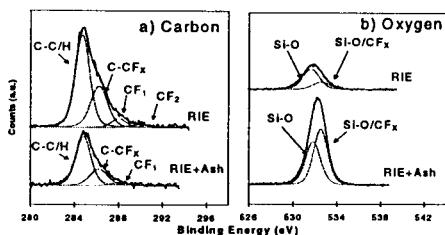


Figure 2 - XPS spectra after RIE and RIE + oxygen ash processing.

#### 3.2 Removal of the Contaminating Films

RIE +  $\text{O}_2$  ashed samples were subjected to an integrated cleaning process as illustrated in the bottom of Figure 3. XPS spectra for the integrated cleaning process are shown in Figures 4a and 5a. Although spectra were taken for carbon, oxygen, silicon, fluorine, and chlorine, only carbon and oxygen are shown here due to space limitations. Figure 4a shows that most of the carbon contamination was removed by the initial  $\text{UV}/\text{Cl}_2$  process. There is a measurable amount of carbon remaining that cannot be

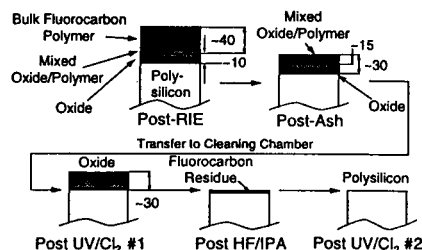


Figure 3 - Schematic diagram of the contaminating films and the removal sequence.

removed by  $\text{UV}/\text{Cl}_2$  at this stage, even with a drastically longer processing time. Correspondingly, the oxygen spectra in Figure 5a show that the fluorocarbon character of the mixed fluorocarbon polymer/oxide layer is removed up by the  $\text{UV}/\text{Cl}_2$  process. This is apparent by the disappearance of the  $\text{Si-O}/\text{CF}_x$  contribution to  $\text{Si-O}$  bonding in both spectra. The total amount of  $\text{Si-O}$  bonding appears to be unchanged. The intensity of the substrate peak (not shown) is also unchanged by the  $\text{UV}/\text{Cl}_2$  process. This indicates that the overall thickness of the contamination layer is not greatly affected by the  $\text{UV}/\text{Cl}_2$  process.

A vapor-phase  $\text{HF}/\text{IPA}$  process was used to remove the oxide film. Figure 4a shows that the intensity of the carbon line increased after  $\text{HF}/\text{vapor}$  processing. The chemical state of the carbon revealed after the  $\text{HF}/\text{IPA}$  oxide strip is very similar to the initial RIE polymer contamination. This residual fluorocarbon is most likely incorporated in the oxide film, and is concentrated on the surface as the oxide is etched away. The residual fluorocarbon was not removed by the vapor phase  $\text{HF}$  process as the oxide film was etched. Figure 5a shows that the oxide film is almost completely removed after vapor-phase  $\text{HF}$  processing. We have estimated the oxygen coverage at  $\approx 1/3$  monolayer.

A second  $\text{UV}/\text{Cl}_2$  process removed most of the remaining carbon from the silicon surface, as shown in Figure 4a. The intensity of the carbon after the second  $\text{UV}/\text{Cl}_2$  process is consistent with the background level of carbon contamination normally observed in our vacuum system. We have estimated the carbon coverage after the second  $\text{UV}/\text{Cl}_2$  exposure at  $\approx 3/4$  monolayer. The oxygen spectra given in 5a was unchanged. The chlorine and fluorine coverage (not shown) have been estimated as  $\approx 1$  and  $2/3$  monolayer respectively after the second  $\text{UV}/\text{Cl}_2$  process.

### 3.3 Comparison Between "Wet " and "Dry" Cleaning Sequences

Figures 4 and 5 illustrate the comparison between the wet and dry cleaning sequences. Generally, the results from the dry cleaning sequence compare favorably with the wet cleaning sequence, and in some respects appear superior due to the inherent advantages of avoiding ambient exposure during processing.

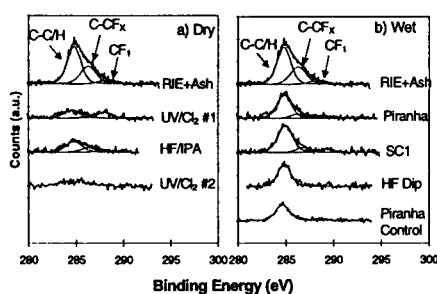


Figure 4-Carbon 1s XPS line from a) a dry and b) a wet cleaning sequence.

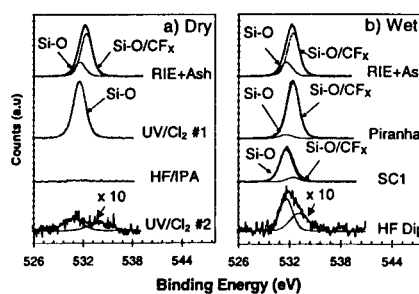


Figure 5-Oxygen 1s XPS line from a) a dry and b) a wet cleaning sequence.

From the carbon 1s spectra in Figure 4, it is apparent that the dry cleaning sequence is at least as effective as the wet sequence in removing polymeric and carbonaceous contamination. It is unclear whether the level of carbon contamination in the wet process sequence is due to inadequate removal or ambient re-contamination (note the high carbon level on the piranha control, a virgin wafer subjected to a piranha clean). In any event, the *absence* of re-contamination in the *dry* sequence illustrated in Figure 4a points out one advantage of a clustered processing regimen.

Figure 5 shows the oxygen 1s spectra from the wet and dry cleaning sequences. The Piranha clean does not significantly effect the fluorocarbon character of the mixed polymer/oxide layer as can be seen by the prominent Si-O/CF<sub>x</sub> component in the oxygen line. In fact, the Si-O/CF<sub>x</sub> component appears to increase in intensity. The SC1 clean removes most of the fluorocarbon in the mixed layer, evidenced by the shift to mostly Si-O bonding in both the oxygen and silicon (not shown) lines. A slight contribution due to Si-O/CF<sub>x</sub> bonding is still resolved in the oxygen spectrum after the SC1 clean in Figure 5b. The SC1 clean also results in slight etching of the oxide film. This is apparent from a reduction in intensity of the Si-O component in both the oxygen and silicon (not shown) spectra. The oxide etching component of the SC1 step could explain why it is more efficient than Piranha at removing the fluorocarbon incorporated in the oxide. Removal of oxide could expose residual fluorocarbon that was protected from the Piranha clean, which is known to cause oxide growth. The final oxygen coverage is significantly lower for the dry sequence as compared to the wet sequence. The bottom spectra in Figure 5 have been scaled so that this effect can be more clearly seen.

The surface roughness of samples subjected to: 1) the etch and ash sequence, 2) the etch and ash sequence plus the wet cleaning sequence, and 3) the etch and ash sequence plus the dry cleaning sequence was measured as 68.5, 69.3, and 51.3 Å rms respectively. The surface roughness of all of the samples is comparable.

#### 4. Conclusions

We have demonstrated an all-dry integrated cleaning sequence that is capable of removing blanket fluorocarbon and oxide films from poly- and single-crystal Si substrates that result after RIE + O<sub>2</sub> ashing. A UV/Cl<sub>2</sub> process removed fluorocarbon polymer and residual carbon contamination. A reduced pressure vapor-phase HF/IPA process removed silicon oxide contamination. The cleaning sequence outlined here produces a silicon surface with negligible carbon and oxygen contamination. Small amounts of chlorine and fluorine are present on the surface after the cleaning sequence. The dry cleaning sequence compares favorably with a standard wet cleaning sequence, and results in a lower oxygen coverage.

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## **A Novel Vapor Phase Process for Clean Silicon Surface Preparation**

L. Li, R. Weimer, A. Kepten\*, R.P.S. Thahur, L. Breiner

Micron Technology Inc., 8000 S. Federal Way, Boise, ID 83707

\*A.G. Associates Ltd., Ramat Gabriel Industrial Park, Migdal Haemek 10551, Israel

### **1. Introduction**

Fabrication of advanced semiconductor devices imposes stringent requirements on the contamination control during the wafer process. The surface preparation for some critical processes, i.g., pre-gate oxide clean, can directly impact the performance and reliability of the device.<sup>1</sup> After traditional wet batch cleaning, wafers are exposed to the clean room ambient which could cause hydrocarbon contamination on the surface. Contamination on the surface at this point can influence the device characteristics.<sup>2</sup> Therefore, the clustered processes with in situ cleaning and vacuum wafer transferring appear to be an interesting approach for ultraclean manufacturing.

The HF vapor clean is known to be compatible with cluster wafer processing, due to its vacuum compatibility. The vapor phase clean can etch silicon oxide from the wafer and provide a hydrogen passivated silicon surface. However, unlike the wet HF clean which removes metallic contamination effectively, the HF vapor clean leaves a high metal concentration on the wafer surface. The UV/Cl<sub>2</sub> process has been applied after the HF vapor step to eliminate trace metallic contamination, but the active chlorine species etches the bare silicon surface increasing the surface roughness.<sup>3,4</sup>

In this paper, we report a new vapor phase process of combining the UV/Cl<sub>2</sub> with HF vapor clean for metal removal with minimized surface roughening.

### **2. Experimental**

Substrates used for this study were 150 mm Si(100), p-type with a resistivity of 10-20  $\Omega$  cm. The wafers were started with a SC1 clean, so the surface was covered with a thin chemical oxide before the vapor clean test. The cleaning tests were carried out in a HF/methanol, UV/Cl<sub>2</sub> module (Submicron Primaxx) which is incorporated in a cluster tool (AG Integra). For HF vapor clean, HF vapor 300 sccm, methanol 75 sccm, N<sub>2</sub> 100 sccm, pressure 100 Torr, and temperature 40 °C were chosen. The cleaning time took 90 sec. For UV/Cl<sub>2</sub> process, Cl<sub>2</sub> 500 sccm, pressure 10 Torr and temperature 150 were chosen. The process time took either 30 sec. or 120 sec. Silicon surface morphology after different cleaning was characterized with atomic force microscopy (AFM). The surface metal concentration was measured by vapor phase decomposition-total reflection x-ray

fluorescence (VPD-TXRF). The surface chemistry of silicon wafers was studied by x-ray photoelectron spectroscopy (XPS).

### 3. Results and Discussion

#### 3.1. Surface roughening

In the UV/Cl<sub>2</sub> metal removal process, chlorine radicals generated by UV activation reacts with surface metal atoms forming a volatile species. The chlorine radicals also etch the silicon surface causing surface roughening. Since the roughness is a critical factor for surface preparation, we will address the roughness issue first. Figure 1 shows the surface morphology after the cleaning processes. Figure 1(a) presents the wafer surface for only HF vapor clean. Since the HF etched the thin chemical oxide on wafer surface and the etching stopped at SiO<sub>2</sub>/Si interface, we obtain a smooth surface. Figure 1(2) presents the surface roughness of the wafer run through the conventional HF vapor + UV/Cl<sub>2</sub> process, i.e., HF vapor clean followed by a UV/Cl<sub>2</sub> treatment. The HF vapor clean removed the surface oxide completely. A bare silicon surface was exposed to the active chlorine radicals during the UV/Cl<sub>2</sub> process, and we see serious roughening on the wafer surface. Figure 1(3) shows the surface of the wafer after treatment with our new process sequence, i.e., UV/Cl<sub>2</sub> process followed by HF vapor clean. It is easy to see, with the chemical oxide protecting the wafer surface, the surface roughening was significantly reduced in the UV/Cl<sub>2</sub> process. A very strong UV/Cl<sub>2</sub> process ( 120 sec. ) was chosen here because we wanted to clearly see the influence of changing process sequence. A smooth silicon surface close to that seen in Figure 1(1) can be obtained with our new process by running the UV/Cl<sub>2</sub> step for a reduced time.

#### 3.2. Metal removal

In our new vapor clean process, the surface roughening is reduced by running the UV/Cl<sub>2</sub> treatment with a thin chemical oxide covering the silicon surface. Leaving the thin chemical oxide on silicon surface can not influence the metal removal efficiency of the UV/Cl<sub>2</sub> process. Otherwise, this process will not be useful since the purpose of applying the UV/Cl<sub>2</sub> treatment is for eliminating metallic contamination. Table 1 shows the surface metal concentration measured by VPD-TXRF after different clean processes. One can clearly see the processes of applying the UV/Cl<sub>2</sub> treatment before HF vapor step provided the same metal removal efficiency as that of HF vapor step followed by UV/Cl<sub>2</sub> treatment. Therefore, the high metal removal efficiency with minimized surface roughening can be achieved with our UV/Cl<sub>2</sub> + HF vapor clean process. It is also interesting that the new clean processes with different UV/Cl<sub>2</sub> treatment times ( 30 sec. and 120 sec. ) provided a wafer surface with very low metallic contamination. The UV/Cl<sub>2</sub> process time can be decreased to further reduce the surface roughening while maintaining a low level of metallic contamination.



### 3.3. Surface passivation

A hydrogen passivated silicon surface is desired after a HF cleaning. Table 2 shows the atomic percentage concentration of fluorine and chlorine on the wafer surface after each clean processes. Typically, the chlorine residue is detected on the surface of the wafer run through the HF vapor + UV/Cl<sub>2</sub> process. In our UV/Cl<sub>2</sub> + HF vapor process, the final HF vapor step cleans up the chlorine residue completely.

### 4. Conclusions

Using a thin chemical oxide to prevent direct reaction of active chlorine radicals on silicon surface, the UV/Cl<sub>2</sub> + HF vapor cleaning process minimizes the silicon surface roughening as compared with the conventional HF vapor + UV/Cl<sub>2</sub> process. The new cleaning process provides the same metal removal efficiency as the conventional process, and a completely hydrogen passivated silicon surface can be obtained by the UV/Cl<sub>2</sub> + HF cleaning process because the last HF vapor step removes the Cl residue on the wafer surface.

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Table 1. The surface metal concentration ( $\times 10^9$  atoms/cm) measured by VPD-TXRF for different clean processes. The UV/Cl<sub>2</sub> step was run for 30 and 120 seconds respectively.

|                            | K     | Ca   | Fe   | Cu  | Zn   |
|----------------------------|-------|------|------|-----|------|
| HF                         | 197.1 | 15.9 | 32.3 | 3.6 | 57.5 |
| HF, Cl <sub>2</sub> (30")  | 91.5  | 21.3 | 4.4  | 0.8 | 30.5 |
| HF, Cl <sub>2</sub> (120") | 3.5   | 3.1  | 1.5  | -   | 37.5 |
| Cl <sub>2</sub> (30"), HF  | 3.4   | 3.9  | 4.9  | -   | 6.8  |
| Cl <sub>2</sub> (120"), HF | 32.0  | 2.1  | 3.7  | -   | 4.2  |

Figure 1. AFM profiles of the wafer surface after a vapor phase clean of HF vapor (1), HF vapor + UV/Cl<sub>2</sub> (2), and UV/Cl<sub>2</sub> + HF vapor (3).

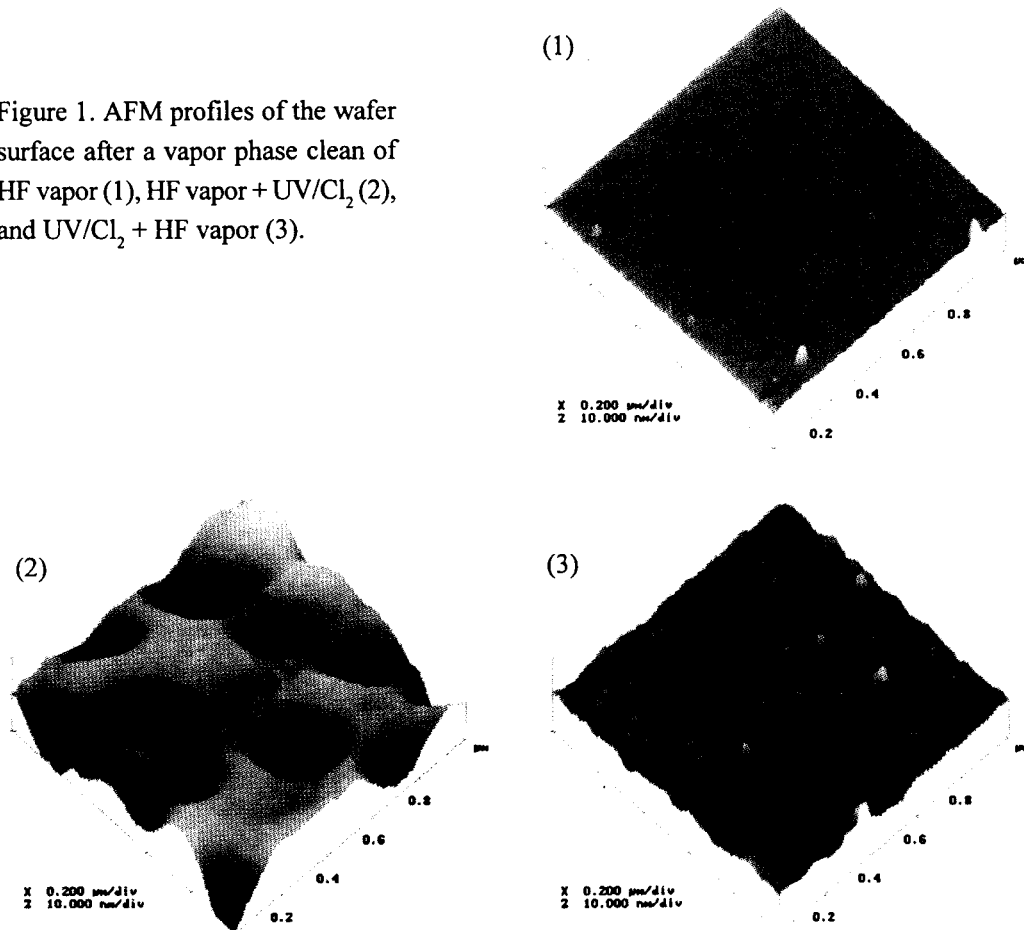


Table 2. XPS analysis on wafers processed through different clean processes.

|                            | F   | Cl  |
|----------------------------|-----|-----|
| HF                         | 3.0 | -   |
| HF, Cl <sub>2</sub> (30")  | 1.8 | 1.5 |
| HF, Cl <sub>2</sub> (120") | 1.7 | 1.1 |
| Cl <sub>2</sub> (30"), HF  | 4.6 | -   |
| Cl <sub>2</sub> (120"), HF | 1.3 | -   |

## IN SITU MEASUREMENT AND CONTROL OF SC-1 CHEMISTRIES

P. G. Lindquist, J. N. Butler, S. A. Velichko, J. A. Fahrenkrug and J. J. Rosato  
SCP Global Technologies, 400 Benjamin Lane, Boise, Idaho 83704

### 1. INTRODUCTION

Shortly after mixing and heating an SC-1 bath, ammonia begins to evaporate and hydrogen peroxide starts to decompose[1]. Many semiconductor manufacturers desire an in situ method for concentration measurement, along with a feedback method of controlling SC-1 bath chemistry[2]. Control of the bath chemistry results in longer bath lifetimes, higher equipment up-time, less frequent bath qualification, fewer particle monitor wafers, less lot-to-lot variation in surface roughness, and constant particle removal efficiency. This work describes a prototype system to measure and control the ammonia and hydrogen peroxide in an SC-1 bath. Additionally, we studied the process performance of an SC-1 bath as it aged for 48 hours under concentration control. On the wafer surface, we looked for changes in particle removal efficiency, surface roughness, surface charge, iron deposition, and etch rates. In the bath, we monitored trace metal impurities over the bath lifetime.

### 2. EXPERIMENTAL

For a schematic of the SC-1 concentration monitor and control system see Figure 1. A pump, filter, and heat exchanger mixed, filtered and heated the SC-1 bath. An SC-1 concentration monitor measures the ammonia and hydrogen peroxide concentration. Metering pumps precisely control the amount of concentrate injected from the chemical reservoirs, as the chemicals' concentration changes. This system is installed on a Model SPS 9400 system configured for RCA cleans of 200 mm wafers.

### 3. DISCUSSION AND RESULTS

For a typical SC-1 decomposition curve see Figure 2. Both components of the SC-1 bath follow a pseudo first order rate law, as reported by Meerakker[3].

$$[A] = [A]_0 e^{(-kt)} \quad (1)$$

Where  $[A]_0$  is the initial concentration of component A,  $k$  is a rate constant, and  $t$  is time. The ammonia losses are because the process tank is not refluxed or sealed. For hydrogen peroxide the rate constant,  $k$ , depends on temperature, chemical purity, and chemical ratio of ammonia. For these tests, we used ppb grade

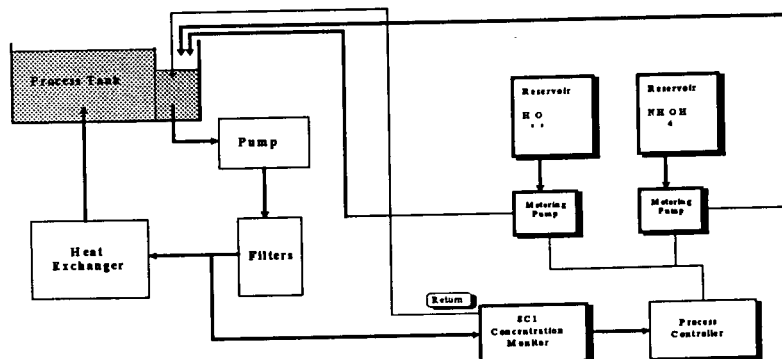


Figure 1. Schematic diagram of the SC-1 concentration monitor and control system. An SC-1 concentration monitor measures the ammonia and hydrogen peroxide concentration. Metering pumps precisely control the amount of concentrate injected as the concentration changes.

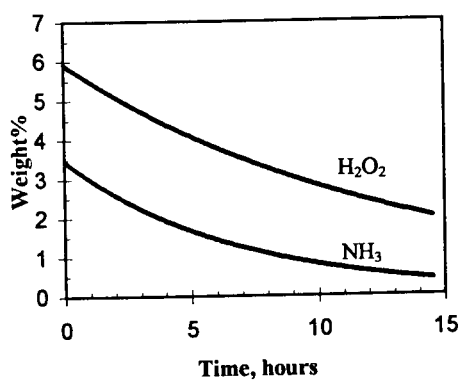


Figure 2. SC-1 decomposition curve of a 1:1:5 (ammonia:peroxide:water) bath at 70 C.

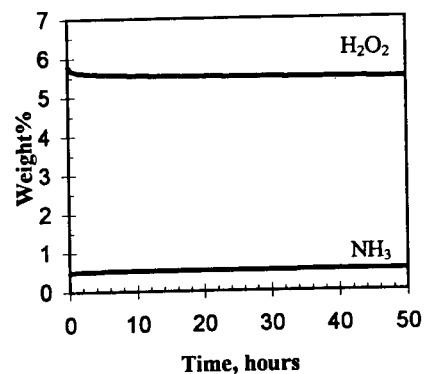


Figure 3. Concentration control of a 0.1:1:5 (ammonia: peroxide: water) SC-1 bath at 50 C. This system performed very well when tested between 50 and 75 C.

chemicals, a setpoint temperature of 70 C and a fixed ammonia concentration using the closed loop control system. The hydrogen peroxide concentration data fit equation (1) very well. We compute  $k = 0.0318 \text{ hr}^{-1}$  for a 0.1:1:5 bath and  $k = 0.2176 \text{ hr}^{-1}$  for an 1:1:5 bath, with correlation coefficients were greater than 0.97. Aside from determining a practical rate constant for our equipment, it is interesting that the hydrogen peroxide rate constant,  $k$ , depends on the ammonia concentration,  $k$  increases as ammonia is added. This is additional evidence that dilute SC-1 chemistries will decrease chemical consumption. For dilute SC-1 baths, lowering the ammonia concentration extends the half life of the hydrogen peroxide from 3.2 to 21.8 hours, comparing standard SC-1 chemistry to a dilute one.

The decomposition curve clearly demonstrates the need for concentration control of the SC-1 when one expects consistent process results. The performance of the system under closed-loop concentration control is very good; see Figure 3. The system performed well for concentration ratios between 0.1:1:5 and 1:1:5 (ammonia:hydrogen peroxide:water). and temperatures between 50 to 75 C.

Using the closed-loop concentration control, we wanted to examine the effect of SC-1 bath aging on the wafer cleaning performance; see Table 1. A dilute SC-1 process optimized for maximum particle removal efficiency and minimal surface roughness was used[4]. The SC-1 wafer cleans were ten minutes at 50 C, using 400 W megasonic power. Approximately five hundred 200 mm wafers went

| SC-1 Performance 0.1:1:5 at 50C<br>Wafer Surface | Time (hrs.) |      |      |
|--------------------------------------------------|-------------|------|------|
|                                                  | 0           | 24   | 48   |
| AFM Surface Roughness, RMS (angstroms)           | 1.3         | 1.5  | 1.4  |
| Particle Removal Efficiency, PSL spheres         | >99%        | >99% | >99% |
| Oxide Etch Rate, (angstroms/min)                 | 0.2         | 0.2  | 0.3  |
| Surface Charge, (x10E10C/sq.cm)                  | 2.5         | 2.2  | 1.7  |
| Fe Surface Concentration, (x10E12 atoms/sq.cm)   | 0.9         | 1.2  | 1.7  |
| <b>Trace Metals in SC-1 Bath (ICP/MS)</b>        |             |      |      |
| Fe (D.L. 2.0 ppb)                                | <2.0        | <2.0 | <2.0 |
| Al (D.L. 0.1 ppb)                                | 0.7         | 1.3  | 0.8  |
| Sum of 16 elements in SC-1 Bath Above D.L.       | 6.1         | 9.3  | 11.2 |

Table 1. SC-1 bath performance of a 0.1:1:5 (ammonia:peroxide:water) bath operated under concentration control for 48 hours. Approximately 500 wafers processed through an SC-1, rinse and dry cleaning sequence.

through the tank in 48 hours, fifty wafers per lot. The AFM surface roughness, particle removal efficiency, and oxide etch rates remained constant during the test because of concentration control. Without control, all of the ammonia would have evaporated from the tank long before the test completed. The fact that these parameters, along with the SC-1 chemical concentration remained constant, supports extending the SC-1 bath lifetime beyond 4 to 8 hours, without process degradation. The SC-1 bath lifetime is now limited by concentration of trace metals that can be tolerated in the manufacturing process, not decomposition or evaporation of the chemicals. Trace metals may collect slowly in baths used for pre diffusion cleans or quickly in baths used for post implant cleans.

#### 4. CONCLUSION

In situ measurement and control of SC-1 chemistries is achievable. We showed that: Hydrogen peroxide decomposition is modeled by a first order rate law; The decomposition rate constant,  $k$ , depends on ammonia concentration; And dilute SC-1 chemistries optimized for high particle removal efficiency and low surface roughness can be controlled. The forty eight hour process tests showed it is possible to extend the bath life beyond the 4 to 8 hours currently practiced by semiconductor companies. The benefits of using this proposed system are longer SC-1 bath lifetime, the ability to integrate dilute SC-1 chemistries into manufacturing, and a lower cost of ownership. The cost of ownership will be lowered because equipment availability increases, the frequency of chemical change outs and process qualifications decreases (less monitor or test wafers used, fewer particle scans, and less labor), less chemicals are used, and consistent process performance are predicted. These factors are even more important for manufacturing processes still using standard SC-1 chemical ratios and temperatures. A standard SC-1 is extremely dynamic with respect to decomposition and evaporation.

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## OPTIMIZED CLEANING PROCESSES FOR SILICON WAFER BONDING

Karin Ljungberg<sup>#</sup>) and Stefan Bengtsson<sup>\*</sup>)

<sup>#</sup>)Microelectronics Centre, Technical University of Denmark, Bldg. 345e  
DK-2800 Lyngby, Denmark

<sup>\*</sup>)Solid State Electronics, Chalmers University of Technology  
S-412 96 Göteborg, Sweden

The use of SPFM ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{HF}$ ) at low HF concentrations (10-1000 ppm) has been investigated as a pre-cleaning procedure for silicon direct bonding. This cleaning procedure can be tuned to *simultaneously* give hydrophilic surface properties, ensuring good bondability, *and* excellent electric properties, crucial for the application of direct bonding in device applications.

### 1. INTRODUCTION

Wafer bonding [1] allows formation of structures by joining solid materials. In silicon technology, commercial applications are found in the production of SOI (Silicon-On-Insulator) materials, in substitutes for thick epitaxially grown silicon and in the formation of novel sensor structures. In the case of bonded Si/Si junctions, the ability of the silicon surface to form a successful high yield bond is critically dependent on microroughness, surface termination, and particle removal. Furthermore, the electrical properties of Si/Si junctions are strongly affected by cleaning procedures and by the presence of a chemical oxide at the interface. Many of the common cleaning procedures, e.g. APM, HPM or SPM, create a highly hydrophilic chemical oxide at the surface. Hydrophilic surfaces bond quickly and show relatively strong adhesion already at room temperature [2]. On the other hand, HF-dipped (H-terminated) hydrophobic surfaces, which are oxide-free and thus preferable for electronic applications, are characterized by a slower contact wave as well as a weaker adhesion [3]. The reason for this is weaker attraction forces between the terminating atoms. This makes the bonding procedure and handling more complicated. We present results on the use of  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{HF}$  (SPFM) [4] as the cleaning procedure prior to formation of Si/Si interfaces by wafer bonding. Surface preparation is optimized to enhance room temperature bonding as well as to achieve good electrical characteristics.

### 2. SURFACE PREPARATION AND CHARACTERIZATION

Silicon (100) wafers were dipped in diluted HF, rinsed in water, and cleaned for 2 minutes in  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  4:1 (SPM), to which 10 to 1000 ppm of HF was added. An XPS analysis was performed to investigate the surface chemistry and the chemical oxide thickness. Figure 1 shows the Si 2p spectra obtained from the differently treated samples. The peak at 103,4 eV is attributed to Si in  $\text{SiO}_2$ . Its height can be used to calculate the oxide thickness. The thickest oxide, achieved in pure SPM, can be estimated to be about 10 Å thick [5]. The thickness of the oxide decreases with increasing HF-concentration in the SPFM, reaching virtually zero thickness at an HF concentration of 1000 ppm. In the SPFM mixture there is a competition between oxidation and oxide etching. The result is a steady-state thickness of the oxide, determined by the ratio of the oxidizer and the etchant.

Figure 2 shows F 1s spectra obtained from samples cleaned in SPFM with different HF concentrations prior to water rinse. The surfaces appear to be terminated by F to a large extent. This is supported by the fact that they are hydrophobic. The F signal first increases with HF concentration, but then decreases at the highest HF concentration. This is believed to be due to a higher degree of H termination of the Si dangling bonds. Rinsing the surfaces in water causes substitution of F by OH, which makes the surface hydrophilic. The rinsed 1000 ppm-samples are less hydrophilic, supporting the assumption of a partly H terminated surface.

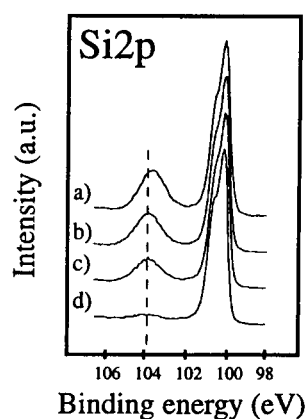


**Fig. 1.** Si 2p spectra.  
SPFM with a) no HF, b) 10 ppm  
c) 100 ppm, d) 1000 ppm HF added.

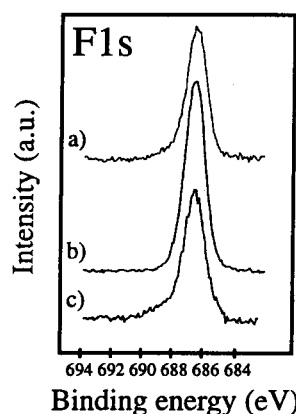


**Fig. 2.** F 1s spectra.  
SPFM with a) 10 ppm, b) 100 ppm  
c) 1000 ppm HF added.

Increasing HF concentration in the SPFM from 10 ppm to 1000 ppm increases the silicon etch rate by approximately a factor of 20 [5]. Nevertheless, the surface roughness, as measured by AFM, is practically independent of HF concentration at concentrations of 10 to 1000 ppm. The r.m.s surface roughness value was found from AFM measurements on  $0.2 \times 0.2 \mu\text{m}$  scan areas to be 0.70 Å, 0.67 Å and 0.62 Å after cleaning in SPFM solutions with 10, 100 and 1000 ppm HF respectively. As a comparison the fresh wafers exhibited r.m.s values of 0.35 Å.

### 3. BONDING CHARACTERISTICS

The bonding properties of the surfaces were investigated by measuring the speed at which the contacted area grew, the contact wave velocity. This is observed in transmitted IR light. Also the surface energy of the bond was determined, by inserting a thin blade between the wafers and measuring the crack length [6]. Figures 3 and 4 show mean values of measured contact wave velocities and surface energies for wafers treated in SPFM with different HF concentrations, after DI water rinse. The surface energy measurements were made immediately after cleaning and room temperature bonding of the wafers, prior to any high temperature annealing. For comparison, data from the literature for hydrophilic surfaces prepared in oxidizing chemicals [2] and hydrophobic surfaces prepared in 10 % HF [7] are indicated as dotted lines in the figures.



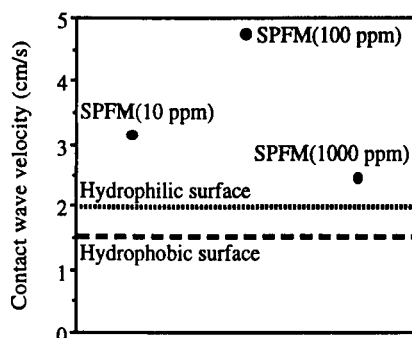


Fig. 3. Contact wave velocity for different pre-cleaning procedures.

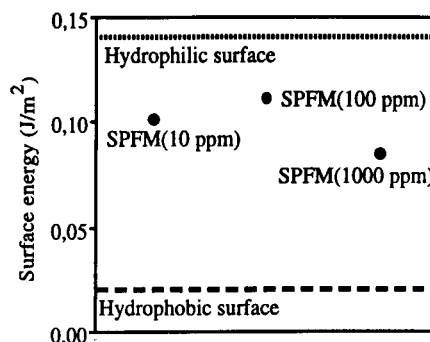


Fig. 4. Surface energy for different pre-cleaning procedures.

#### 4. ELECTRICAL CHARACTERIZATION

The use of SPFM offers an interesting alternative to HF-dipping for applications where an oxide-free interface is required. This cleaning process makes it possible to produce a hydrophilic (OH terminated) surface, thereby achieving a strong room temperature bond with a minimum of interfacial oxide. In addition, hydrophilic surfaces have less tendency to attract particles from air and chemicals, which decreases the particle contamination probability at the interface. To investigate the influence of SPFM treatment on electrical properties Si/Si junctions were made by bonding n-type wafers (FZ, (1-0-0), 6-9  $\Omega\text{cm}$ ) after surface preparation using 2% HF, SPFM(1000 ppm), SPFM(10 ppm), APM/HPM and  $\text{HNO}_3$ . The bonded pairs were annealed at 1000° C for 10 minutes in  $\text{N}_2$ . Figure 5 shows the results of IV-measurements across such n-type/n-type junctions having areas of 25 mm<sup>2</sup>.

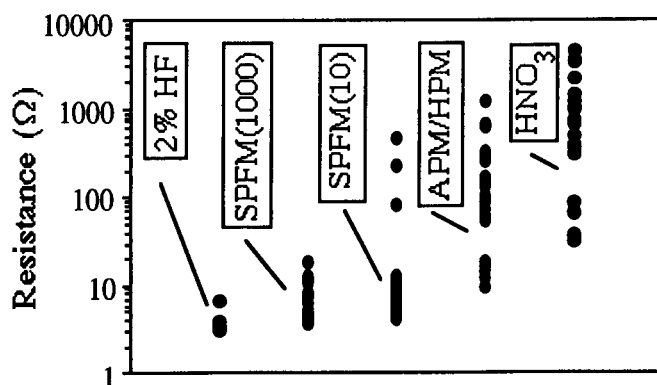


Fig. 5. Resistances of n-type/n-type Si/Si junctions (area: 25 mm<sup>2</sup>) formed by wafer bonding after surface cleaning in different solutions. The IV characteristics were measured across the bonded structures.

The use of SPFM produces Si/Si junctions with properties similar to those obtained using HF-dipping before wafer bonding. It can also be seen that when the HF concentration in the SPFM mixture is lowered some high resistance samples result. This is presumably due to some islands of thicker oxide occurring locally on the surface. The influence of the chemical oxide on the electrical properties of Si/Si junctions formed by wafer bonding has been thoroughly investigated [8]. The chemical oxide gives rise to interface states causing a current-limiting potential barrier at the interface. SPFM cleaning can be expected to influence the interface state density at the Si/Si interface reducing of the thickness of the chemical oxide and possibly through a defect passivating effect of fluorine.

## 5. CONCLUSIONS

The surface cleaning step used prior to wafer bonding has a large impact both on the bondability of the surfaces and on the electrical properties of Si/Si junctions. We have shown how the use of a cleaning mixture, SPFM, consisting of both an oxidizing and an oxide-etching agent can be used to *simultaneously* optimize the bondability of silicon surfaces *and* the electrical properties of bonded Si/Si junctions. Some drawbacks of HF-dipping in bonding applications can be circumvented by use of SPM ( $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ ) with small (10 - 1000 ppm) amounts of HF added without negative effect on the electrical properties.

## 6. ACKNOWLEDGEMENTS

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## Rinsing Efficiency of a SPM added HF Solution

R. Messoussi\* , S. Verhaverbeke\*\* , T. Ohmi\*

### 1. INTRODUCTION

The Sulfuric acid hydrogen Peroxide Mixture (SPM) which was originally developed to remove photoresist, has been widely used as a main cleaning step in different wet cleaning processes [1,2]. SPM solution is commonly used to remove organic contaminants as well as metallic contaminants when followed by a dilute HF step. However, because of the viscous character of the sulfuric acid, sulfur is difficult to remove completely from the surface. In this paper we report on the use of SPM solution added with a small amount of HF which reduces significantly sulfur contamination on cleaned surfaces.

### 2. EXPERIMENTAL

Cz (100) wafers were used with a resistivity range of 8-25  $\Omega$ -cm. Both bare Si surfaces and field oxide surfaces were used. The field oxide was 600-700 nm thick, obtained by wet oxidation at 1000 °C. SPM treatment was carried out at a constant time of 1min. XPS analysis were carried out on a SCIENTA 300 ESCA equipment. TRXRF analysis were performed on a THECNOS 601T equipment.

### 3. RESULTS AND DISCUSSION

Although SPM (Sulfuric acid - hydrogen Peroxide - Fluoric acid Mixture) solution includes an etching agent, a chemical oxide of about the same thickness as a SPM chemical oxide is still grown for HF concentrations up to 10<sup>-2</sup> volume %. For this range of HF concentrations, AFM observations showed no change in surface microroughness [3]. These two observations can be explained as fellows. In this range of HF

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\* Tohoku University, Sendai, Japan

\*\* CFM Technologies, West Chester, PA

concentrations, immediately after immersion in a SPFM solution the oxidation rate of the solution is very high compared to its etching rate, so that at first this latest can be neglected, and when the etching rate becomes significant surfaces are already covered with chemical oxide which protect them from roughening. The etching rate of the used SPFM solutions is very low and was evaluated to be less than 1 Å/min for HF concentrations lower than 10<sup>-2</sup> vol.%.

SPFM solutions produce passivated surfaces with higher contact angles (CA) than SPM treated surfaces. This effect is obtained on bare silicon surfaces (Fig.1) as well as on field oxide covered Si surfaces (Fig.2). The CA of the treated surfaces was evaluated either right after SPFM cleaning, i.e. before DI water rinsing, and after DI water rinsing. From Fig.1 and Fig.2 one can see clearly that the passivation produced after SPFM cleaning is removed from the surface by DI water rinsing.

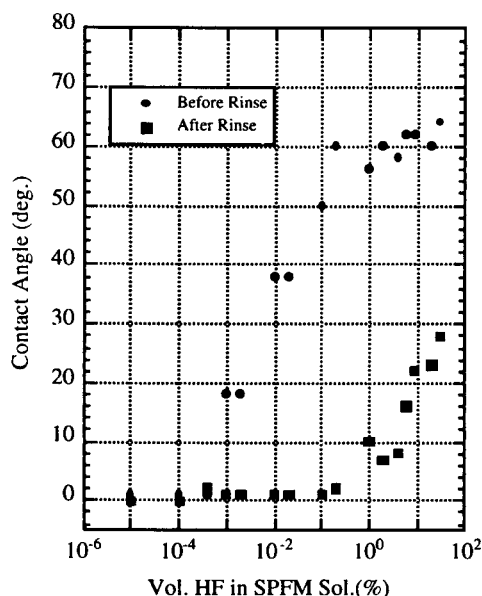


Fig.1 The contact angle on bare Si as a function of the HF concentration in SPFM solutions before and after rinsing

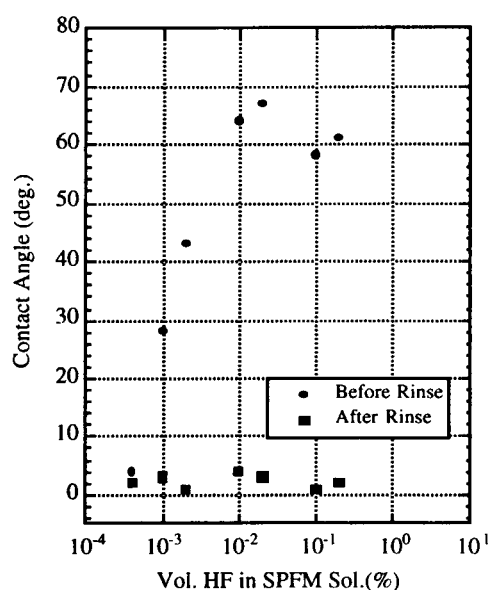


Fig.2 The contact angle on thermal oxide as a function of the HF concentration in SPFM solutions before and after rinsing

XPS analysis (Fig.3a & 3b) show that the passivation produced after SPFM cleaning results from fluorine termination on both chemical oxide and field oxide surfaces. From the energy position of the F1s and O1s peaks we can say that most of

fluorine ( $\approx 97\%$ ) is bounded to the surface as SiOF, only a small proportion of fluorine ( $\approx 3\%$ ) exist as SiF. XPS analysis confirmed that DI water rinsing removes fluorine passivation immediately after surfaces get in contact with water, probably by replacing F terminations by OH terminations. An estimation of fluorine concentration is found to be ranging from  $10^{14}$  at/cm<sup>2</sup> to  $10^{15}$  at/cm<sup>2</sup> after SPFM treatment for HF concentration ranging from  $2 \times 10^{-4} \%$  to  $2 \times 10^{-2} \%$ . The improvement in rinsing efficiency of DI water

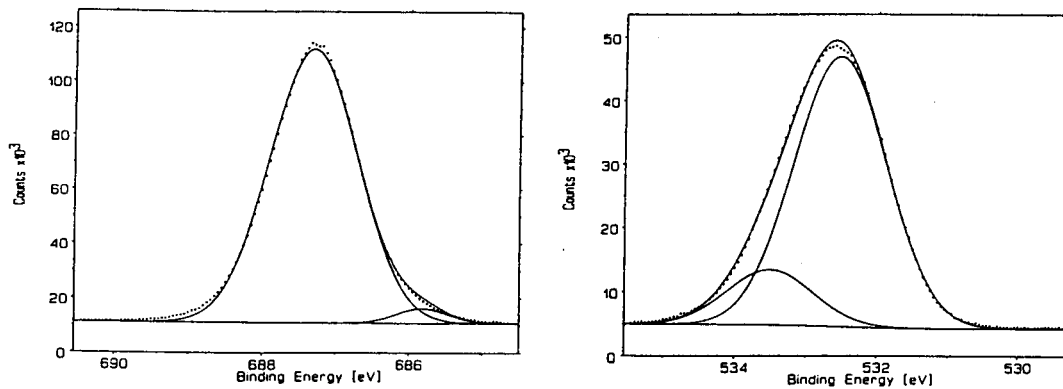


Fig.3. XPS spectra after SPFM cleaning

(a) after deconvolution of the F1s peak

(c) after deconvolution of the O1s peak

after SPFM cleaning is shown in Fig.4. The resistivity of rinsing DI water at the outlet of the overflow tank after SPFM cleaning reaches saturation ( $\approx 18 \text{ M}\Omega\cdot\text{cm}$ ) faster than in the case of SPM cleaning. The difference in efficiency of these two cleaning solutions results from the morphology of the surfaces after cleaning. SPM cleaning produces surfaces with very low CA; since SPM is a viscous solution, therefore chemicals stick to the surface and are difficult to remove by DI water rinsing. The irregular behavior of the resistivity is not reproducible, but similar behaviors after SPM treatments are observable from time to time. This may be due to random removal of sulfuric acid contamination. On the other hand, SPFM cleaning produces surfaces with higher CA than SPM solution, which prevent chemicals from sticking to the surface, therefore rinsing is faster than after SPM cleaning. These results are confirmed by TRXRF evaluation of sulfur contamination, sulfur contamination after a SPFM dip is at least one order less than after SPM treatment.

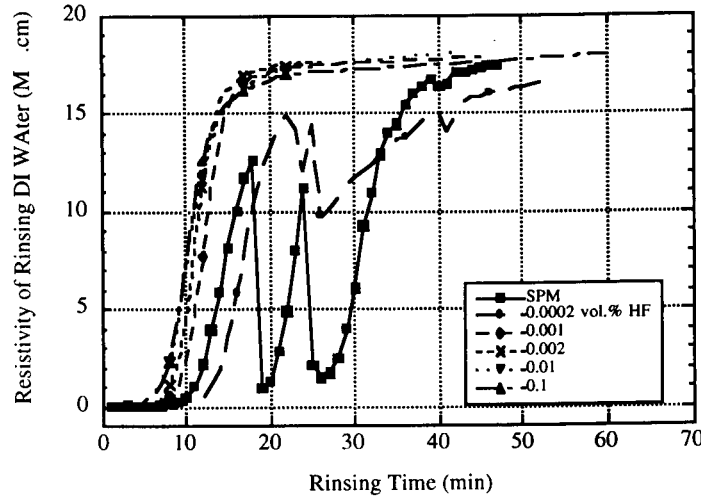


Fig.4 Variation in resistivity of DI water during rinsing of samples which were treated in different SPFM solutions and conventional SPM mixture

#### 4. CONCLUSION

We have shown that SPFM solutions produce fluorine terminated surfaces, as well oxide as bare Si surfaces. Fluorine concentration ranges from about 0.1 monolayer to 1 monolayer for the used HF concentrations. This passivation results in better sulfur removal and shorter rinsing time, in addition to the power of particle removal [4]. Concurrently a chemical oxide still can be formed on the treated surfaces and the fluorine passivation layer is removed during DI water rinsing. Furthermore no roughening is observed for the range of HF concentrations used.

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## Point of use HF purification for Si surface preparation

W. Fyen, L. Mouche\* , M. Meuris, M.M. Heyns

IMEC, Kapeldreef 75, 3001 Leuven, Belgium

J. Zahka

Millipore, 80 Ashby Road, Bedford, MA 01730

### INTRODUCTION

To prevent noble and near noble metallic deposition in HF, several solutions can be used, such as adding  $H_2O_2$  to the HF [6], adding HCl to the HF [7] or using sub ppb grade chemicals. This last possibility is the most widely used. However, once a certain number of dirty wafers are processed into a bath, the HF is loaded with impurities and it is not sub ppb grade anymore. For now two choices are possible, (i) dump the HF between every batch, (ii) use the HF for a certain time or a certain number of batches with the risk of processing wafers with impurity concentrations out of the specification of process. To avoid this problem, a Point Of Use (POU) metal purifier must be installed in a recirculation loop in series with a particle filter. Several purification techniques have already been applied to HF such as ion exchange [8], reverse osmosis [9] and metal displacement [10]. Interesting results have been obtained with all of these techniques. However, there is still a lack of data to compare them.

In this paper, the performance of a POU ion exchange purifier is investigated in HF 0.5 %. The impact of the purifier on metallic concentration in the bath; metallic, particle and organic contamination on wafers; MCLT (Minority Carrier Life Time); surface roughness and 5 nm GOI (Gate Oxide Integrity) will be presented and discussed.

### EXPERIMENTAL

All the experiments were performed under class 10 environment except the TOF SIMS and AFM analysis. Table 1 shows the analytical techniques that were used for these experiments.

A Millipore Chempure™ Dilute HF purifier was used as ion exchange purifier. The experimental system in which the purifier was tested is presented in figure 1. Sub ppb grade concentrated HF was diluted with DI water to prepare HF 0.5 %. After HF treatment, the wafers were rinsed for a few seconds in DI water and were transferred to a dry carrier with nitrogen blow dry if necessary. The experiments were carried on p and n type 6" wafers, precleaned with an IMEC™ clean (SPM 4:1, 90°C, 10' followed by HF 0.5 %, 20°C, 2').

For the MCLT measurements, the wafers were annealed in pure oxygen for 30' at 900°C. For GOI, a 5 nm oxide was grown in  $O_2/N_2$  without chlorine additive.

### RESULTS

First of all, the extractable from the purifier was measured with HF 0.5%. The results are presented in table 2. Except for a slight Fe contamination inherent to the recirculation loop, no extractable was detected.

To look at the performance of the purifier, the metallic concentration in solution was measured after spiking with 10 ppb of  $Ni(NO_3)_2$ ,  $Fe(NO_3)_3$  and  $Cu(NO_3)_2$  versus the number of bath turnovers through the purifier. The three curves for Ni, Fe and Cu have the same shape, so only the Fe results are plotted in figure 2.

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\* Present address: Motorola Semiconducteurs, Avenue Eisenhower, 31023 Toulouse CEDEX, FRANCE

One can see that with less than 5 turnovers the Fe concentration decreases below 0.5 ppb, where the equilibrium between the impurities in solution and the impurities adsorbed on the membrane is reached.

To quantify the influence of the purifier on wafer cleaning, fresh HF 0.5% was recirculated through the bypass. Then, the bath was spiked with 10 ppb of  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$ . After this, the HF flow was switched from the bypass to the purifier. Before spiking, after spiking and after purification some wafers were dipped for ten minutes into the bath and some HF samples were taken from the top of the tank. Results from these samples are presented in table 3 and figure 3.

Finally, to get information on the purifier capacity, the HF impurity concentration after purification was investigated versus the cumulative loading level (figure 4).

### DISCUSSION

The results presented above illustrate that an ion exchange POU purifier can be used for Silicon processing in HF. Metallic impurities in HF 0.5% are removed to sub-ppb level in less than 5 bath turnovers, without additional particle or organic contamination. This can reduce Cu outplating, since Cu is known to deposit in HF proportionally to its bath concentration. This also improves the MCLT of n type wafers, confirming the correlation between Cu surface concentration and MCLT of n type wafers established in the literature [11]. The lack of significant influence of the purifier on GOI is logical if we take into account the fact that Cu can diffuse very quickly in Si wafers, and is therefore not located in or near the gate oxide.

The test performed to study the concentration in solution after purification versus the total bath loading shows that the purifier has a very high capacity. This proves that the number of adsorption sites is sufficiently high to ensure an adequate purifier lifetime. One interesting point with ion exchange is that the purifier is used only when it is necessary, in others words, if the HF is always very clean the purifier lifetime is practically infinite.

### CONCLUSION

The results presented in this work show that an ion exchange POU purifier can have a beneficial impact on Si surface preparation. The experimental and theoretical aspects of this study will be soon developed in detail in a journal.

### ACKNOWLEDGEMENTS

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**Table 1.** Characterisation techniques and detection limits.

| Measurement         | Method               | Equipment               | Det. limit                       |
|---------------------|----------------------|-------------------------|----------------------------------|
| Metals in HF        | Droplet drying /TXRF | Atomika XSA 8000        | <0.05 ppb for Cu, Fe and Ni      |
| Metals on wafer     | VPD/DSE TXRF         | Atomika XSA 8000        | $10^9$ atoms.cm <sup>-2</sup>    |
| Particles on wafers | Light Scattering     | Censor ANS 100          | 0.15 $\mu$ m PLSE                |
| Organic contam.     | TOF SIMS             | Trift I (Charles Evans) | $10^9$ atoms.cm <sup>-2</sup>    |
| MCLT                | $\mu$ PCD            | Phoenix MRM             | $10^{10}$ atoms.cm <sup>-2</sup> |
| Roughness           | AFM                  | Digital Dimension 3000  | 0.05nm                           |

**Table 2.** Extractable from the purifier. The solution was 0.5% HF.

|                                 | Cu conc. (ppb) | Fe conc. (ppb) | Ni conc. (ppb) |
|---------------------------------|----------------|----------------|----------------|
| through bypass                  | <DL            | 0.28           | <DL            |
| through purifier (5 turnovers)  | <DL            | 0.34           | <DL            |
| through purifier (10 turnovers) | <DL            | 0.58           | <DL            |

**Table 3.** Impact of a POU purification on HF last cleaning.

|                                                   | Fresh HF 0.5 %                      | After Ni, Fe and Cu spike (10 ppb) | After purification                |
|---------------------------------------------------|-------------------------------------|------------------------------------|-----------------------------------|
| Ni in HF (ppb)                                    | < 0.05                              | <b>9.73 <math>\pm</math> 0.05</b>  | <b>0.75 <math>\pm</math> 0.05</b> |
| Fe in HF (ppb)                                    | 1.16 $\pm$ 0.05                     | <b>11.9 <math>\pm</math> 0.05</b>  | <b>0.53 <math>\pm</math> 0.05</b> |
| Cu in HF (ppb)                                    | < 0.05                              | <b>9.89 <math>\pm</math> 0.05</b>  | <b>0.26 <math>\pm</math> 0.05</b> |
| Ni on p type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.05                              | < 0.05                             | < 0.05                            |
| Fe on p type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.3 (*)                           | < 0.3 (*)                          | < 0.3 (*)                         |
| Cu on p type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.07                              | <b>51.12 <math>\pm</math> 0.07</b> | <b>0.31 <math>\pm</math> 0.07</b> |
| Ni on n type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.05                              | < 0.05                             | < 0.05                            |
| Fe on n type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.3 (*)                           | < 0.3 (*)                          | < 0.3 (*)                         |
| Cu on n type Si ( $10^{10}$ at./cm <sup>2</sup> ) | < 0.07                              | <b>37.75 <math>\pm</math> 0.07</b> | <b>0.75 <math>\pm</math> 0.07</b> |
| LPD's > 0.15 $\mu$ m PLSE per wafer               | 147 $\pm$ 47                        | 116 $\pm$ 40                       | 143 $\pm$ 60                      |
| Organic contam.on p type Si                       | no difference between the 3 samples |                                    |                                   |
| AFM/RMS (nm) on p type Si                         | 0.13                                | 0.17                               | 0.14                              |
| AFM/RMS (nm) on n type Si                         | 0.18                                | 0.15                               | 0.16                              |
| MCLT ( $\mu$ s) in p type wafers                  | 128 $\pm$ 17                        | 214 $\pm$ 48                       | 291 $\pm$ 39                      |
| MCLT ( $\mu$ s) in n type wafers                  | 630 $\pm$ 39                        | <b>108 <math>\pm</math> 30</b>     | <b>880 <math>\pm</math> 176</b>   |

(\*)for Fe, a practical background noise value of a few  $10^9$  atoms/cm<sup>2</sup> is assumed, resulting from the VPD-DSE technique.

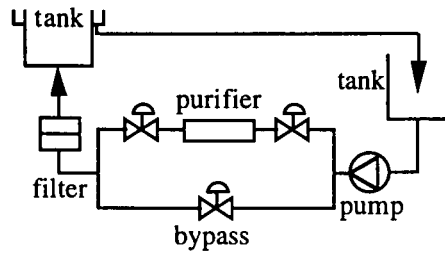


**Figure 1.** Experimental set up.

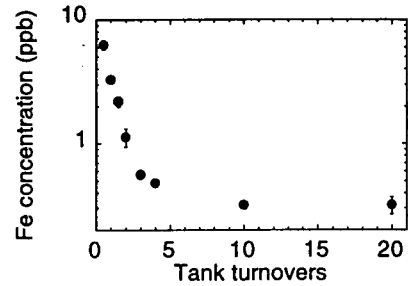


**Figure 2.** Fe concentration after spiking vs number of turnovers through the purifier.

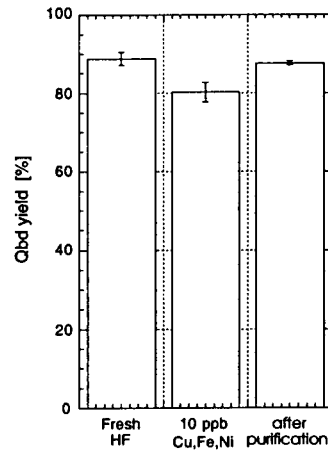
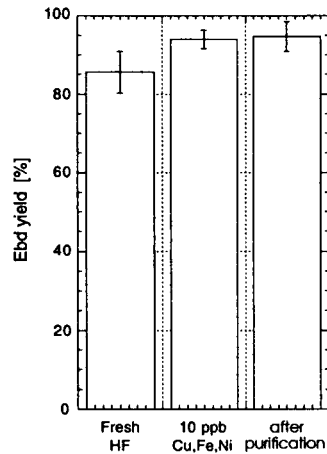


**Figure 3.** EBD and QBD results for 5 nm gate oxide on 1.12 mm<sup>2</sup> capacitors. Intrinsic breakdown at 11 MV/cm (EBD) and 0.1 C/cm<sup>2</sup> (QBD).

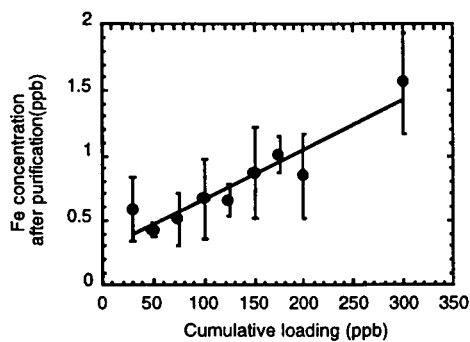


**Figure 4.** Fe concentration after purification vs cumulative Fe loading.

# Impact of Gold and Copper on the Recombination Activity of a Hydrogen Terminated Silicon Surface

G. J. Norga, K. A. Black, J. Michel, L. C. Kimerling

Department of Materials Science and Engineering, Massachusetts Institute of Technology  
Cambridge, MA 02139, USA

## Abstract

A superior control over the surface chemistry of crystalline silicon in wet and dry ambients is an essential requirement for achieving high product yield in integrated circuit manufacturing. Because of their deleterious effects on device yield and performance, control and detection of trace metals on silicon is especially critical. Meanwhile, increases in process complexity have created a need for fast, *in situ* diagnostic techniques for early detection of process contamination. We demonstrate surface-sensitive carrier lifetime measurements for *in situ* control of metal surface chemistry on hydrogen terminated silicon.

## 1 Introduction

The detrimental effects of metallic contaminants on submicron electron devices are well documented [1], [2]. When present in silicon, heavy metals often form midgap states, which act as efficient generation-recombination centers, increasing the leakage current of junctions. Due to their high diffusivity and low solubility, they exhibit a strong tendency to precipitate and decorate extended defects, leading to junction shorting and degradation of the gate oxide integrity (GOI).

Electrical techniques have long been used successfully for in-line detection of bulk defects and impurities. We have developed a new wafer-scale characterization technique for surface-sensitive minority carrier lifetime measurements, based on radio-frequency photoconductance decay (RF-PCD) [3, 4]. Under optimal conditions, this method is capable of detecting down to  $10^8 \text{ cm}^{-2}$  electrical defects without the need for a thermal drive-in step. In this paper, the application of RFPCD for *in situ* studies of metallic contaminant deposition during wet cleaning will be discussed.

## 2 Experimental

### 2.1 Wafer surface preparation

The MIT clean consists of 2 minutes in dilute (1:100) HF, a 10s DI rinse, followed by immersion in hot piranha ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) at  $70^\circ\text{C}$  for 4 minutes. The purpose of the first cleaning step is to remove any native oxides, while the second step grows a 2-3 nm thick chemical oxide, which traps any contaminants present in the top silicon layer. After the piranha step, the wafer is thoroughly rinsed in DI for 1 minute, followed by immersion in dilute (1:100) HF for 2 minutes.

### 2.2 Controlled contamination

We use standard solutions with a precisely known concentration of a specific ion to obtain controlled, low concentrations of metallic ions in HF solution. We used both AAS standard solutions (Alpha Aesar Specpure) and ICP-MS standard solutions (Aldrich Chemical co.). Volumetric amounts of the standard solutions were added to the cleaning solution using Fischer Scientific Digital Micropipettes (1-10 ml, 40-200  $\mu\text{l}$ , 5-50  $\mu\text{l}$ ).

### 2.3 Wafer materials

Two types of ( $> 5$  ms) wafers were used:

- n-type, CZ, 12.5 cm diameter wafers, resistivity 10-25  $\Omega\text{cm}$ ,  $\tau_{bulk} > 5$  ms;
- p-type, CZ, 15 cm diameter wafers, resistivity 10-15  $\Omega\text{cm}$ ,  $\tau_{bulk} > 6$  ms.

### 2.4 Analysis methods

A Fisons Plasma-Trace 1 High Resolution ICP-MS was used to verify the accuracy of metallic impurity concentrations and the absence of cross contamination in the controlled contamination experiments. The effect of metallic contaminants on the surface minority carrier lifetime was measured by radio-frequency photoconductance decay (RFPCD). The use of this technique for sensitive detection of surface chemical processes was previously demonstrated [4].

## 3 Results and Discussion

### 3.1 In situ detection of gold and copper deposition on silicon from 1:100 HF

After precleaning, the wafers were immersed in 1:100 HF solution while the surface lifetime was monitored continuously. The effect of adding 10 ppb  $\text{Au}^{+++}$  (as  $\text{AuCl}_3$ ) to the cleaning solution is shown in Figure 1.

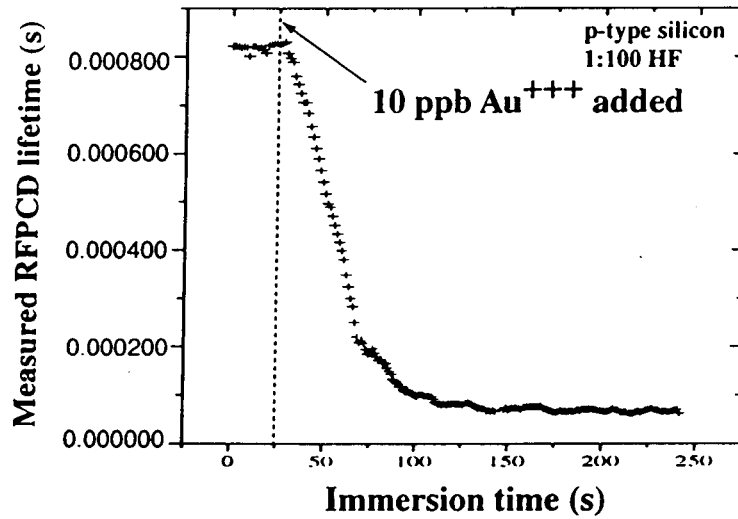


Figure 1: In situ detection of  $\text{Au}^{+++}$  deposition from 1:100 dilute HF.

Because of the high carrier lifetime of the wafer material used, bulk recombination can be neglected and the measured lifetime is inversely proportional to the areal density of surface recombination centers, introduced by chemisorbed Au atoms [5, 6]. The steep drop in the lifetime for  $\text{Au}^{+++}$  is in agreement with a fast reduction process by hole injection in the silicon valence band [7].

Figure 2a compares the deposition kinetics of copper and gold. The relatively slow decrease of the lifetime for copper deposition is caused by the nucleation of nanometer sized precipitates [8, 9, 10, 11, 12]. The detailed mechanism of copper deposition from dilute HF will be reported elsewhere [7].

Instantaneous reduction of gold ions at the Si/HF interface leads to a diffusion-limited deposition process, as expressed by the Cottrell Equation (Figure 2b):

$$N_{Au}(t) = 2 \cdot D^{1/2} C \pi^{-1/2} t^{1/2} \quad (1)$$

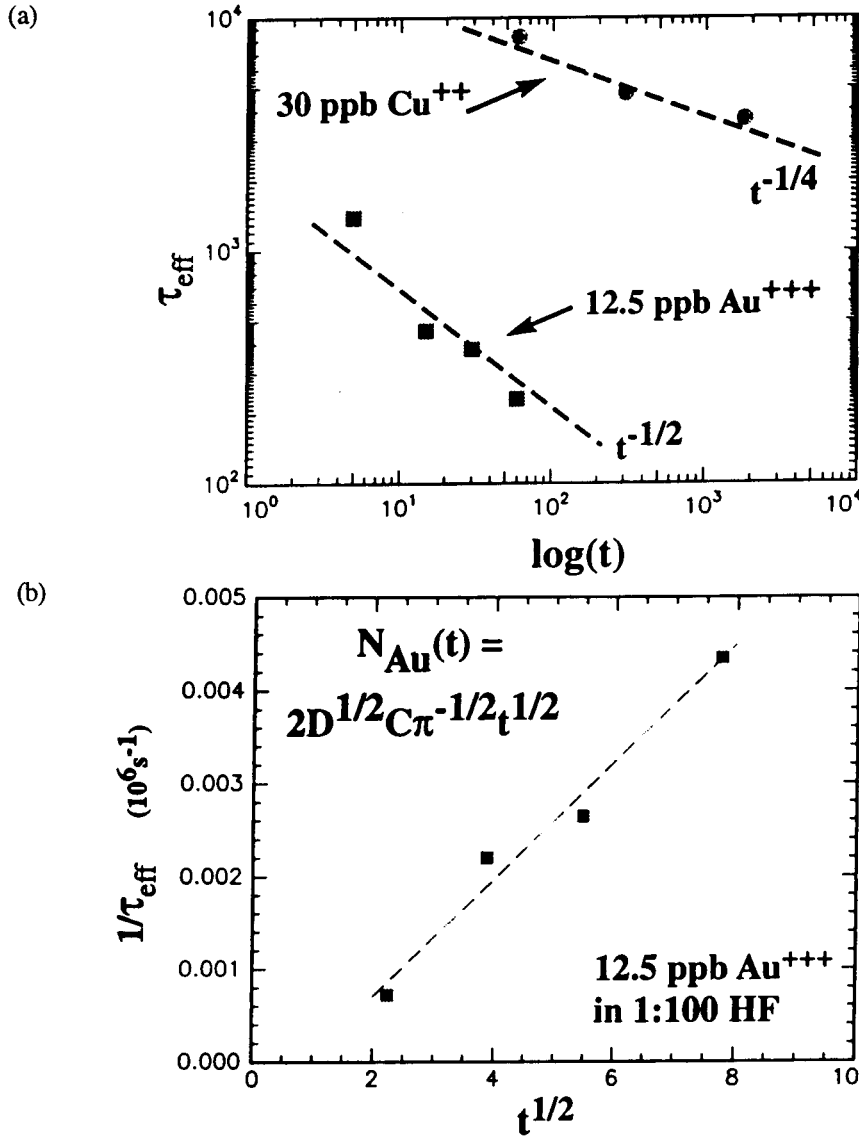


Figure 2: (a)  $\tau$  vs  $\log(\text{exposure time})$  for exposure of CZ Si to 1:100 HF solutions containing 30 ppb  $\text{Cu}^{++}$  (as  $\text{CuNO}_3$ ) and 10 ppb  $\text{Au}^{+++}$  (as  $\text{AuCl}_3$ ). (b)  $1/\tau$  vs  $t^{1/2}$  for exposure to 10 ppb  $\text{Au}^{+++}$ . All the measurements were performed in 48 % HF.

### 3.2 The effect of air exposure on recombination activity of copper

The influence of air exposure following the contamination treatment on the surface lifetime measured by RFPCD is shown in Figure 3a. A strong increase in the recombination activity of the copper is observed as a result of air exposure step. A possible explanation for this effect is illustrated in Figure 3b. The formation of dangling bonds during native oxide growth in air [13] gives rise to reduction of physisorbed copper ions to metallic copper. While the native oxide is removed by subsequent immersion in 48 % HF, the copper remains chemisorbed and acts as an effective surface recombination center.

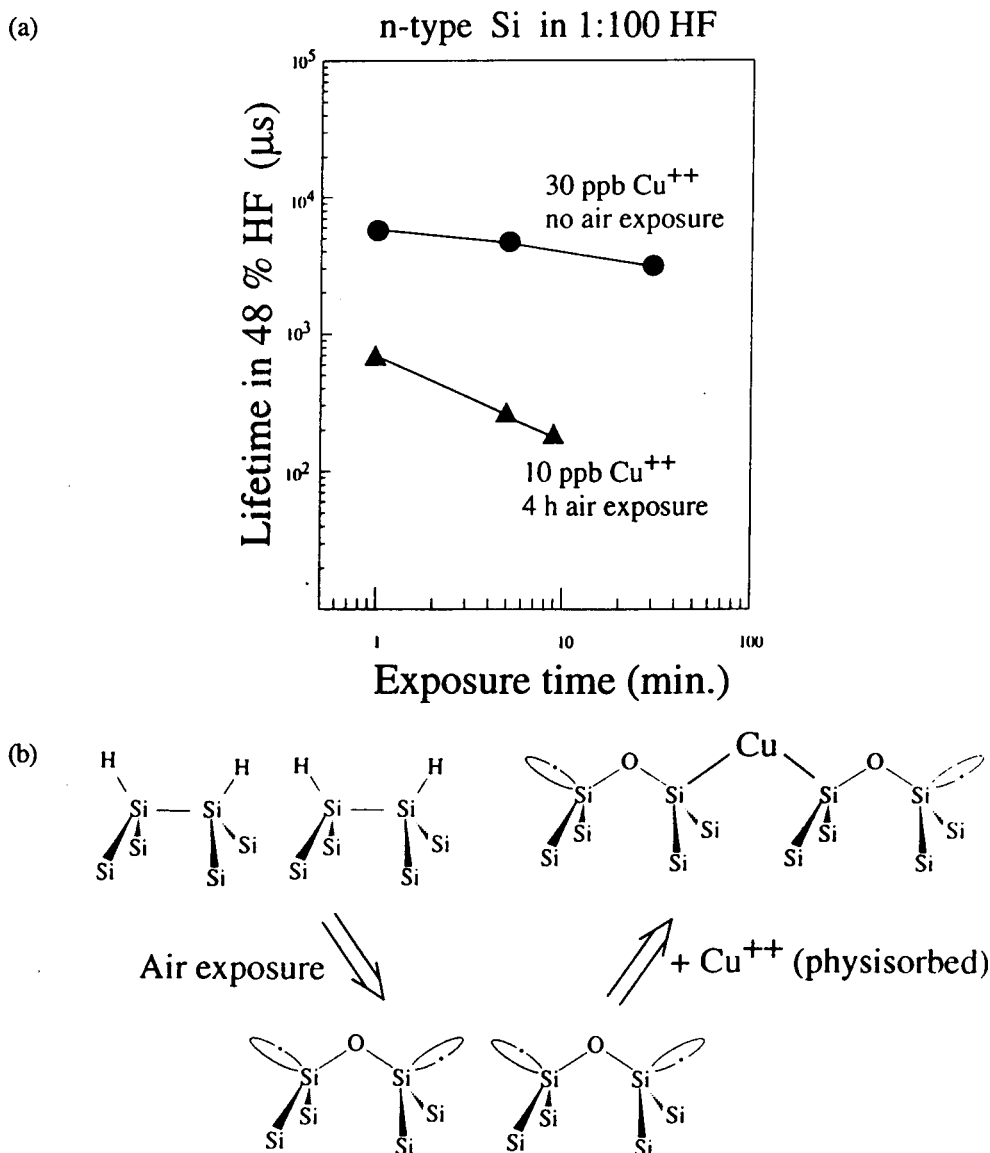


Figure 3 (a) Effect of air exposure on the recombination activity of copper. (b) Proposed mechanism for the effect of air exposure on the recombination activity of physisorbed copper.

## 4 Conclusions

A metal's chemical bonding state and distribution over the hydrogen terminated silicon surface determine its effect on surface recombination velocity (SRV). For copper, which deposits from HF by a conduction band mechanism, SRV scales with the areal density of copper precipitates. Reduction of physisorbed copper during air exposure introduces additional recombination centers. Because gold deposits by a hole injection mechanism without nucleation of precipitates, a linear relationship between SRV and gold coverage is obtained.

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### THREE-ZONES "IN-DEPTH" DISTRIBUTION OF THE INTRINSIC CHARGED TRAPS THROUGHOUT SiO<sub>2</sub> ON Si ON THE SUBNANOSCALE

O.V.Romanov\*, I.A.Kotov, V.P.Letavin\*\*

The notion of the interface and its "intermediate layer" or "disturbed or transition layer" (IL) rests ambiguous for insulator/semiconductor (IS) systems in general and for IS-system in particular. Different experimental techniques give variable evaluation of the "intermediate layer" (or interface) thickness. High Resolution Transmission Electron Microscopy (HRTEM) characterized the border Si/a-SiO<sub>2</sub> as structurally abrupt with low roughness, about 1 monolayer. X-ray and other photoelectron spectroscopy techniques (XPS, UPS, SPS) showed the existence at the interface Si/thermal SiO<sub>2</sub> of "intermediate zone" of 5-10 Å width with some specific quantity of the silicon suboxides Si<sub>1+</sub>, Si<sub>2+</sub>, and Si<sub>3+</sub> for the low indexes surface orientations. There are some papers with results on different physical-chemical properties of the "intermediate layer" of Si/SiO<sub>2</sub> structures (IR optical absorption and refraction, SiO<sub>x</sub> stoichiometry distribution, chemical etching velocity, "transition layer" density etc.), where its width was evaluated in limits from 2 nm to 7 nm. So the principal parameter of the interface Si/a-SiO<sub>2</sub> - the width of the "intermediate layer" is still controversial subject and demands elaboration of new high precision and sophisticated methods for its control and evaluation. The main goal of our research was the detailed "in-depth" distribution of the intrinsic charged traps throughout thin and super-thin SiO<sub>2</sub> layers on Si and the new approach to the interpretation of the IS-system electronic properties [1-5].

The IS-structures of investigation were fabricated after standard flattening and RCA cleaning procedures before oxidation in two groups. The first group of IS-samples (Middle Temperature Oxide- MTO) was prepared on p-Si (4÷11 Ohm·cm) (100) wafers by the Electron-Cyclotron Resonance (ECR) Plasma Oxidation at the substrate temperature 400°C, microwave power 600 W, and process pressure 2.5 mTorr. The second one of IS-specimens (High Temperature Oxide - HTO) was formed on n- and p-Si (4÷8 Ohm·cm) (100) wafers by the standard low pressure thermal oxidation in dry pure O<sub>2</sub> at the temperature 1050°C. Oxide layers of both groups were not annealed and were as-grown oxides with varied thickness of SiO<sub>2</sub> layers from 10 nm to 60 nm.

The dependencies of the High Frequency (1 MHz) and Quasistatic capacitances (C, C<sub>qs</sub>), Photocapacitance (C<sub>ph</sub>), Transversal current (j), and Photocurrent (j<sub>ph</sub>) of the system Silicon-Silicon Dioxide layer-proper aqueous electrolyte on electrochemical potential were measured by the Combined Field Ef-

\* St-Petersburg Univ., POB - 178 St-Petersburg-198216, RUSSIA; Fax: +7-(812)-428-724; E-mail: oroman@ont.niif.spb.su

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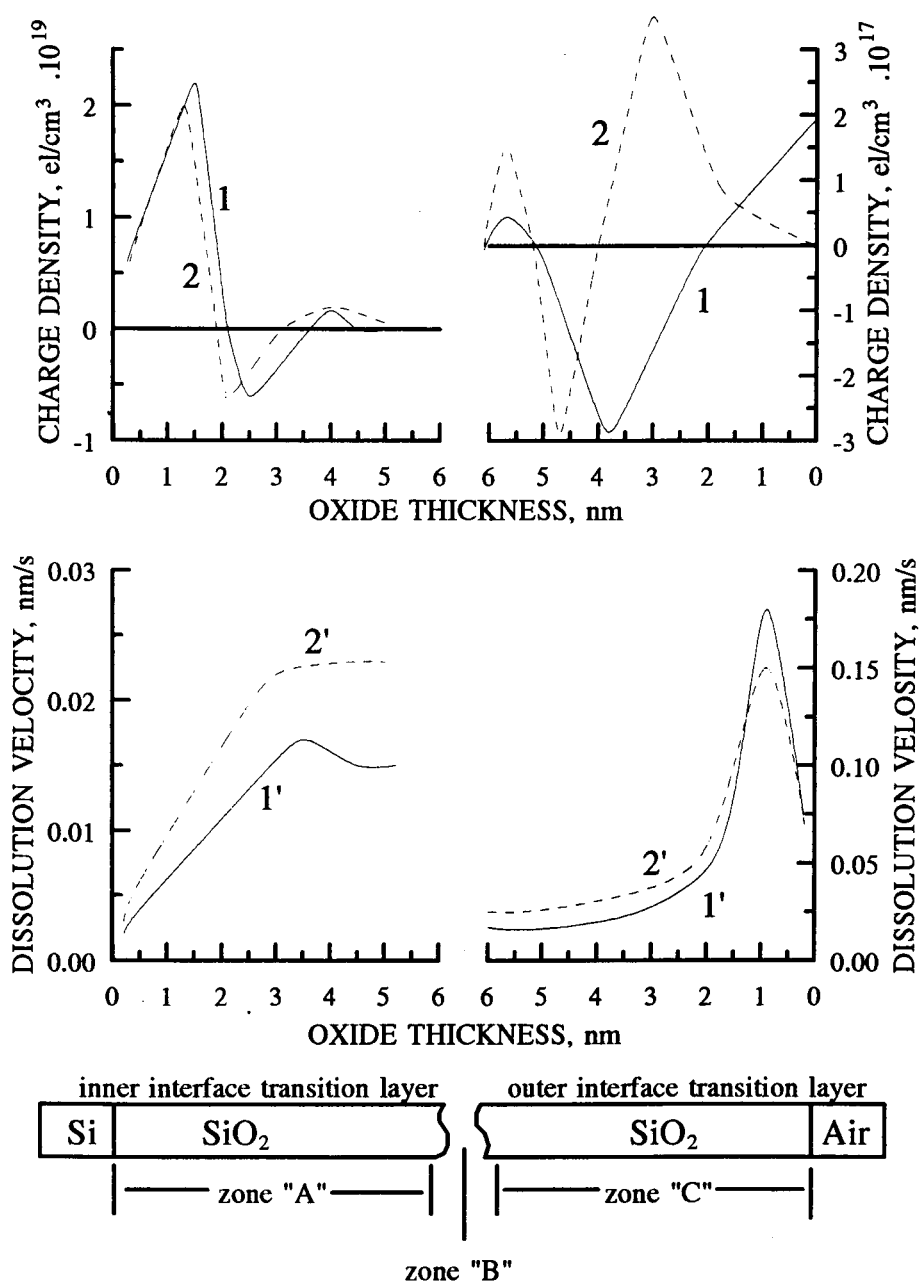


Figure 1. "In-depth" distribution of the intrinsic charged trap density (1, 2) and the chemical dissolution velocities (1', 2') through the Silicon Dioxide layers prepared by the High - Temperature (1, 1') and the Middle-Temperature (2, 2') oxidation

fect in Electrolytes (CFEE) Method [6] after each dissolution treatment. All measurements were performed at 295 K into special electrochemical cell. Statistical processing of these characteristics enabled us to calculate some electronic and physical-chemical parameters of system in question and its variation with the thickness of a-SiO<sub>2</sub> layers.

The results of statistical processing of our experiments are presented in the Fig.1. Total positive electric charge at the Si/SiO<sub>2</sub> interface was  $Q_{tot}=+(5.61\pm 0.41)\cdot 10^{11}$  el·cm<sup>-2</sup> for the MTO samples and  $Q_{tot}=+(4.55\pm 0.26)\cdot 10^{11}$  el·cm<sup>-2</sup> for the HTO specimens. The samples of MTO group had the main maximum of fast Electronic Surface States (ESS) density into the upper half of the band gap  $E_{ss}-E_v=0.7$  eV. But the specimens of HTO series had the main maximum of ESS density into the down half of the band gap  $E_{ss}-E_v=0.4$  eV and more weak maximum into the upper half of the band gap  $E_{ss}-E_v=0.7$  eV. For both types of specimens the ESS density decreased sharply when the thickness of SiO<sub>2</sub> layer becomes smaller than 1.0 nm.

Independently of the initial oxide layer thickness, the distribution of intrinsic charged traps had some common features for two types of oxide (Fig.1). We revealed three zones of the intrinsic charged traps location - "A", "B", and "C" through SiO<sub>2</sub> layer. The first zone "A" of total thickness 5-6 nm near the Si/SiO<sub>2</sub> interface includes three sub-zones of charged traps density distribution: donor-type traps with density  $\rho=+(0.3-1.8)\cdot 10^{18}$  el·cm<sup>-3</sup> into an interval  $x_i=3.5-5.0$  nm from the Si/SiO<sub>2</sub> interface; acceptor-type traps with density  $\rho=-(0.5-6.0)\cdot 10^{18}$  el·cm<sup>-3</sup> at  $x_i=2.0-3.5$  nm; and dramatic rise of the positively charged traps density to  $\rho=+(0.7-2.2)\cdot 10^{19}$  el·cm<sup>-3</sup> into the sub-zone with coordinates  $x_i=0.2-2.0$  nm.

Totally ignored in earlier experiments the zone "C" of charged intrinsic traps location is situated at the SiO<sub>2</sub>/Air interface into an interval of 4÷6 nm. It consists of two (or three) sub-zones: sub-zone of positively charged traps with  $\rho=+(1-3.5)\cdot 10^{17}$  el·cm<sup>-3</sup> is the nearest to the interface under discussion; sub-zone of negative traps with  $\rho=-(0.5-3)\cdot 10^{17}$  el·cm<sup>-3</sup> and another possible sub-zone of donor-type traps with  $\rho=+(0.3-1.5)\cdot 10^{17}$  el·cm<sup>-3</sup> are more remote correspondingly from the SiO<sub>2</sub>/Air interface (Fig.1).

There is very low charged traps density  $\rho < |\pm 3\cdot 10^{16}|$  el·cm<sup>-3</sup> into the middle chemically and structurally uniform (Fig. 1, zone "B") part of SiO<sub>2</sub> layers.

"In-depth" location of intrinsic charged traps throughout zones "A", "B", "C", and its sub-zones correlates with the "in-depth" distribution of SiO<sub>2</sub> layers etching velocities ( $v_{dis}$ ) measured at the same time in our experiments (Fig.1, curves 1', 2'), which partly supports the results of [4,5].

The most important results of this work are the thicknesses evaluation and the revelation of detailed "in-depth" distribution of the intrinsic charged electron/hole traps near interior (Si/SiO<sub>2</sub>) and exterior (SiO<sub>2</sub>/Air) borders of thin and super-thin SiO<sub>2</sub> layers. It is important to underline that there are a consecutive "damping oscillation" distributions of donor- and acceptor-type intrinsic charged traps near the borders of SiO<sub>2</sub> layer on c-Si with the donor-type traps at the limits. Specific "intermediate (transition) layer" at the Si/SiO<sub>2</sub> interface with enhanced trap density extends to 5-6 nm, and consists of three or more types of structural

defects, which play the role of hole and electron traps. The principal cause of this "A"-zone creation is the misfit of Si and SiO<sub>2</sub> crystallographic structures and associated stretching/compressive stress, which is accommodated into SiO<sub>2</sub> "intermediate layer" by revealed charged defects (traps). The possible existence of the acceptor-type traps into this layer was supposed by [7]. The existence of an extended ( $x_i=2-7$  nm) compressive stress zone into SiO<sub>2</sub> near Si/SiO<sub>2</sub> interface was revealed by various techniques for the spectroscopy of interfaces [3-5]. Our trap distribution results support the model of the extended "intermediate layer" created by the compressive stress. From our point of view the zone "A" is the region which prescribes the quality and the perfectness of MOSFETs.

Revelation by CFEE-method of some specific charged traps distribution into SiO<sub>2</sub> layer near exterior SiO<sub>2</sub>/Air interface and its "in-depth" distribution correspondence to the local chemical dissolution velocity (Fig.1) points another important zone throughout SiO<sub>2</sub> layers which can limit the quality and reliability of MOS devices. It seems more probable that the main causes of the "C"-zone generation are the finishing step of the silicon oxidation procedure and the processes of adsorption, diffusion, and chemical interaction of the laboratory atmosphere components such as H<sub>2</sub>O, CO<sub>2</sub>, and O<sub>2</sub> with the free outside surface of SiO<sub>2</sub> layers as soon as its were formed. This zone may be more responsible on the reliability of MOSFET ICs than zone "A".

In summary, the application of experimental CFEE-method revealed complex "in-depth" distribution of intrinsic charged electron/hole traps through thin and super-thin SiO<sub>2</sub> layers on Si created by the High (1050°C) and Middle (400°C) temperature oxidations, which consisted with the same of the chemical etching velocity; confirmed the existence of extended ( $x_i=4-6$  nm) "intermediate layer" near the Si/SiO<sub>2</sub> interface and revealed complex "in-depth" distribution of intrinsic charged electron/hole traps near exterior SiO<sub>2</sub>/Air interface. General and particular features of two types Si/SiO<sub>2</sub> systems were outlined. "In-depth" distributions of the acceptor- and donor-type traps throughout SiO<sub>2</sub> layers consists of three zones: "A" - interior, "B" - middle, and "C" - exterior, and some sub-zones specifically located in-depth of layer in a certain order. The presented model takes in consideration the misfit of Si and SiO<sub>2</sub> crystallographic structures and stress (compressive and stretching) at the Si/SiO<sub>2</sub> interface, and impact of surrounding atmosphere components on the free outside surface of SiO<sub>2</sub> layer.

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## MONITORING OF HF-LAST CLEANS USING THE SURFACE CHARGE PROFILING METHOD

P. Roman, J. Staffa, M. Brubaker, S. Fakhouri, J. Ruzyllo and E. Kamieniecki\*

### 1. INTRODUCTION

The increased cost of wafers and processing in deep-submicron device manufacturing calls for broader, more rigidly executed monitoring of processes at various stages of microchip manufacturing. To be effective, the process monitoring should be carried out in-line, in real time which requires quick and non-invasive methods. Presently, methods of surface characterization that are quick and non-invasive typically address specific surface characteristics, and hence, a broad range of surface characteristics go uncontrolled in the course of device manufacturing.

The HF:H<sub>2</sub>O etch is a commonly used step in silicon surface cleaning and conditioning operations. The condition of the surface following the HF:H<sub>2</sub>O etch has a significant bearing on the outcome of the subsequent step. Hence, the effect of the HF:H<sub>2</sub>O etch should be carefully monitored, but unfortunately available methods, such as XPS, or wetting angle measurements are not compatible with the requirements of in-line process monitoring.

In this work, the Surface Charge Profiler (SCP), a new tool designed to fill the gap in front-end-of-the-line process sampling is introduced. The SCP is used here to monitor the outcome of an HF:H<sub>2</sub>O etch involving varied parameters.

### 2. EXPERIMENTAL

A commercial SCP system is used in this study [1]. The operation of the SCP is based on the surface photovoltage (SPV) effect which in this particular case is induced by illumination of the Si surface with a beam of chopped, shortwavelength (450 nm), low intensity light having photon energy higher than the silicon bandgap. The light penetration depth is very shallow (.4  $\mu$ m) which means that the outcome of the measurement is dominated by characteristics of the surface and sub-surface region. The SCP method does not utilize external bias voltage or corona charging, and the probe does not come into contact with the wafer surface during measurement. The SCP measures both recombination lifetime at the surface and either surface charge density or active dopant concentration at the surface.

The basic experimental sequence in this investigation consisted of two steps: (i) etching of the native/chemical oxide on the silicon wafer using 1%

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The Electronic Materials and Processing Research Lab, Department of Electrical Engineering, Penn State University, University Park, PA 16802, US.

\* QC Solutions, Inc., 150-U New Boston St., Woburn, MA 01801, US.

HF:H<sub>2</sub>O followed by a 5 min. rinse and N<sub>2</sub> drying and (ii) SCP measurement. Wafers (p-type, <100>, CZ, 100 mm diam., 2.5-4 Ωcm) as received from the manufacturer were used. Additional information on the condition of the surfaces following HF treatment was obtained from wetting angle measurements.

### 3. RESULTS AND DISCUSSION

It was previously observed that HF:H<sub>2</sub>O etching adds positive charge to the surface typically in an amount that for p-type Si is sufficient to induce inversion [2]. Under this condition, further subtle variations in surface charge density may go unnoticed as the depletion width,  $W_d$  will not change beyond its maximum value,  $W_m$ . This state will only change when negative charge sufficient to bring the surface out of inversion will be added to the surface. Therefore, the surface charge density determined using the SCP may not respond adequately to accomplish effective monitoring of HF-last cleaning sequences. However, under inversion, the surface recombination lifetime measured using the SCP is an independent parameter, and due to the electrical field in the inversion layer that sweeps photogenerated electrons toward the surface, it is expected to reflect the condition of the Si surface or Si/oxide interface.

In the first part of this study, the time of immersion in HF:H<sub>2</sub>O solution was varied to determine whether this parameter would respond adequately to incomplete removal of the native oxide. A good correlation is observed between the surface recombination lifetime measured using SCP (Fig. 1) and the wetting angle (Fig. 2).

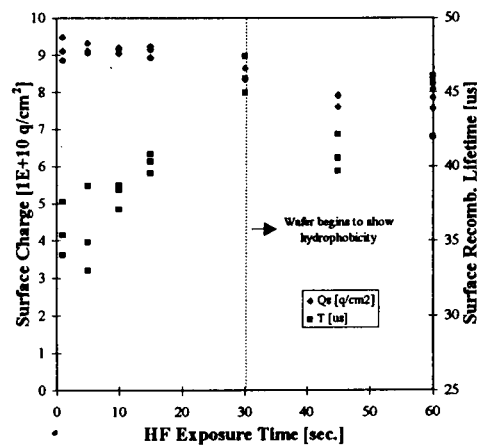


Figure 1. Surface charge and surface recombination lifetime vs. time of exposure to HF(1):H<sub>2</sub>O(100).

Following this, surface charge was measured as a function of time of exposure to ambient air following HF:H<sub>2</sub>O 1:100 and 1:500 treatments. For the hydrophobic HF(1):H<sub>2</sub>O(100) treated surface, the surface charge is highly positive and stable (Fig. 3). For the hydrophilic HF(1):H<sub>2</sub>O(500) treated surface, the

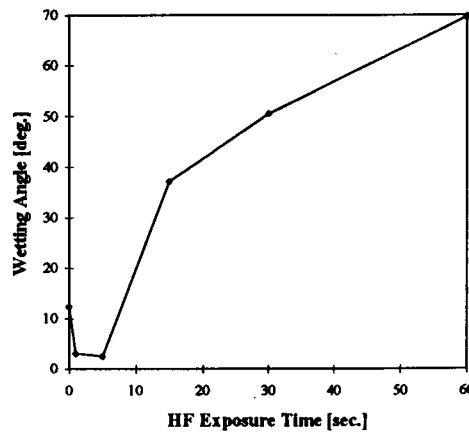


Figure 2. Wetting angle vs. time of exposure to HF(1):H<sub>2</sub>O(100).

surface charge is initially highly positive, but begins to decrease after only 30 min. in ambient air. The increased activity in ambient air of native oxide covered surfaces has been attributed to Si-OH condensation and hydrolization of bridging Si-O-Si sites by water vapor while the near ideal electrical passivation of HF-last treated silicon surfaces has been mostly attributed to the presence of Si-H groups [3].

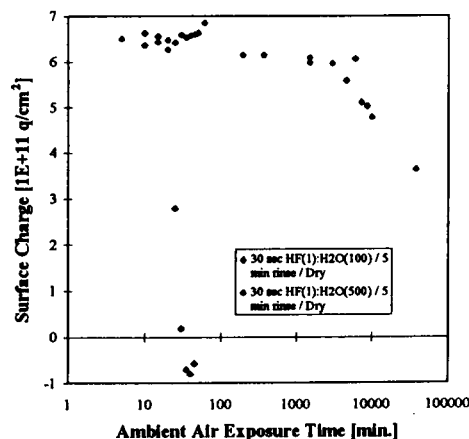


Figure 3. Surface charge vs. time of exposure to ambient air on surfaces treated in HF:H<sub>2</sub>O 1:100 and 1:500.

Next, the SCP was used to measure the doping concentration in the space charge region,  $N_{sc}$ , for a wafer following HF(1):H<sub>2</sub>O(100) treatment. The SCP-measured doping concentration is initially lower than the bulk value obtained from four-point resistivity measurements. It has been reported that hydrogen [4] and metals such as Cu [5], which is introduced during chemomechanical polishing, and Fe [6] in silicon form pairs with boron which render the boron electrically inactive.

To verify boron deactivation in the near surface region, wafers were annealed on a hot plate for 15 min. in ambient air prior to the HF(1):H<sub>2</sub>O(100) treatment and SCP measurement. The results (Fig. 4) indicate that the surface doping concentration measured using SCP increases with annealing temperature and approaches the bulk value obtained from the four-point measurements.

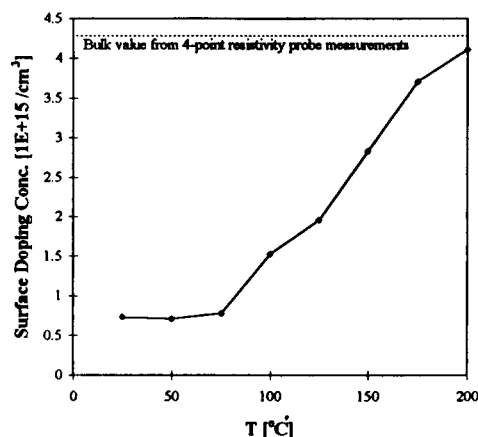


Figure 4. Surface doping concentration vs. anneal temperature.

#### 4. SUMMARY

Results of this study demonstrate the usefulness of the SCP method in the monitoring of HF:H<sub>2</sub>O treated surfaces. A good correlation is observed between the surface recombination lifetime measured using SCP and the wetting angle following an HF:H<sub>2</sub>O etch. Further, oxide remaining on the surface following etching is also reflected in the instability of the surface charge as a function of time of exposure to the ambient air. It is therefore postulated that the SCP can be an effective method for the in-line monitoring of native/chemical oxide removal and surface doping concentration following cleaning sequences ending with an HF step.

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## DEVELOPMENT OF A REDUCED CLEANING PROCESS FOR APPLICATION IN A SPRAY PROCESSOR

P.M.Snee\*, L.Mouche\*\*, P.W.Mertens, M.Meuris, H.F.Schmidt\*\*\*, M.Heyns  
IMEC, Kapeldreef 75, B3001, Leuven, Belgium

\* Currently assigned to IMEC from Motorola SPS, East Kilbride, Scotland. \*\* Formerly with IMEC, now with Motorola SPS, Toulouse, France. \*\*\*Formerly with IMEC, now with IBM Inc.

**1. Introduction:** The introduction of dilute chemistry cleaning processes over the last few years has enabled large cost and environmental benefits to be realised. Unfortunately the application of dilute chemistries is not straightforward in all types of currently used cleaning tools. This is particularly true for spray processors where the flow control range is the main limitation. To achieve dilute chemistries pre-diluted chemical can be used or blending/diluting systems can be installed. The net result is increased complexity and the full benefits of dilute chemistries are not realised.

Alternatively, for this type of system it is possible to examine the existing process and look at ways to reduce the chemical usage, while maintaining the performance, without the need for dilute chemistries. In this work we have developed a reduced cleaning recipe based on the RCA B-clean (SPM, DHF, SC-1, SC-2) for application in a spray processor which has enabled chemical and cost savings of approximately 50%. This has been done by applying the concept of the IMEC clean to the RCA B-clean carried out in a spray processor.

In the classical RCA B-clean the SPM (Sulphuric Acid and Hydrogen Peroxide mixture) is used to oxidise organic contaminants. The dilute HF acid step removes the chemical oxide formed by the SPM treatment allowing the subsequent SC-1 step to remove particles by continuous dissolution and re growth of the chemical oxide. The SC-2 step acts as a metallic contamination removal step.

In the IMEC clean [1] particle and metallic contamination are removed by an oxidising step, such as SPM, followed by an oxide etching step typically utilising Hydrofluoric acid. The oxidation of the silicon surface and dissolution of the oxide causes particles and metals to be removed from the surface. The surface can then be rinsed and dried to give a hydrogen terminated surface or a chemical oxide can be grown using ozonated DI water for example, if a hydrophilic surface condition is required.

Applying this concept to the B-clean in a spray processor leads to the conclusion that the SC-1 and SC-2 steps can be optimised for clean chemical oxide re growth only and not for particle or metal removal, since this has already been achieved using SPM and DHF steps. This clean protective oxide allows particle and drying spot free rinsing and drying in the spray processor. The SC-1 step is no longer required to have a high particle removal efficiency and the SC-2 step should be optimised only to remove metallic contamination deposited from the SC-1 step. This allows the possibility of making the following reductions in the spray B-clean process: -

- The SC-1 step can be applied at room temperature instead of at elevated temperature since the oxide growth rate is faster at lower temperature. This has been demonstrated by open circuit potential measurements (OCP) made on HF treated silicon dipped in SC-1 baths at various temperatures [2]. See fig 1. The oxide growth is actually faster at room temperature since at low temperature and high pH the competing oxide dissolution rate is much reduced. This allows the SC-1 time to be reduced still further and has the added advantage that metal deposition from the SC-1 solution is reduced at low temperatures [3], thus decreasing the metal contamination required to be removed by the SC-2. A reduced temperature also means that the danger of silicon roughening or etching is also reduced somewhat, allowing the pre and post SC-1 peroxide dispenses to be reduced.

- If the SC-1 step is not required to have high particle removal efficiency, then the step time can be reduced with the only boundary condition being the growth of sufficient oxide to achieve a low contact angle (hydrophilic surface).

- It has been shown that for tank processes the peroxide in the SC-2 step is unnecessary for metal removal [4]. It is also possible to dilute the remaining HCl and achieve good metal removal with low particle addition from HCl [4].

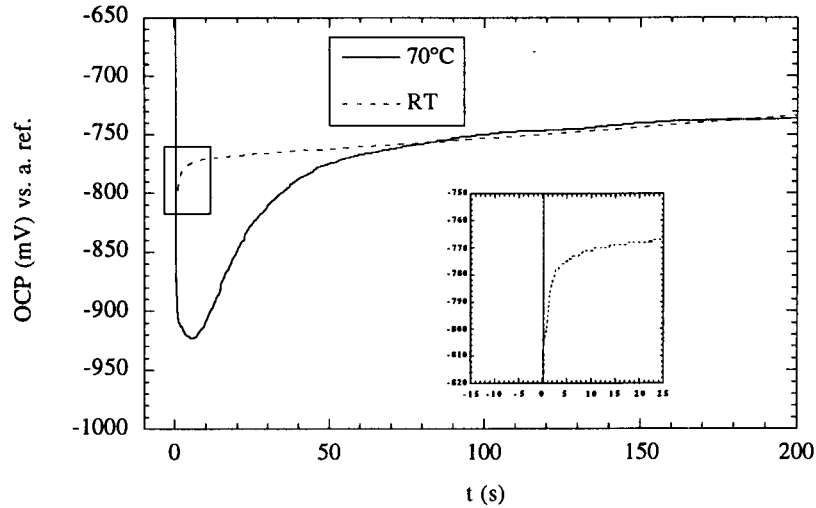


Figure 1: OCP curves for a p-type substrate when immersed in a hydrophobic state into an SC-1 mixture of different temperature (0.25:1:5, pre-treatment: 0.5% HF, 5 minutes followed by 4 minutes DI water rinse).[2].

**2. Experimental:** All tests were carried out using 150 mm p-type CZ material. A Censor ANS100 system was used for the LPD (light point defect) measurements. Metal contamination was evaluated using VPD-DSE-TXRF. Surface condition (hydrophobic/hydrophilic) was determined by measuring the contact angle of a water droplet on the surface using a home built apparatus. All tests were carried out in a Mercury single cassette processor manufactured by FSI inc. For all tests the DI water heater setpoint was 85°C. An appropriate challenge was chosen to evaluate the changes detailed above. For evaluation of the SC-1 changes the challenges chosen were clean bare silicon wafers and wafers contaminated with Si<sub>3</sub>N<sub>4</sub> particles deposited from a water suspension onto HF treated wafers. The SC-1 test sequence included the standard SPM and DHF steps which remained unchanged throughout the investigations. The metal removal in HCl has also been studied using clean SC-1 and contaminated SC-1 challenges. Contaminated SC-1 was spiked with Fe and Ca to give  $2.10^{11}$  and  $3.10^{12}$  at/cm<sup>2</sup> respectively on the wafer. Different blends of HCl(37%) and hot DI water were studied from 1:1000 dilution to 1:5 and times from 30s to 90s.

**3. Results and Discussion:** Table 1 shows the contact angle results obtained for various SC-1 treatments. From the contact angle measurements it can be seen that a 15s cold treatment is sufficient to achieve a hydrophilic surface condition after SPM/DHF.

Table 1: Contact angles for various SC-1 treatments(pre treatment SPM + DHF in situ)

| <u>DI temp (°C)</u> | <u>time (s)</u> | <u>vol. ratio</u> | <u>contact angle</u> |
|---------------------|-----------------|-------------------|----------------------|
| 85                  | 0               | *                 | 80                   |
| 85                  | 15              | 0.5:0.6:5         | <5                   |
| 85                  | 90              | 0.4:0.5:5         | <5                   |
| 22                  | 15              | 0.4:0.5:5         | <5                   |
| 22                  | 90              | 0.4:0.5:5         | <5                   |

\*0s is comprised of pre and post dispenses of H<sub>2</sub>O<sub>2</sub>:DI H<sub>2</sub>O (0.5:5) for 30 s total

The Si<sub>3</sub>N<sub>4</sub> particle removal efficiency for processes comprising SPM and DHF treatments followed by different SC-1 treatments is depicted in fig 2. SC-1 only has an extremely low particle removal efficiency compared to SP/DHF/SC-1 with either hot or cold SC-1.

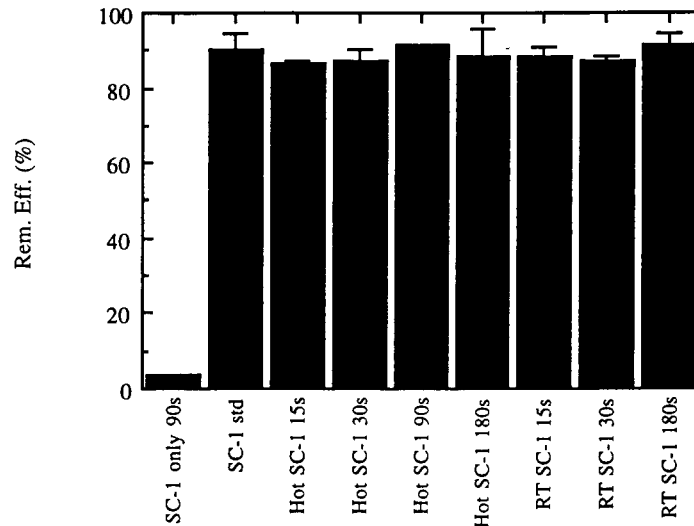


Figure 2: Silicon Nitride particle removal efficiency for various SPM/DHF/SC-1 sequences and SC-1 only (LPDs > 0.15 micron starting count 1000 +/- 200 LPDs)

This illustrates that the SP/DHF combination alone is responsible for the particle removal of the B-clean. The particle addition of the same processes is depicted in fig 3.

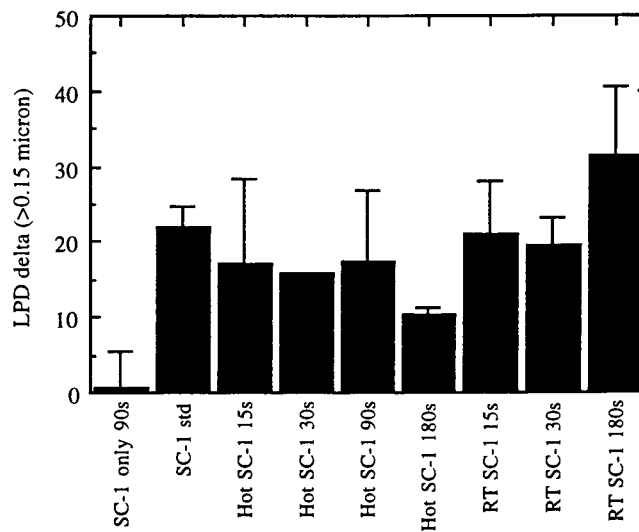


Figure 3: Added number of light point defect values for various SPM/DHF/SC-1 sequences and SC-1 only

TXRF measurements carried out before and after the HCl experiments showed the challenge metals had been removed to below the TXRF detection limits. The VPD-DSE-TXRF measurements showed some systematic variation with HCl blend although there was no significant difference between clean or contaminated SC-1 challenges. It appears that in the range of contamination studied, the final level of contamination on the wafer is determined by the outplating of the HCl solution even for the short times studied. This outplating of HCl has been studied in ref. 5. In this reference outplating data obtained for Fe in HCl in a tank process have been subjected to a curve fitting exercise to be able to predict

the final level of metal concentration on the wafer depending on HCl concentration, concentration of Fe in the HCl and in the DI water. In fig 4 the experimentally obtained data from the spray processor for Fe is plotted against the flow rate of HCl (37%) with the DI water flow constant at 1000 cc/min. Also the model obtained by curve fitting in reference [5] has been used to calculate the surface concentration of Fe as a function of HCl flow. This is plotted as 'Csurf calc' in fig 4. For the calculation the Fe concentration was taken as 2ppb in the HCl and 0.02ppb in the DI water. The actual HCl used in the experiment had an upper specification limit of 10 ppb for Fe, so this is quite reasonable.

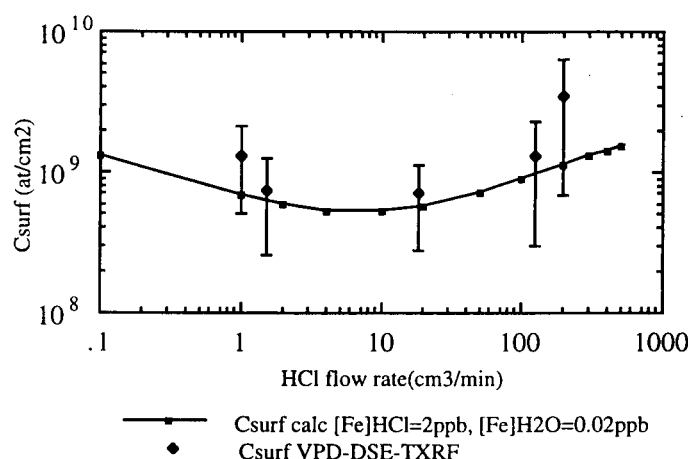


Figure 4: Experimentally obtained and calculated Iron surface contamination as a function of HCl flow with DI flow fixed at 1000 cm<sup>3</sup>min<sup>-1</sup>.

There is quite a good agreement between the two. It appears that in general a spray processor behaves in a similar way to a tank in terms of metal outplating from HCl solutions. In fact the spray processor has the advantage that there is no solution loading from the incoming wafers since the chemical is always fresh. It is possible to calculate curves for different DI and HCl qualities to predict the final level of contamination. This can be used to pick an appropriate flow rate for the grade of HCl used.

Based on the results described above a recipe has been tested with the SC-1 step reduced to 30s and the SC-2 step changed to 1:10 HCl:DI. The pre and post SC-1 peroxide dispenses were also reduced somewhat. GOI testing of this recipe yielded equivalent results to the standard RCA B-clean.

**4. Conclusions:** Data have been presented which demonstrate that the SC-1 and SC-2 steps of the RCA B-clean carried out in a spray processor can be reduced while maintaining performance.

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**A Quantitative Model of SC-1 Wet Processing**  
**Steven Verhaverbeke, Jennifer Parker and Chris McConnell**  
**CFM Technologies Inc., 1336 Enterprise Drive, West Chester, PA 19380**

### Introduction

The Standard Clean 1 consists of a mixture of Ammonium-Hydroxide/ Hydrogen-Peroxide/ Water and is therefore also called the Ammonium-hydroxide hydrogen Peroxide Mixture (APM). In this paper we will discuss a quantitative model for the SC1 cleaning. Equations are developed describing the etching and oxide growth in SC1 cleaning solutions.

### Oxide etching rate in SC-1

The species responsible for the etching of SiO<sub>2</sub> is [OH<sup>-</sup>] which is determined by the pH of the solution. The oxide etching rate in SC-1 is also a function of temperature. Since the reaction is occurring on the surface of the oxide, the reaction rate is independent of thickness (or equivalently time). Data from Sugihara et al. (1) suggest that the oxide etching is directly proportional to [OH<sup>-</sup>]. The experimentally determined activation energy for etching of CVD oxides in SC-1 solutions is of 14.6 kcal/mol.(2) The etching rate for chemical oxides grown in SC-1 solutions has been measured and is reported in the literature. (1, 2, 3, 4, 5). From this data, a value of  $5.21 \times 10^{11}$  for the proportionality constant  $a$  was determined. All of this data (1,2,3,4,5) confirms a first order reaction kinetics with OH<sup>-</sup>. Also the etching of thermal oxides follows this first order reaction kinetics with OH<sup>-</sup> (6). However, the proportionality constant is smaller for thermal oxides.

The [OH<sup>-</sup>] concentration is dependent on the composition of the SC1 solution and on the temperature. In previous studies (7), we have shown that the [OH<sup>-</sup>] concentration can be expressed in terms of the formal NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> concentration in the SC-1 mixture by using the following formula (7):

$$[OH^-] = \sqrt{\frac{K_b K_w c_{NH_3}}{K_a c_{H_2O_2}}} \quad [1]$$

The total expression describing the etching of chemical oxides in SC-1 solutions becomes

$$r_e = 5.21 \times 10^{11} \frac{nm.l}{min.mol} \cdot \sqrt{\frac{K_b \cdot K_w}{K_a}} \cdot \sqrt{\frac{c_{NH_3}}{c_{H_2O_2}}} \cdot e^{\frac{-14.6 \frac{Kcal}{mol}}{1.987 \cdot 10^{-3} \cdot T}} \quad [2]$$

In Figure 1, the chemical oxide etch rate in SC-1 solutions is shown as a function of C<sub>NH3</sub> and C<sub>H2O2</sub>, or the formal ammonia and hydrogen peroxide concentrations at 70 °C. These results provide a very accurate model for the etching of chemical oxides and therefore also of silicon in SC-1 solutions and agree with the data reported in the literature (1,2,3,4,5).

### Oxide Growth Kinetics in SC-1

Oxide growth is occurring at the boundary between the existing oxide and the silicon. Since the reactive species must diffuse throughout the existing oxide before reacting with the silicon, the reaction is diffusion limited and therefore a function of oxide thickness. The oxide thickness changes as a result of the concurrent etching and oxide growth. Therefore, thickness is a function of reaction time.

The Deal-Grove model (8) for the oxide growth rate can be used for the initial stages of the reaction between a bare silicon wafer and an SC-1 solution. This model assumes only diffusion as a driving force for mass transport of the oxidizing species to the silicon

surface. The oxide growth according to the Deal-Grove model can be described by the following equation :

$$t_{ox} = a \cdot e^{\frac{-Q_d + E_r}{kT}} \cdot \left( \sqrt{1 + b \cdot [O] \cdot t \cdot e^{\frac{-2E_r + Q_d}{kT}}} - 1 \right) \quad [3]$$

Oxide thickness has been reported in the literature for several temperatures as a function of time for pure  $H_2O_2$  solutions. (2,9) The oxide thickness has also been reported in literature for several SC-1 solutions.(10) Unlike pure  $H_2O_2$  solutions, the oxide thickness is a combination of both etching and oxidation in SC-1 solutions. Therefore, in our study we first modeled the oxide growth rate in pure  $H_2O_2$  solutions, and then coupled the results to the etching rate described by equation 2 for SC-1 solutions.

Clearly, the main uncertainty in the Deal-Grove Model is the identification of oxidizing species [O].

Since the true oxidizing species is not known at this time, we have considered two different oxidizing species,  $H_2O_2$  and  $HO_2^-$  in our study. Since hydrogen peroxide does not dissociate significantly, even in alkaline solutions, the  $H_2O_2$  concentration is approximately equal to the formal  $H_2O_2$  concentration after mixing the chemicals.

In contrast,  $HO_2^-$  results from a dissociation and the  $HO_2^-$  concentration must be calculated by solving the equilibrium equations. In pure  $H_2O_2$  solutions, the  $HO_2^-$  concentration defined by equation 2 is approximately given by the following expression :

$$[HO_2^-] = \sqrt{K_a \cdot c_{H_2O_2}} \quad [4]$$

In SC-1 solutions, the  $HO_2^-$  concentration must be determined by solving equation 1-3 (7) and is given approximately by the following expression (7):

$$[HO_2^-] = \sqrt{\frac{K_a \cdot K_b}{K_w}} \sqrt{c_{H_2O_2} \cdot c_{NH_3}} \quad [5]$$

In these expressions  $C_{H_2O_2}$  and  $C_{NH_3}$  are the formal hydrogen peroxide and ammonia concentrations of the mixture of chemicals.

The oxide growth rate is mainly dependent on oxide thickness. The oxide growth rate,  $g$ , where  $g = dt_{ox}/dt$ , can be determined from equations 3,4 and 5. In either pure  $H_2O_2$  solution or SC-1 solutions, if it is assumed that  $HO_2^-$  is the oxidizing species, the oxide growth is dependent on the square root of the hydrogen peroxide concentration and is inversely dependent on the oxide thickness. A comparison of the oxide etch rates in the two solutions is then:

$$\frac{g_{SC-1}}{g_{H_2O_2}} = \sqrt{\frac{K_b}{K_w}} \cdot \sqrt{c_{NH_3}} \quad [6] \text{ and } \sqrt{\frac{K_b}{K_w}} \text{ is of the order of 11,000 to 40,000 depending}$$

on temperature. Equation 6 shows that for the same hydrogen peroxide solution the oxide growth rate will be much faster in SC-1 solutions than in pure hydrogen peroxide solutions if the oxidizing species is the  $HO_2^-$  ion.

This explains why the surface is still covered with oxide in SC-1 solutions even though the oxidation rate is so slow in neutral hydrogen peroxide solutions. In SC-1 solutions, typically the oxidation rate is about 10 000 times faster (or more) than in neutral hydrogen peroxide solutions.

Similar modeling can be completed with  $H_2O_2$  as the oxidative species in equation 3 and then it is found that the oxide growth rate is directly proportional to  $H_2O_2$  if the oxidizing species is  $H_2O_2$  for both SC-1 solutions and pure  $H_2O_2$  solutions.

Moreover, the oxide growth rates in the two solutions shows an equal growth rate if  $H_2O_2$  is the oxidizing species :

$$\frac{g_{SC-1}}{g_{H_2O_2}} = 1 \quad [7]$$

Meaningful results are obtained only if the oxidizing species is  $\text{HO}_2^-$ . Experimental data for oxide growth (11) indicates that oxide growth in neutral  $\text{H}_2\text{O}_2$  solutions follows a square root dependency on hydrogen peroxide concentration. Additionally, when wafers are exposed to SC-1 solutions, even for a very short time at 70 °C, the final oxide thickness is similar to the oxide thickness found when wafers are exposed to pure  $\text{H}_2\text{O}_2$  of similar peroxide concentration at 90 °C for 50 minutes. (9) In the SC-1 solution, etching is occurring simultaneously with the oxide growth. Therefore, the oxidation must occur much faster in SC-1 solutions than in neutral  $\text{H}_2\text{O}_2$  solutions. Based on these results,  $\text{H}_2\text{O}_2$ , alone, cannot be the active species in the oxidation of silicon in SC-1 or  $\text{H}_2\text{O}_2$  solutions. These results are not surprising given the fact that  $\text{HO}_2^-$  has a higher oxidation potential than  $\text{H}_2\text{O}_2$  (2.119 V for  $\text{HO}_2^-$  versus 1.776 V for  $\text{H}_2\text{O}_2$  solutions. (12)) One of the most important findings of this model is that the oxidizing species in hydrogen peroxide solutions is likely to be  $\text{HO}_2^-$ . The fact that a charged species is responsible for the oxidation creates the possibility that mass transport through the oxide is not merely a diffusive transport, but may be enhanced by electrical fields.

The Deal-Grove model, based only on diffusive flux, cannot quantitatively describe oxide growth for long oxidation time. The fact that the oxidation results from a charged species and that the oxide growth virtually stops at a thickness of 1 nm suggests that an additional driving force is involved in the mass transfer of the oxidizing species. Electrostatic interaction is known to affect the oxidation kinetics when charged species are involved. (13,14). Both The Cabrera-Mott model (13) and the electrostatic image interaction as in the model by Stoneham and Tasker (14) show significantly different mass flux when charged species are involved as opposed to neutral diffusion.

#### Equilibrium condition during SC-1 cleaning

In the case when the oxidizing species is  $\text{HO}_2^-$ , and the Deal-Grove diffusion model is assumed, the final oxide thickness can be determined by equating the etch rate with the oxide growth rate. The minimum hydrogen peroxide concentration required to assure a final oxide thickness of at least 0.5 nm can be determined as a function of temperature. Considering two extreme operating temperatures provides the limits on required  $\text{H}_2\text{O}_2$  concentration. At 70°C, the minimum hydrogen peroxide concentration necessary to obtain a oxide layer of 0.5 nm is 0.008 mol/l. This molarity corresponds to a dilution of 1500:1 ( $\text{H}_2\text{O}$ : 30wt%  $\text{H}_2\text{O}_2$ ) when a proportional amount of  $\text{NH}_4\text{OH}$  is in solution, which is roughly necessary for adequate particle removal due to etching (7). Reducing the temperature reduces the risk of producing an oxide that is too thin to provide wafer protection. This temperature dependency is often intuitively accepted although by no means obvious. Indeed, reducing the temperature obviously reduces the etching rate, but at the same time the oxidation rate is also reduced. Clearly the very dilute concentrations suggested by our equilibrium model are significantly lower than standard operating conditions used today.

#### Conclusions

A model has been developed for the oxide thickness, the etching rate and the oxide growth kinetics in the SC-1 solution. Using this model and comparing the results to oxide growth rates in neutral hydrogen peroxide solutions as well as SC-1 solutions indicates that  $\text{H}_2\text{O}_2$  is not the dominant oxidizing species, and that a more likely candidate is  $\text{HO}_2^-$ . Although in our current model, only diffusion is assumed as a driving force, our results show that another force (i.e., electrostatic forces) must be involved in the mass transfer of the oxidizing species through the chemical oxide. In future work, electrical field assisted mass transfer will be modeled.

Additionally, the preliminary results from the diffusion limited equilibrium model show that extremely dilute SC-1 solutions are adequate to provide a protective oxide. Currently, SC1 solutions with dilutions around 100:2:1 ( $\text{H}_2\text{O}$ :  $\text{H}_2\text{O}_2$  :  $\text{NH}_4\text{OH}$ ) are

commonly in use in production; diluting such solutions by a factor of 10 will still yield oxide protection.

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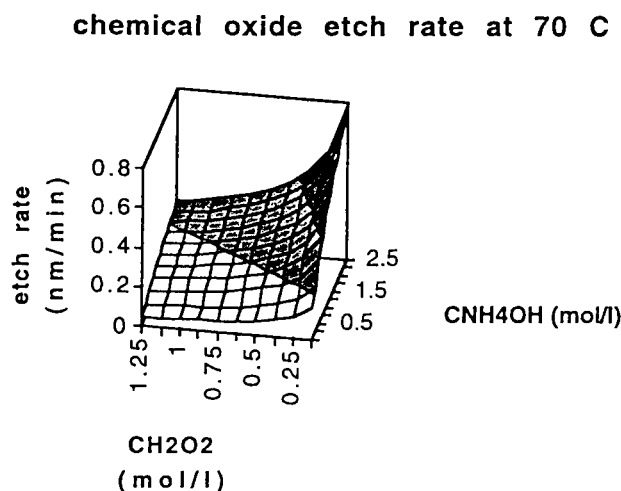


Fig. 1. Chemical oxide etch rate in SC-1 solutions at 70 C as a function of formal NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> concentration.



## THE CHANGE OF SILICON SURFACE MICROSTRUCTURE BY WET CHEMICAL PROCESSING

R. Stömmmer\*, A. R. Martin\*\*, H. Göbel\* and W. Hub\*\*

*\*Siemens AG, Corporate Research and Development,  
Otto-Hahn-Ring 6, 81739 München, Germany*

*\*\*Siemens AG, Semiconductors Division,  
Otto-Hahn-Ring 6, 81739 München, Germany*

### ABSTRACT

For the investigation of the silicon surface microstructure after wet chemical processing, x-ray scattering from silicon surfaces and atomic force microscopy complement one another. For the silicon samples under investigation, X-ray scattering results demonstrate the diluted SC1 ( $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) to decrease the surface roughness. Atomic force microscopy on small length-scales shows the increase of surface frequencies due to the etching process of the diluted SC1. During the cleaning process, the adhesion of oxygen bubbles on the surface can prevent effective etching at the area covered. Emerging columns of silicon of heights up to 10nm are observed, which allow to calculate the etching rate to values exceeding 2nm/min.

### 1. INTRODUCTION

The chemical cleanliness and physical smoothness of silicon (Si) surfaces are important prerequisites to improve speed, complexity and density of silicon ultra large scale (ULSI) integrated circuits. For scaling down thin gate oxides, metallic and organic contamination of the Si surface have to be prevented to maintain the insulating function of the oxide. The Si-SiO<sub>2</sub> interface roughness  $\sigma$  degrades the mobility of free carriers in ULSI circuits. Additionally,  $\sigma$  can affect the growth and the homogeneity of the gate oxide [1]. The chemical processing of silicon surfaces with SC1 removes contaminants such as particles, organic materials and metallic impurities [2]. The conventional SC1 (1/1/5  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) increases the surface roughness due to the high etching rate [3].

In this work, we apply x-ray scattering (XRS) and atomic force microscopy (AFM) to investigate the effects of the diluted SC1 (0.25/1/5) on the Si surface microstructure. The statistics of the surface topography is usually described by parameters such as rms roughness  $\sigma$  and lateral correlation length  $L$ . The rms roughness  $\sigma$  is the mean amplitude fluctuation of the height-profile perpendicular to the surface, whereas  $L$  is an estimation for the lateral order of the surface under investigation.  $L$  is comparable to the mean wavelength ( $\lambda$ ) by means of a Fourier description of height profiles. Specular XRS is sensitive to changes of the electron density normal to the sample surface. It provides the density and the roughness of a Si surface as well as the density, the thickness and the roughness of SiO<sub>2</sub> layers. For different length scales, AFM provides height profiles from the Si surface which allow to calculate the surface roughness  $\sigma$  and the lateral correlation length  $L$ . The

precision of XRS in determining  $\sigma$  and the capability of AFM in imaging small-scale surface features provide comprehensive information about the changes Si surfaces can undergo.

## 2. EXPERIMENTAL CONDITIONS

The storage of silicon wafers leads to adhesion and bonding of impurities degrading the surface quality. The SC1 cleaning in its diluted form of 0.25/1/5 was applied to clean surfaces of such wafers at a cleaning temperature of 70°C. The etching time varied in 5min intervals (0, 5, 10, 15, 20, 25min) and in 10min intervals (0, 10, 20min). The samples under investigation are n-type CZ (100) wafers doped with phosphorus. All samples were HF-dipped before and after cleaning to remove native oxid layers and to slow down oxidation. The changes of  $\sigma$  and  $L$  were measured ex situ in dependence on the etching time  $t$  by XRS and AFM. XRS measurements were carried out at the Siemens D 5000 diffractometer at a wavelength  $\lambda$  of 0.154nm (CuK $\alpha$ ). Afterwards, AFM measurements were made in contact mode on a Nanoscope of Digital Instruments. Sample preparation and measurements were accomplished within three days.

## 3. RESULTS AND DISCUSSION

### 3.1. XRS results

Fig. 1 proofs the smoothing capability of the diluted SC1 for the Si samples under investigation. To stress the dependence of XRS on the surface roughness  $\sigma$ , the reflectivity  $R$  is multiplied by  $q_z^4$  giving  $R^*$ .  $q_z$  is the wavevector transfer normal to the Si surface. The dependence of  $q_z$  on the angle of incidence  $\theta$  is given as inset in fig. 1.

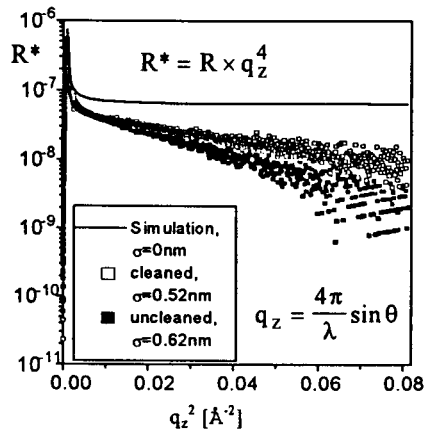


Fig. 1: XRS from the cleaned and from the uncleaned Si surface (diluted SC1,  $t=20$ min). Cleaning reduces the surface roughness  $\sigma$ . For comparison, the simulation shows the XRS curve for a Si surface with no roughness.

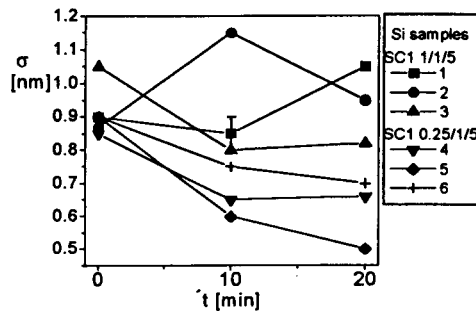


Fig. 2: Roughness  $\sigma$  from six Si samples plotted versus cleaning time  $t$ .  $\sigma$  is calculated from reflectivity data. The bar denotes the mean error of measurement ( $\pm 0.05$ nm). In contrast to conventional SC1 (1/1/5), the diluted SC1 (0.25/1/5) can smoothen the Si surface.

If  $R^*$  is plotted versus  $q_z^2$ , the decrease of  $R^*$  for increasing  $q_z^2$  is due to surface roughness  $\sigma$  only. Fig. 2 compares the effect of the conventional and the diluted SC1 cleaning onto  $\sigma$  obtained by XRS for increasing etching time  $t$ . Up to  $t=20\text{min}$ , diluted SC1 reduces the surface roughness  $\sigma$  from  $0.9\text{nm}$  to values below  $0.7\text{nm}$ . For the conventional SC1 the functional dependence of  $\sigma$  on the etching time  $t$  remains ambiguous.

### 3.2 AFM results

Fig. 3 compares Si surface images prior to and after diluted SC1. Particles

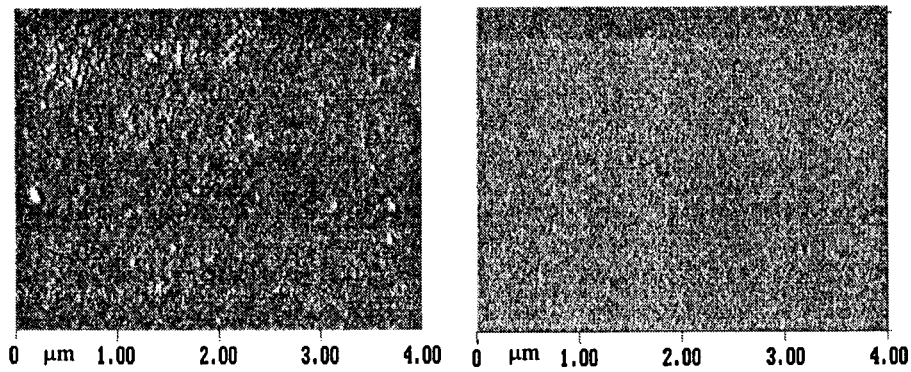


Fig. 3: Left: AFM image prior to diluted SC1 cleaning. Right: AFM image after diluted SC1 cleaning. Surface impurities are removed.

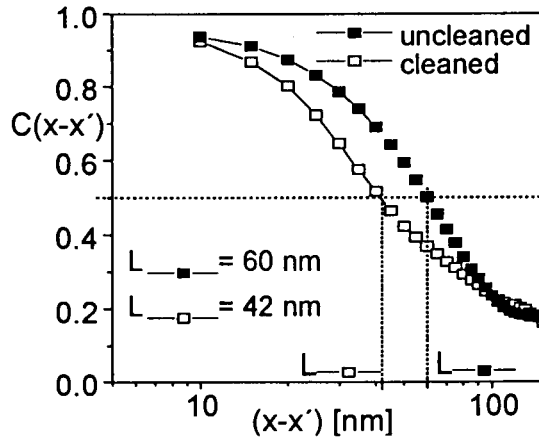


Fig. 4: The plot of the correlation function  $C(x-x')$  gives the lateral correlation length of the uncleaned ( $L_{\blacksquare}$ ) and of the cleaned ( $L_{\square}$ ) surface.

are removed. Fig. 4 shows the decrease of the lateral correlation length  $L$  due to the etching process. The decrease of  $L$  is accompanied by an increase of surface frequencies. This can be interpreted as a decrease of lateral order at the surface.

Under certain conditions, cleaning leads to the formation of oxygen bubbles [4]. The adhesion of oxygen bubbles (diameter:  $30\text{nm} - 200\text{nm}$ ) on the surface prevents effective etching at the area covered. Emerging silicon-columns with

heights up to  $10\text{nm}$  are observed, regularly covering the surface with mean column-to-column-distances in the  $\mu\text{m}$  range (see Fig. 5).

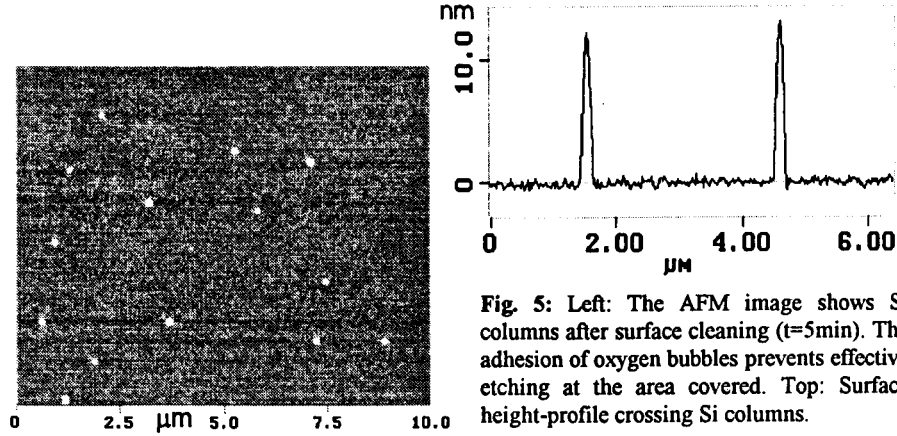


Fig. 5: Left: The AFM image shows Si columns after surface cleaning ( $t=5\text{min}$ ). The adhesion of oxygen bubbles prevents effective etching at the area covered. Top: Surface height-profile crossing Si columns.

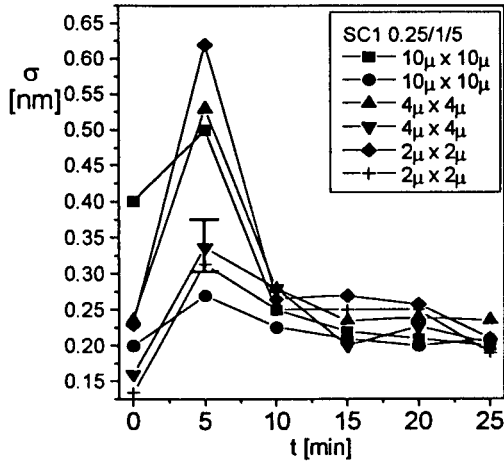


Fig. 6: Roughness  $\sigma$  versus etching time  $t$  obtained from AFM data. Two different Si samples are measured on three different length-scales. The peak at  $t=5\text{min}$  is due to Si column formation. The bar denotes the mean error of measurement ( $\pm 0.038\text{nm}$ ).

Fig 6 shows the dependence of the surface roughness  $\sigma$  on the etching time  $t$  obtained from the AFM data of two samples. For all length-scales, the roughness spike at  $t=5\text{min}$  is due to Si column formation. If the etching time is taken too short ( $t < 10\text{min}$ ) these columns remain, increasing  $\sigma$ . Therefore, diluted SC1 can lead to roughening of surfaces. The limited resolution of the AFM-tip leads to roughness values smaller than the roughness values obtained from XRS (Fig. 2). For  $t=0\text{min}$ , the roughnesses are below  $0.4\text{nm}$ . For  $t \geq 10\text{min}$ , the roughnesses vary between  $0.20\text{nm}$  and  $0.28\text{nm}$ . Unusual surface features like silicon columns and particles cause the roughness  $\sigma$  to be dependent on

the area and the length-scale measured. Taking the mean error of measurement of  $\pm 0.038\text{nm}$  into consideration, the diluted SC1 does not seem to affect the surface roughness for cleaning times  $t \geq 10\text{min}$ . From the height of the silicon columns remaining on the surface, the etching rate of diluted SC1 calculates to values exceeding  $2\text{nm/min}$ .

#### 4. CONCLUSIONS

XRS data show that the diluted SC1 smoothens the Si surfaces. Sensitive to electron density changes, XRS determines the roughness at the Si-air interface with high precision, ignoring surface particles. The main advantage of AFM is its direct

imaging of unusual surface features and particles even at low surface coverage. Nevertheless, the interpretation of AFM data remains ambiguous: roughness  $\sigma$  and lateral correlation length  $L$  are dependent on the lateral length scale, the number of data points and the AFM-tip thickness determining the resolution of the instrument. Based on AFM results only, there is no evidence that diluted SC1 smoothens the Si surfaces. The lateral correlation length  $L$  should not be compared to values obtained by other techniques such as x-ray diffuse scattering or transmission electron microscopy [5]. But for identical instrumental settings,  $L$  is a good measure for the relative change of surface order due to chemical processing.

#### ACKNOWLEDGEMENTS

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**" JUST-CLEAN-ENOUGH" RINSING CONDITIONS  
AND  
REAL-TIME ULTRA-TRACE ANALYSIS OF ULTRA PURE WATER**

Laszlo Fabry, Siegfried Pahlke, Ludwig Kotz, Peter Blöchl,  
Wacker Siltronic AG, D-84479 Burghausen  
Thomas Ehmann and Knut Bächmann,  
Fachbereich Chemie, Technische Hochschule, D-64289 Darmstadt

**Abstract**

Depending on the length of rinsing time, detrimental iron concentrations can be absorbed on the wet native oxide surface even from the purest semiconductor grade water ( $\text{Fe} < 7 \text{ pg/mL}$ ,  $\text{Na} < 20 \text{ pg/mL}$ ). The real-time method of  $\mu$ -wave reflection photoconductive decay method ( $\mu$ -PCD) proved, that by locating and reducing the iron sources and adsorption, we increased the rinsing efficiency even when not the highest grade of water purity was applied. Iron adsorption on the native oxide surface is reduced when rinsed with ultra pure water (UPW) that is saturated with carbon dioxide.

**Economical and ecological relevance of process hygiene and real-time monitoring**

The economy of a device fab is a direct function of the yield of each process step in the line. Competitive fabs must process wafers correctly, with perfect consistency and repeatability. The only way to do that is to measure, characterize, optimize, and control all of the highly complex and variable tools and processes [1]. Chip fabrication abounds in cleaning steps to remove inevitable metallic impurities, that set the limits to the chip vintage. Thus, cost-effective monitoring of process cleanliness is the key to economical semiconductor manufacturing. Monitoring methods must perform with high repeatability in the analytical range of interest. Particular requirements for monitoring methods are real-time results and analytical equipment with high up-time. Recently, we have reviewed the application of microanalytical tools suitable for monitoring process hygiene in large scale silicon wafer manufacturing [2, 3].

Manufacturing one 200 mm wafer requires more than 200 L of water [4]. Water has now been considered to be 'the oil of the semiconductor industry'. Saving water in the semiconductor industry became a high public priority. Rinsing operations consume most of the water in the line, usually, water of highest purity. Applying 'just-clean-enough' processes and 'just-clean-enough' media saves natural water resources and manufacturing costs [5]. Maintaining these optimal process conditions requires real-time monitoring methods and a practical knowledge of materials and processes.

We report here investigations on mixed-bed (MB) ion exchange resins as crucial metal, particularly, iron contamination sources, a real-time monitoring method that is suitable to monitor UPW cleanliness and 'just-clean-enough' rinsing conditions.

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### Leaching tests of MB ion exchange resins for polisher use

According to common engineering knowledge [6, 7] and to our leaching tests, the specifications for commercially available MB polisher resins, such as grade of cross-linking, ion exchange capacity, ignition residue etc. do not sufficiently guarantee the required water cleanliness. Particularly, iron and sodium are unpredictable, detrimental contaminations of MB resins. On the other hand, there is no larger portion of alien surface in the line, than the intrinsic surface of the ion exchange resin: For conventional polisher gel resins it is a value of 100-200 m<sup>2</sup>/g ! Our leaching results showed, that even MB resins selected for polisher application might release metals in varying concentrations during resin-cleaning, even if ignition assay results show about the same level. In many cases, the outer layers of polisher MB resins were found to be a particularly rich reservoir of magnesium, iron and nickel, whereas sodium, aluminum and zinc were gradually leaching out. The less extraction steps necessary to remove the metallic contamination and to achieve the specified ppt-levels the less cleaning water and, resp., the shorter treatment time are necessary for the start-up cleaning period before resumed rinsing operation after maintenance work.

### Real-time analysis of UPW

Ion-coupled plasma mass spectrometry (ICP-MS), ion chromatography (IC) and capillary electrophoresis (CE) are the standard analytical tools of elemental and, resp., anion analysis in pure deionized water [8]. Tedious calibration procedures must include standard addition procedure for both ICP-MS and IC and CE. Before the measurement starts, the samples must be preconcentrated under controlled conditions, in order to be able to analyze with the required detection limit. Necessary analysis times of more than 8 hours extend the time frame, that is requested for real-time results [9].

Recently, we have reported the application of injection level spectroscopy to iron determination in silicon wafers using  $\mu$ -PCD [10]. Defect-free, freshly cleaned [11], hydrophilic wafers (float zone crystal, (100), 50 ohm cm D-doped,  $[O]_i < 5 \cdot 10^{15} \text{ at.cm}^{-3}$ ,  $Fe < 1 \cdot 10^{10} \text{ at.cm}^{-3}$ ) were rinsed with UPW of controlled flow rate in a quartz apparatus. Subsequently, a drive-in treatment during thermal oxidation (900 °C, dry oxidation without TCA, 20 nm, about 1 h) provided reproducible conditions for the analysis of iron that had been adsorbed from the UPW on the wafer surface [12].

### Diminishing iron adsorption in rinsing operations

The ICP-MS results showed that the decrease of lifetime is a function of iron and sodium concentration in UPW. Except oxalate, carbonate and hydrogencarbonate, small anions did not affect the iron adsorption from UPW onto the surface under the experimental conditions. Addition of oxalate or carbon dioxide diminished the iron adsorption in rinsing cascades [13] and increased rinsing efficiency by eliminating the detrimental effect of increasing iron and sodium concentration (Fig.).

We rationalize our findings by the increased solubility of iron hydrogen carbonate due to the presence of excess carbon dioxide. By the increased solubility of iron averted the precipitation of iron hydroxide on the wafer surface [14]. On the other hand, the carbonic acid is a stronger acid than the surface silanol groups of the native oxide [15] and, as such, can efficiently prevent the formation of surface iron silicates [16, 17].



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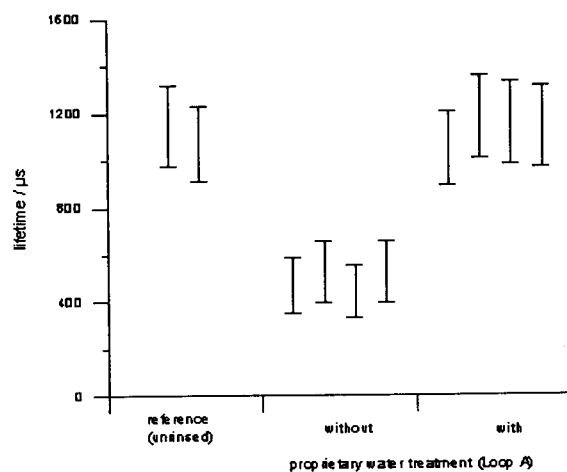


**Fig.:**  
**Comparison of effective pure water quality.**  
**Even quality "Loop A" can satisfy the quality requirement,**  
**provided hydrocarbonate anions render Fe more soluble and,**  
**simultaneously, reduce the adsorption capacity of the native oxide.**

## SI-WAFER SURFACE CHARACTERIZATION BY TOF-SIMS

G. Egbers, M. Deimel, B.-C. Schwede, A. Benninghoven  
Physikalisches Institut der Universität Münster,  
Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany

### INTRODUCTION

Si-wafer surfaces feature a complex chemical composition and structure, depending on pretreatment, storing conditions, etc. Usually the bulk material is covered by a native or chemical oxide. The surface contains metal contaminants, hydrogen (especially on HF-treated wafers), OH-groups, anions and organic molecules.

In the last years Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has developed into a well suited analytical tool for the characterization of this surface region. Table 1 shows different TOF-SIMS operation modes, the supplied information and the related process technologies.

*Table 1 : TOF-SIMS operation modes, supplied information and related process technologies.*

| TOF-SIMS Operation Mode | Information                                | Process Technology  |
|-------------------------|--------------------------------------------|---------------------|
| Surface spectroscopy    | $Y(X_i^q) \rightarrow$ Surface composition | Contaminants        |
| Surface sputtering      | Disapp. cross section $\sigma_i(X_i^q)$    | Sputter cleaning    |
| TP-SSIMS spectroscopy   | Binding energy $E_b(M)$                    | Thermal cleaning    |
| Imaging TOF-SIMS        | Diffusion coefficient $D(M)$               | Surface migration   |
| Depth profiling         | Oxide characterization                     | Oxidation processes |

In this paper we report on our systematic investigations of Si-wafer surfaces by combining different TOF-SIMS operation modes including surface spectroscopy, Temperature Programmed Static SIMS (TP-SSIMS) spectroscopy and imaging TOF-SIMS (marked grey in table 1).

### EXPERIMENTAL

#### 1. Investigated Samples

We investigated three silicon wafer surfaces after different pretreatments:

- Si as recieved (Si as rec.)
- Si, 10 min etched by HF (1%) and 2 min rinsed with water (Si/HF)
- Si, 2 min HF-treated and 10 min uv/ozone treated (Si/OZ)

and a Si-wafer covered with a monolayer of the isolated polydimethylsiloxane oligomer with 17 repeat units (PDMS D17).

## INSTRUMENTAL

Table 2 : Used TOF-SIMS instruments and selected features.

| Instrument    | Primary Ion (PI) species | Analyzer                | Mass Resolution | used for              |
|---------------|--------------------------|-------------------------|-----------------|-----------------------|
| TOF IIIa      | Ar, 11 keV               | Reflectron              | 10 000          | spectroscopy          |
| SNMS/SIMS-TOF | Ar, 11 keV               | double stage Reflectron | 3 000           | TP SSIMS (100 - 700K) |
| TOF IIIk      | Ga, 30 keV               | Reflectron              | 3 000           | imaging TOF-SIMS      |

## RESULTS AND DISCUSSION

### A. Surface Spectroscopy

Positive and negative spectra of the investigated wafers show a number of species characteristic for the different wafer pretreatments. High mass resolution is required for an unambiguous determination of the atomic composition of these ion species.

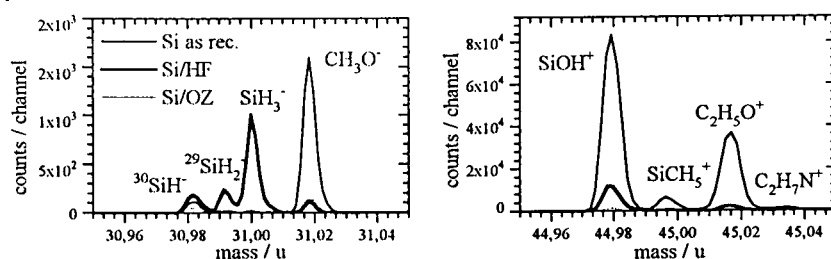


Fig. 1 Detail of negative and positive spectra of different Si-wafer surfaces at mass 31u and 45u.

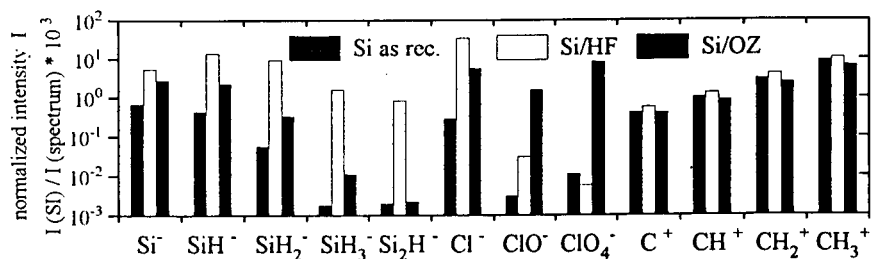


Fig. 2 Relative intensities of selected ions emitted from different Si-wafer surfaces. The secondary ions  $\text{SiH}_3^-$  and  $\text{Si}_2\text{H}^-$  are most characteristic for the Si-H bond.

The results may be summarized as follows:

- $\text{ClO}_x^-$ -ions are most intense for ozone treated surfaces.
- $\text{SiH}_x^+$  and  $\text{Si}_2\text{H}^+$ -ions are more intense for Si/HF than for Si/OZ.
- The intensity of the hydrocarbon ions is not much affected by the wafer pretreatment.

By the spectral data the lattice valence may be determined from the  $\text{SiO}_x^-$  emission from different Si-wafer surfaces according to the valence model [1]. This is shown in fig. 3. For all three surfaces the experimental values fit excellently with the

expected emission pattern. The lattice valency  $G^-$  (valency in the maximum of the parabole) is identical for the "as rec." and the HF treated surfaces.

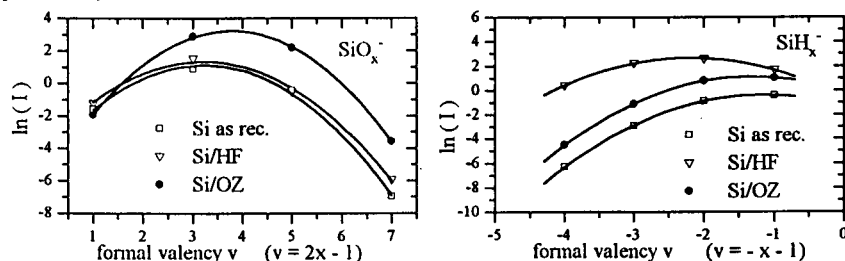


Fig. 3 Determination of the lattice valence of Si from the  $\text{SiO}_x^-$  and  $\text{SiH}_x^-$ -emission.

Table 3: Lattice valence  $G^-$  of Si determined from  $\text{SiO}_x^-$  and  $\text{SiH}_x^-$ .

| Pretreatment | $G^- (\text{SiO}_x^-)$ | $G^- (\text{SiH}_x^-)$ |
|--------------|------------------------|------------------------|
| as recieved  | $3.22 \pm 0.08$        | $-1.16 \pm 0.05$       |
| HF           | $3.21 \pm 0.09$        | $-2.20 \pm 0.02$       |
| OZ           | $3.78 \pm 0.02$        | $-1.32 \pm 0.05$       |

The lattice valence  $G^-$  for Si determined from  $\text{SiO}_x^-$  is higher for Si/OZ than for Si/HF and Si as recieved. The absolute value of the lattice valence  $G^-$  for Si determined from  $\text{SiH}_x^-$  is higher for Si/HF than for Si/OZ and Si as recieved. The Si lattice valence calculated from the  $\text{SiH}_x^-$  and  $\text{SiO}_x^-$ -emission patterns allows to distinguish between the investigated wafer surfaces.

#### TP-SSIMS of silicon wafers

Investigating the temperature dependence of secondary ion (SI) emission according to [2] we found almost no difference between the three types of Si-wafer surfaces except for  $\text{ClO}_x^-$ . But different SI-species show different temperature behaviour. We found three different types of behaviour, as shown in figure 4a.

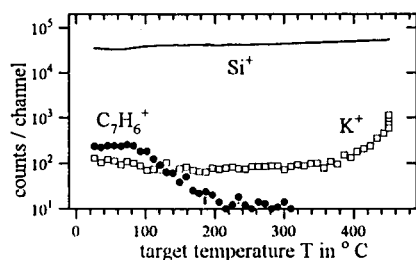


Fig. 4a: Temperature behaviour of different ions from Si/OZ.

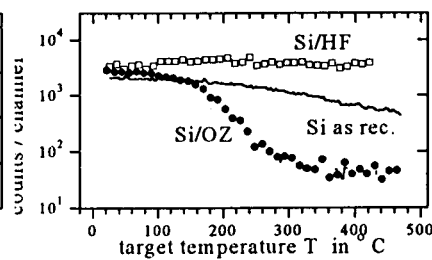


Fig. 4b: Temperature behaviour of  $\text{Cl}^-$  from different pretreated surfaces.

$\text{Si}^+$ : The increase with T indicates the subsequent removal of molecular overlayers (e.g.  $\text{C}_7\text{H}_6^+$ ) from the oxidized Si-wafer surface.

$\text{C}_7\text{H}_6^+$ : The decrease with T indicates the evaporation of organic molecules from the surface.

$\text{K}^+$ : The temperature dependence of  $\text{Na}^+$  indicates the increasing bulk mobility of Na atoms and their trapping at the surface.

### Surface Diffusion

Some polymers, e.g. PDMS, show a surface mobility, which enables the regeneration of a depleted area by intact molecules from neighbouring undisturbed areas. This surface diffusion can be investigated by imaging TOF-SIMS [3]. Therefore PDMS is desorbed from a defined area by primary ion bombardment. The recovered area  $A_r$  is determined by imaging TOF-SIMS.  $A_r$  is given by

$$A_r(t) = \sqrt{\frac{2D}{A}} t \quad [4].$$

A plot  $A_r(t)$  versus  $t^{1/2}$  yields the diffusion coefficient  $D$ .

Field of view:  $240 \times 240 \mu\text{m}^2$

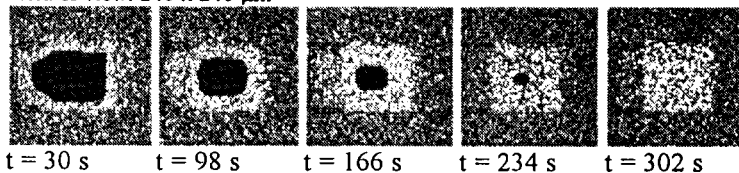


Fig. 5: Time dependence of the lateral distribution of the fingerprint ion  $\text{Si}(\text{CH}_3)_3^+$  ( $m = 73 \text{ u}$ ) from the polymer PDMS D17 on Si  
 Prebombardment conditions:  $120 \times 120 \mu\text{m}$ , PIDD:  $10^{15} \text{ cm}^{-2}$   
 Imaging conditions:  $240 \times 240 \mu\text{m}$ , PIDD:  $2 \times 10^9 \text{ cm}^{-2}$

In figure 5 the time dependence of the lateral distribution of PDMS D17 on Si is shown. The prebombarded area is recovered by PDMS molecules from undisturbed neighbouring areas. After 300s the whole prebombarded area is again covered by PDMS molecules.

The diffusion coefficient  $D$  was determined to  $D = 3 \cdot 10^{-7} \text{ cm}^2/\text{s}$

### CONCLUSIONS

The combination of different TOF-SIMS operation modes (see tabel 1) supplies detailed insight into the surface chemistry of Si-surfaces and allows the

- Identification of the surface oxidation state by application of the valence model
- Identification of molecular surface species as hydrocarbons,  $-\text{NH}_4$ ,  $-\text{ClO}_4$  and other process residues by TP high mass resolution spectroscopy
- Determination of activation energies for desorption by TP-SIMS
- Determination of the surface diffusion behaviour of molecular species by imaging TOF-SIMS

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## Protective films formed by RIE of Co and Ti silicides and ways of their removal.

M.R.Baklanov, S.Vanhaelemeersch, Y.B.Kim, W.Storm, W.Vandervorst and K.Maex  
IMEC, Kapeldreef 75, B-3000 Leuven, Belgium

Dry etching of silicon and its compounds is based on the reaction with atomic fluorine generated by a glow discharge of fluorine-carbon chemistries. At room temperature atomic fluorine etches Si 40 times faster than SiO<sub>2</sub>[1]. For this reason it is not obvious to etch SiO<sub>2</sub> selective to silicon. Nevertheless, it was found that with certain process conditions, the etch process in a CF<sub>4</sub>-based plasma can provide good selectivity in the SiO<sub>2</sub>-Si system. Two decades ago, Heinecke found an explanation of this phenomenon: CF<sub>x</sub> radicals formed in the discharge, can polymerise forming a Teflon-like polymer[2]. The polymerisation reaction strongly depends on the material of the substrate: the degree of polymerisation on Si is much higher than on SiO<sub>2</sub>. For this reason a polymer film starts to build up on the Si-surface after completion of the SiO<sub>2</sub> etch and blocks the etching of silicon. During the last two decades, many works were devoted to the study of these processes. At present there is a good understanding of the mechanisms of these processes and as a consequence, many practical recommendations for the control of polymerisation processes and removal of polymer residues are available for different etch tools..

The metal silicides are important for advanced microelectronics due to their well-known advantages [3]. The traditional problem of the etch selectivity of SiO<sub>2</sub> in this case requires a new approach because the mechanisms of the protective film formation on silicides have several peculiarities. The most important difference is given by the fact that during the etching of silicides with fluorine a non-volatile metal fluoride film is formed, together with the volatile SiF<sub>4</sub>. For this reason complex protective films are formed on the silicide surfaces, containing both the metal fluorides and teflon-like polymers. Metal fluorides covered on the silicide surface promote the polymerisation process not so effectively as Si [4]. For this reason the role of metal fluorides for providing a good selectivity is very important.

In our work we present the study of the protective film formation during contact etch. All the etch processes were done in a LAM Rainbow 4520 oxide etch tool using a classic CF<sub>4</sub>/CHF<sub>3</sub>/Ar etch chemistry. Both XPS and ellipsometry were used for observation of the residue composition and the dynamics of residue formation and their removal in the after etch cleaning process.

Fig.1 shows XPS spectra of F1s signals after the RIE etching of TiSi<sub>2</sub> and CoSi<sub>2</sub> with different gas compositions. We can see that the relative amount of metal fluoride and polymer in both cases depends on the gas composition. In the case of CoSi<sub>2</sub> etching, the observed trend is straightforward. When the etch is done in a pure CF<sub>4</sub>/Ar etch plasma, the residue contains mainly Cobalt fluoride and only a small amount of polymer. With increasing CHF<sub>3</sub> concentration, the relative amount of polymer is increased while for pure CHF<sub>3</sub> plasmas, a preferential formation of polymer is observed. This is consistent with the observation of stimulated polymerisation with increased H<sub>2</sub> or CHF<sub>3</sub> in the etch plasma [2]. The result is also consistent with the very low volatility of the Cobalt fluorides e.g. the CoF<sub>2</sub> boiling

point is 1400 °C. In view of this, the ion-induced sputtering of  $\text{CoF}_x$  in the etch process is expected to be low.

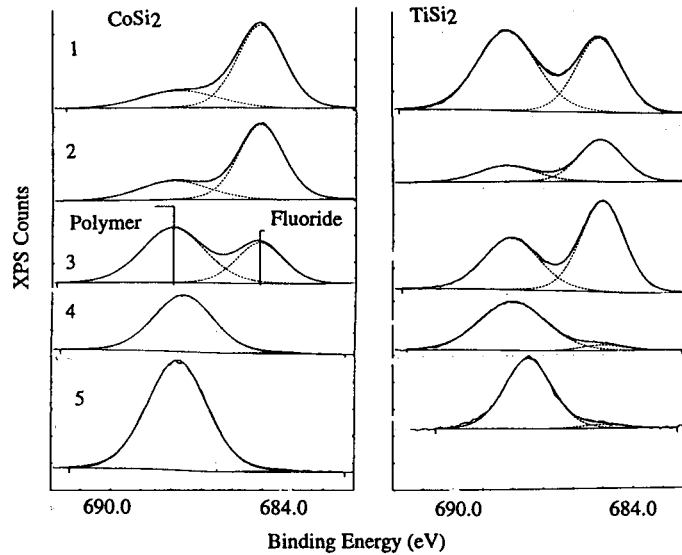


Fig. 1. XPS: F1s for  $\text{TiSi}_2$  and  $\text{CoSi}_2$  after RIE (LAM Rainbow 4520) at different ratios  $x=\text{CF}_4/\text{CHF}_3$ . 1:  $x=40/0$ ; 2:  $x=20/20$ ; 3:  $x=0/40$ ; 4 and 5: after treatment by SPM and HF. From this figure we can see that SPM and HF remove metal fluoride but can't remove the polymer film.

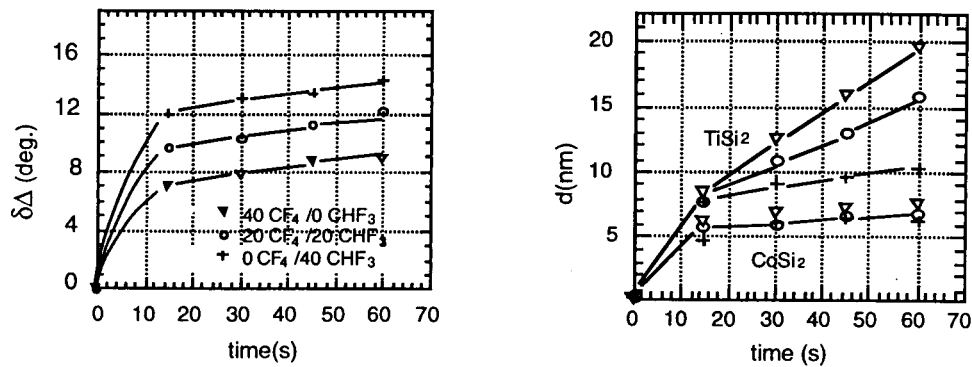


Fig.2 Change of the ellipsometric angle  $\Delta$  during the RIE with different gas composition at  $P=210$  mtorr;  $R_f=440$  W.  $\delta\Delta$  values are proportional to the change of the protective film thickness[5].

Fig.3. Change of  $\text{TiSi}_2$  and  $\text{CoSi}_2$  thicknesses versus etch time. Experimental conditions and symbols on this figure are similar to Fig.2.



Different results are found in the case of  $\text{TiSi}_2$  : even in a pure  $\text{CHF}_3$  plasma the amount of polymer is less than metal fluoride. This fact shows that the Ti fluoride promotes the polymerisation process not so effectively as Co fluoride. In a 1:1  $\text{CF}_4/\text{CHF}_3$  mixture the amount of polymer decreases as compared to pure  $\text{CHF}_3$  as well as in the case of  $\text{CoSi}_2$ . It is surprising that in pure  $\text{CF}_4$  the amounts of fluoride and polymer again become comparable. This phenomenon deals with the low sublimation temperature of  $\text{TiF}_4$  ( $284^\circ\text{C}$ ). Therefore, the ion-induced sputtering during the RIE can be significant. The rate of polymer formation in pure  $\text{CF}_4$  plasma decreases, leading to an increase of the  $\text{TiF}_4$  sputtering. Factually this hypothesis is equivalent to the supposition that polymer protects the titanium fluoride from sputtering. If this is true, the resulting thickness of protective films in  $\text{CF}_4$  plasma has to be much less than in  $\text{CHF}_3$ .

Thicknesses of the protective films were estimated from XPS results and ellipsometry [5]. From data presented in fig.2 we can see that the residue thickness on  $\text{TiSi}_2$  after the  $\text{CHF}_3$  plasma is 1.5 times higher than after the  $\text{CF}_4$  plasma. All these phenomena have strong influence on the etch selectivity. We can see from Fig.3 that in distinction to  $\text{SiO}_2$  the etch rate of both silicides is not constant in time. However, for thin film technology it is more important to know the effective selectivity as calculated from the loss of silicide thickness after 1-2 minutes overetch. In this case the influence of the transition period after the etching of  $\text{SiO}_2$  and the moment where protective film thickness reaches his equilibrium value can not be ignored. This is another problem that is discussed in paper [5].

Let's now consider another important problem. It is difficult to find the conditions not only for controlled polymer formation, but also for the surface cleaning after the selective etching. This problem was addressed based on the data about the composition of the residue and their chemical properties.

1. During the plasma etching both teflon-like polymer and metal fluorides are formed. Teflon is a chemically very stable compound and it is practically impossible to find an efficient wet method to remove it. The experience within the silicon technology shows that for the removal of these films atomic oxygen or ozone can be very effective.

2. Co and Ti fluorides are also stable compounds. It is known that they are soluble in hydrofluoric and sulphuric acids. Therefore, these solutions can be used for the removal of the metal fluorides.

In the silicide preparation a  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=4:1$  mixture (SPM) is widely used. Additionally we were hoping that SPM would be able to oxidise the polymer and therefore remove not only metal fluoride but also at least part of the polymer. We can see from Fig.1 that the last hypothesis is not confirmed. Treatment of the wafers in SPM removes the metal fluorides, but polymer remains on the surface.

Therefore, to remove both metal fluorides and polymer it is necessary to use a chemical procedure including both oxygen-plasma and SPM. Fig.4 shows the results of these experiments. After the formation of protective films (region 1), the wafers were treated by an oxygen plasma in a MATRIX System-10. The temperature of the reactor was equal to  $240^\circ\text{C}$ , the pressure was 1 Torr. We can see that the thickness of the protective film is decreased (2). Then the wafers were etched with SPM. The thickness of the film decreases again due to the removal of metal fluorides. The silicide surface after oxygen-plasma and SPM contains 3-4 nm of  $\text{SiO}_2$ . Therefore, the final step of the surface cleaning has to include the HF treatment since. On the other hand, the use of HF-based solutions creates a potential problem knowing that  $\text{TiSi}_2$  and  $\text{CoSi}_2$  are actively etched by HF[6]. Therefore, it is necessary to optimise the concentration of the HF solution and the etch time. Fig.5 shows the results of the experiments, where at the same time the ellipsometric angles and sheet resistance of

silicides have been measured. We can see that at the beginning only the  $\Delta$  value is changing showing the etching of the  $\text{SiO}_2$  film. The time when the silicide starts to etch is obvious from the change of the sheet resistance value. It is therefore possible to control the etch time by diluting of the HF solution.

Interesting experimental fact is the inverse change of ellipsometric angles near an etch time of 30 seconds just before the process of silicide etching starts. This phenomenon is observed during the etching in HF solutions with different concentration and probably deals with the change of surface stochiometry of silicide.

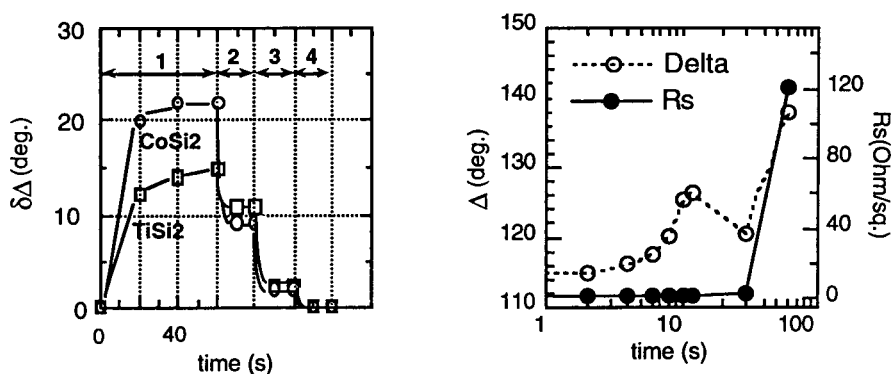


Fig.4. Change of the thicknesses of protective films on top of  $\text{CoSi}_2$  and  $\text{TiSi}_2$  during the RIE and different cleaning procedures. Every region corresponds to the different etch procedures. 1: RIE; 2: Oxygen plasma in System10 (Matrix); 3: SPM; 4:  $\text{HF}+\text{H}_2\text{O}$ .

Fig.5. Optimisation of the final cleaning procedures in HF solution (0.5%). One can see that the sheet resistance of  $\text{TiSi}_2$  changes only after 30 s.  $\delta\Delta$  before this time corresponds to the removal of residues. According to this graph optimal cleaning time (without consumption of silicide) for this experimental conditions is equal to 40 s.

According to XPS experiments, this cycle of the cleaning procedures provide practically clean surfaces of both Ti and Co silicides without the both metal fluorides and polymers. Electrical tests in contact holes also show that after this treatment good contacts of deposited metals with the under layered silicides can be realised.

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## DILUTED DYNAMIC CLEAN : "DDC"

F. Tardif\*, T. Lardin\*,

P. Boelen\*\*, R. Novak\*\*, I. Kashkoush\*\*

\* LETI (CEA-Technologies avancées)

DMEL-CEA/G, 17 rue des Martyrs, 38054 Grenoble cedex 9, France.

\*\* SubMicron System, Allentown, USA

### 1. INTRODUCTION

Usual RCA based cleaning recipes performed in state of the art conditions give performances compatible with most of the advanced application requirements. The next challenge is to achieve the same good performances but at a lower price and with a lower environmental impact. This aim can be achieved by reducing the chemicals and DI water consumptions and by simplifying the cleaning equipment. The use of diluted chemicals at room temperature represents one of the most promising alternatives and enables new technological concepts to be envisaged. The previously exposed<sup>[1]</sup> Diluted Dynamic Clean : "DDC" constitutes an interesting solution. A cleaning process adapted to DDC is proposed here.

### 2. DILUTED DYNAMIC CLEAN CONCEPT

The main idea consists in using a conventional quartz overflow rinsing tank in which small amounts of reactivities are injected alternately or together into the continuous flow of DI water. Both the process and associated rinsing are performed alternately in this same bath. The first consequence is that the space usually occupied by the rinsing bath is saved. If the quantity of chemicals is negligible in the case of diluted cleaning, the overflow can still be connected directly to the drain, thus the wafers always see fresh ultra-pure reactivities. Since for environmental considerations IC manufacturing has to limit its fluoride wastes, another bath dedicated to HF based chemistries completes the whole concept. This bath comprises a conventional HF recirculated/filtered bath including an oxygen desorption device and a chemical purifier to remove noble metals. The DDC concept is constituted by the association of the two baths as represented in figure 1.

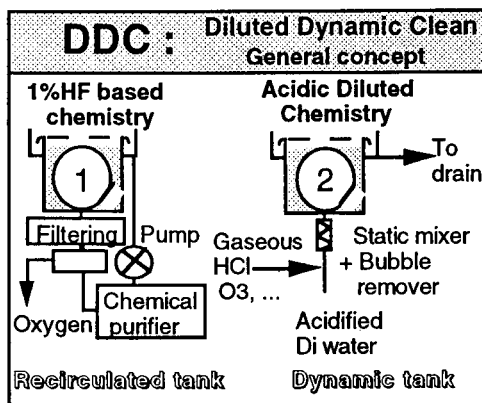


Figure 1 : "DDC" (Diluted Dynamic Clean) concept

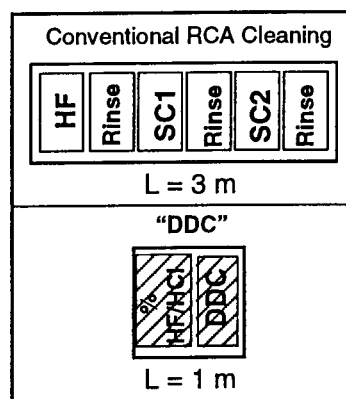


Figure 2 : Foot print for minimal DDC configuration in 200 mm

This minimum configuration thus constitutes a cleaning tool suitable for low throughputs (see figure 2). Higher throughputs can also be achieved by juxtaposing several DDC modules. The industrial success of this new concept is of course closely linked to the set-up of powerful diluted recipes.

### 3. OPTIMIZATION OF DILUTED CLEANINGS FOR DDC

#### 3.1 Oxide removal

In order to avoid the roughening effects of diluted 1%HF we earlier proposed<sup>[1]</sup> to acidify the solution with 1%HCl and to continuously remove the dissolved oxygen. This mixture is called "%" solution. In order to prevent detrimental effects caused by noble metal contamination, we propose to add a purifier in the recirculating loop. Indeed, adding a strong oxidant such as  $H_2O_2$  is only able to reoxidize the metals which have just been deposited back to the solution but leaves the associated roughness. Figure 3 shows the impact of 1 ppm copper in 20% HF in terms of roughness measured next to large defects by AFM in tapping mode. The presence of 20%  $H_2O_2$  in volume does not protect against silicon roughening. In figure 4, big holes left in silicon can be seen in spite of the presence of  $H_2O_2$  as the result of oxidation by Copper (representative of noble metals).

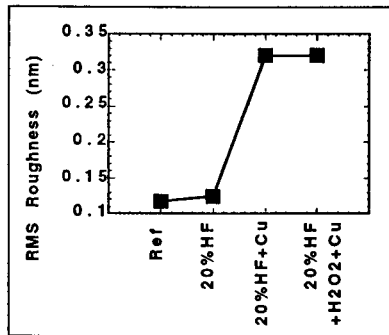


Figure 3 : AFM roughness of wafers dipped in 20% HF spiked with 1 ppm of copper (next to large defects)

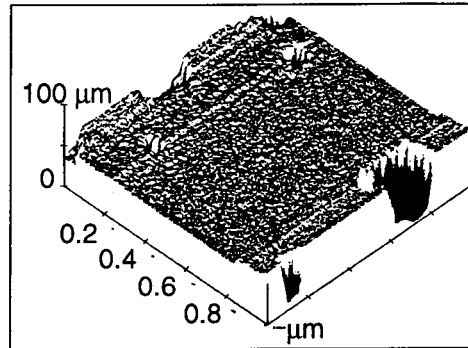


Figure 4 : Silicon oxidation effects by copper in 1%HF "protected" with 20%  $H_2O_2$

#### 3.2 Metallic removal

We earlier demonstrated<sup>[1]</sup> that except for noble metals most of the ionic contaminants are satisfactorily removed by the "%" solution with a 30" oxide overetch. Figure 5 is given as an example for Iron. Furthermore we proposed to protect the neutral pH bath (final rinse and ozone by traces of HCl : 0.01%).

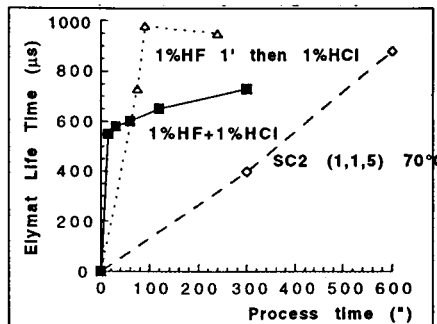


Figure 5 : Iron removal by "%" mixture as measured by ELYMAT

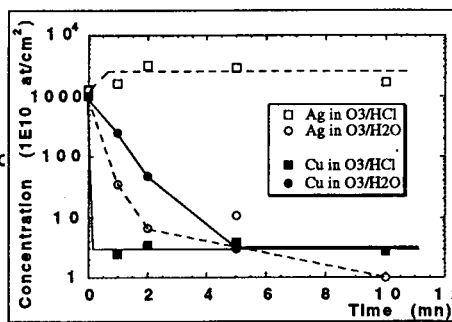


Figure 6 : Cu and Ag removal by diluted ozone chemistries as measured by TXRF

As depicted in figure 6, Copper and Silver can be removed in a DDC bath by ozone-based chemistry. Copper is very rapidly removed in 3 ppm ozone acidified by 0.01% HCl. In the case of Silver, the use of traces of HCl leads to the opposite

behaviour as we locally re-precipitate AgCl to the surface. This phenomenon was confirmed by TXRF as the Silver turns into particles and the Chlorine concentration increases in the same concentration as Silver.

We therefore propose to perform 5' of 3 ppm ozone in water as a first DDC step in order to protect the "%" bath from silver and copper brought by the incoming wafers up to the level of  $10^{13}$  at/cm<sup>2</sup>. Furthermore, this treatment is able to efficiently eliminate part of the organics[2].

### 3.3 Particle removal

Particle removal is the most difficult step to achieve with diluted chemicals. Major works therefore have to be performed in this field as furthermore fine particle removal will also probably be the major challenge in the forthcoming years.

The simplest way to etch both silica and silicon under the particles would have been to use diluted ammonia. Unfortunately, we did not succeed with diluted ammonia because at room temperature the under-etching rates of both Si and SiO<sub>2</sub> are not sufficient. Indeed on oxide, the 2 nm criterion<sup>[3]</sup> for a 10-minute process is only reached at 0.1% ammonia if the bath is heated to 50°C. Furthermore on silicon, the etching is anisotropic even for diluted concentrations (<0.01%) at room temperature resulting in a drastic LPD increase. Ozone injection even directly in the 0.01% ammonia bath does not limit the roughening effect since O<sub>3</sub> is not soluble at alkaline pH.

HF/H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> would be acceptable only if used in conjunction with surfactants and megasonics<sup>[4]</sup> but we did not manage to reproduce this result.

Finally we tried to optimize the two-step under-etching : 3 ppm ozone in water followed by a HF dip for which the mechanism was explained by IMEC. First, in order to enhance the repulsion forces between particles and the substrate the pH given by the weak acid HF has to be lowered. Again but for other reasons, we used our "%" solution to be in the "A" area of figure 7.

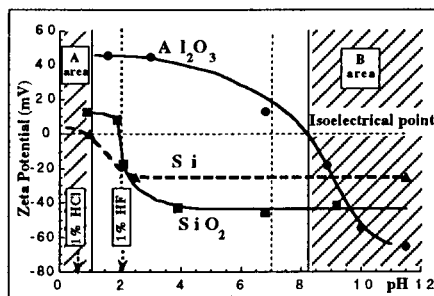


Figure 7 : Zeta potential of materials different as a function of the pH

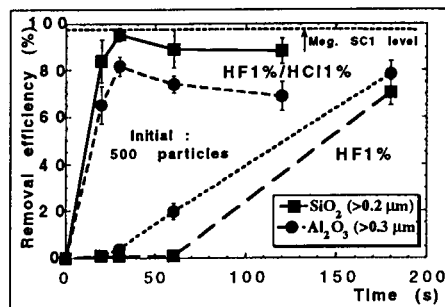


Figure 8 : SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> particle removal on native oxide by 3 ppm O<sub>3</sub> followed by 1%HF or "%" solution

Figure 8 shows the particle removal kinetics of the cleaning processes : 10' in 3 ppm O<sub>3</sub> in water followed by 1%HF acidified or not with 1%HCl starting from 500 particles intentionally deposited. A one-minute dip is therefore sufficient in the case of the "%" solution which limits the detrimental parasitic etchings (on locos edges for example). Furthermore, the removal efficiency is appreciably higher with the "%" solution for the considered particles but is still slightly lower than a conventional SC1 with megasonics (SiO<sub>2</sub> : 97.8% and Al<sub>2</sub>O<sub>3</sub> : 96.4%). In the same way, the first oxidation step : 3 ppm O<sub>3</sub> in water was optimized at 10 min.

### 3.4 Final passivation

As shown in figure 9, the final Silicon surface passivation for 7 nm gate oxide is satisfactorily obtained after 6 to 10' in 3 ppm ozonated water acidified with 0.01% HCl performed in dynamic mode. The irreproducible results obtained with the HFlast process used in the test as a reference can be noted (time delay between cleaning and furnace : 1 hour). The previous cleaning steps performed in this test are those shown in figure 10.

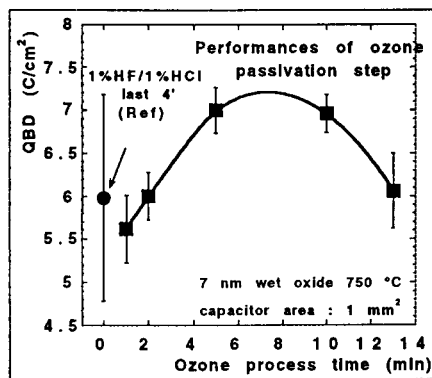


Figure 9 : Final passivation by ozone water in terms of 7 nm gate oxide

| Process (20°C) | Time (min)       | Goal              |
|----------------|------------------|-------------------|
| 3 ppm O3       | 5                | Noble metal + CHx |
| "%"            | + 0.5 (overetch) | Sac. Ox. + metals |
| Rinse          | 5                | Rinse             |
| 3 ppm O3       | 10               | Particle removal  |
| "%"            | 1                | removal           |
| Rinse HCL      | 5                | Rinse             |
| 3 ppm O3 + HCl | 7                | Final passivation |

Figure 10 : DDC process applied in to gate oxidation

### 3.5 Example of DDC recipe : before gate oxide

The previously obtained conclusions have of course to be adapted for each application. Figure 10 shows a cleaning sequence adapted to gate oxidation. The total process time is about 33 min. and consumes about 7 to 30 times less chemicals (as a function of production rate) than a conventional CARO+HF+RCA cleaning performed in an advanced wet bench with chemical spikes (bath life time : 24 hours).

## 4. CONCLUSION

The DDC concept using existing wet bench technology represents one of the most interesting ways of reducing the cleaning costs and environmental impact. The performances of the process proposed here are very close to conventional RCA-based chemistry but can be further improved in particular in terms of particle removal which represents the most difficult challenge for highly diluted chemistries.

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## Effects of Dilute Chemistries on Particle and Metal Removal Efficiency and on Gate Oxide Integrity

Fuyu Lin, Sergio Ajuria\*, Pat Schay, Mike Masquellier, Ron Sanders, and John Stih  
Advanced Custom Technologies, Motorola, 2200 W Broadway Rd., Mesa, AZ 852202

\* Semiconductor Technologies Laboratory, Motorola, 3501 Ed Bluestein Blvd, Austin TX 78721

### INTRODUCTION

While surface preparation continues to draw considerable attention in the areas of gate oxide scaling, surface states, and micro-roughening [1,2], there are a number of mature semiconductor fabs with an equal or greater interest in reducing cleaning costs and chemical waste without affecting yield or device performance [2,3].

RCA cleans with a variety of reduced solution concentrations have been proposed in order to enhance cleaning performance and/or reduce cost of ownership (CoO). Lower ratios of high purity SC1 ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ), originally driven by an interest in reducing ammonia-induced microroughening, are proving to have cost and disposal advantages as well. In addition, the lower pH values of dilute SC-1 have proven to deposit less metalics than concentrated solutions. Metal removal efficiency for SC-2 as a function of temperature and HCL concentration has also been studied [3,4], and suggest that SC-2 dilution may also be possible without impacting metal removal efficiency.

Reduced cleaning steps are another proposed approach to obtaining better surfaces at a lower cost. Pre-gate cleans using  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  and dilute HF/HCL/IPA without SC-1 and SC-2 have been suggested by IMEC[3]. Most pre-gate users are also familiar with HF-last procedures in an RCA+HF sequence to obtain a hydrophobic surface. The main issue associated with HF-last processes is particle contamination, as hydrophobic surfaces are known to promote particle adhesion and Cu plating out on the wafer surface. The IMEC HF-last method circumvents the particulation and Cu problem by growing a sufficiently thick chemical oxide in the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  step to remove particles efficiently in the DHF step, then completely passivating the surface with -H radicals to avoid surface re-oxidation or particle contamination. Surfactant additives, such as Isopropyl Alcohol (IPA), can also lower the surface free energy and increase surface passivation.

In addition to cleaning sequences and chemical mixtures, the type of clean tool can be another major factor in surface cleaning. The most commonly used tools for wet chemistries are spray tools and wet benches. The main advantage of spray tools is the use of fresh chemicals every time, while that of wet benches is greater flexibility for performing mixture modifications. One drawback of spray tools is that it is difficult to incorporate surfactant additives in very small amounts. In addition, its spin-rinse dry (although optimized) can cause residuals in patterned wafers where hydrophobic and hydrophylic surface occur at the same time. Wet benches in turn have bath lifetime considerations due to both chemical decomposition and contaminant accumulation in the bath.

In this paper we evaluate the particle and metallic removal efficiency of various cleaning techniques, and their effects on gate oxide integrity, using wet bench and spray acid tools. All experiments were conducted in a manufacturing environment, suggesting that results are applicable to full-scale production. We demonstrate the existence of a wide cleaning process window in which  $\sim 100\text{\AA}$  gate oxides can be grown with no significant differences in particles, metalics, and gate oxide yield. This in turn allows a manufacturing operation to use criteria such as cost of ownership, tool footprint, waste, or other fab-specific constraints to optimize wafer cleaning procedures.

### EXPERIMENTAL

Particle removal efficiency and metal contaminant levels are the two basic methods for testing the effectiveness of cleaning sequences, surfactant additives, and chelating agents. In this work, particle removal was measured as a function of chemical ratios, bath lifetime, clean sequence, and clean tool. For the wet bench, the SC-1 ratio was reduced to  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}=0.05:1:5$  with bath ages of 2, 4, 6, and 8 hours during a full RCA clean.

For the simplified RCA sequence without SC-1 and SC-2 but with HF-last, the process was optimized using the IMEC recommended process (DI water and a mixture of HF/IPA/HCL = 0.5% 0.1% 0.1%). For the spray tool (FSI Mercury), the SC-1 and SC-2 ratios were 0.4:0.4:6, where 0.4 represents 100cc of flow, the lower limit on the platform's flow controllers. It should be noted that the temperature for SC-1 and SC-2 was 55°C in all experiments.

The initial particle levels for particle removal tests were anywhere from 0 to 1000. The particles were deposited on bare silicon wafers by dipping the wafers in an HF tank with the pump turned off. A SurfScan 4500 was used to monitor particles larger than 0.3µm. Particle removal efficiency was determined from the differences of before and after particle readings plotted as a function of initial particle level. TXRF was used to detect metal contaminants on the wafer surface prior to and after the clean. Wafers were dipped in a tank contaminated with various metals and then cleaned in various clean sequences, similar to those described for particle removal tests.

The effects of dilute chemistries or simplified cleans on gate oxide integrity were evaluated using various capacitors. N<sup>+</sup> poly-gated MOS capacitors with 105Å gate oxides were used for this study. A PBL isolation scheme was used, along with a 6750Å field oxide. After PBL stack removal, a 400Å sacrificial oxide was grown at 1000°C and then removed in 10:1 BOE with 30% overetch. After sacox etch, pre-gate clean splits were performed. Gate oxide was grown in a horizontal furnace at 900°C with 3% HCl followed by poly gate deposition and definition.

Time-zero breakdown and charge-to-breakdown were measured as experimental outputs. Time-zero breakdown was monitored by measuring current during voltage ramping, with the breakdown voltage being defined at 1mA of current. Charge-to-breakdown was measured using a constant current of 0.1A/cm<sup>2</sup>. The capacitors investigated had an area of 0.1cm<sup>2</sup> for determining the defect density and an active perimeter of 6.78 cm (edge-intensive) for evaluating stress.

## RESULTS AND DISCUSSION

Fig. 1 shows the particle removal efficiency of three pre-gate cleans with aggressively reduced or even eliminated chemicals, compared to the standard RCA clean. The removal efficiency of the spray clean with dilute SC-1 & SC-2, for wet bench cleans with IMEC clean, RCA with dilute SC-1, and standard RCA are 93%, 99%, 100%, and 98% respectively. The higher particle removal efficiency for the wet bench cleans with both hydrophylic and hydrophobic surfaces compared to the spray tool may be due to differences in drying techniques. The wet bench uses IPA drying, which has been shown to be superior to spin-rinse-drying (SRD). Water evaporation during drying, the mechanical spinning, and static electricity associated with SRD all result in particle deposition on the wafers[5]. However, it should be noted that initial particle levels were lower for the spray tool than for the wet bench, which may obscure true particle removal comparisons.

It is obvious from Fig. 1C that dilute SC-1 has a removal efficiency comparable to that of conventional chemistry ratios. Furthermore, the wet bench results in Fig. 1 include data from bath lives from 2 to 8 hours. Bath lifetime depends mainly on the decomposition rate, which is a strong function of bath temperature. At 23°C, the time for peroxide to be reduced to the critical concentration is 50 hours, but only 40 minutes at 80°C. Therefore it is very important to set bath life according to the required temperature. The lifetime is also expected to be related to the number of wafers cleaned through the bench. The volatilization of NH<sub>3</sub> from the NH<sub>4</sub>OH and decomposition of H<sub>2</sub>O<sub>2</sub> (which are similar) seem to be insignificant within the 8 hours at 55°C investigated in this work.

Table 1 shows the TXRF results obtained from RCA (dilute SC-1) and IMEC cleans in the wet bench, and RCA cleans in the spray tool. The original contamination level for certain metals is anywhere from mid10<sup>10</sup> / cm<sup>2</sup> to mid10<sup>12</sup> / cm<sup>2</sup>. All of the contaminated wafers were virtually free of metallics after they were run through the above cleans. RCA with dilute SC-1 is expected to be able to remove metals as well as or even better than the standard RCA since dilute SC-1 tends to deposit fewer metallic contaminants. Although the IMEC clean still has its skeptics in manufacturing, our data suggest that it has overcome the Cu contamination and high particle



problems associated with conventional HF-last processes with a significant reduction in chemical usage and cost.

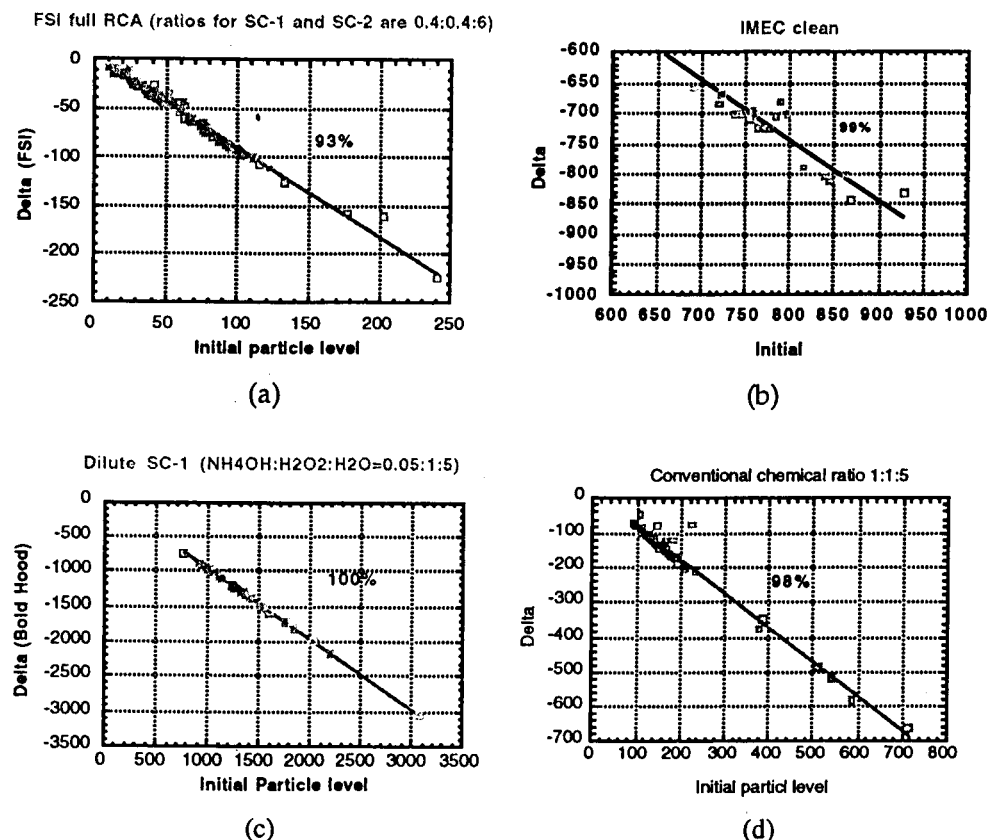


Fig. 1 Particle removal efficiency for various clean sequence and dilute chemistries: (a) dilute SC-1 & SC-2 in the spray tool, (b) Piranha+DHF clean only, (c) dilute SC-1, and (d) standard RCA.

Surface conditions including surface roughness as well as contamination have been known to have a great impact on subsequent gate oxide formation and final gate oxide integrity. Thus, several of the clean sequence variations characterized for particulates and metallics were attempted on both wet bench and spray acid tools to determine their effects on gate oxide integrity. Fig. 2 shows the cumulative plots of breakdown voltage and charge-to-breakdown for 5 different pre-gate clean variations. It should be noted that the HF-last clean was performed in the FSI Mercury using Piranha and 100:1 HF only. The FSI used large droplets during rinse to replace tiny water droplets in order to eliminate drying spots normally found on hydrophobic surfaces dried in SRD's. In addition, RCA with cold, dilute, and short SC-1 was also performed using an FSI recipe to grow chemical oxide.

There is no significant difference between each split in time-zero breakdown behavior on large area capacitors. Similar results were obtained for field edge-intensive structures. These time-zero results indicate that the 5 different pre-gate cleans tested produce similar defect densities using 105Å gate oxides. It thus seems that microroughening, if affected, is not sufficiently different to impact 105Å gate oxide quality. It is also encouraging to see that two hydrogen terminated cleans without SC-1 and SC-2 did not degrade 105Å gate oxides. The optimized HF-last (IMEC) clean may be more robust than the normal HF-last clean in day-to-day performance, but both worked

comparably in this 1-time experiment. The fact that hydrophobic or hydrophylic surface resulted in similar gate oxide yield indicates that oxide and hydrogen passivated surfaces can produce comparable results.

Table 1. Metal removal measured with TXRF using various cleans

|                                          | Ca | Ni<br>( $10^{10}$ atoms/cm $^2$ ) | Cu | Zn | Fe |                         |
|------------------------------------------|----|-----------------------------------|----|----|----|-------------------------|
| Initial metal values                     | 61 | 5                                 | 40 | 55 | 8  | _ below                 |
| RCA with dilute SC-1(0.05:1:5)           | —  | —                                 | —  | —  | —  | the detection           |
| IMEC clean (Piranha+DHF/HCL&IPA)         | —  | —                                 | —  | —  | —  | limit which is          |
| FSI (0.4:0.4:6)                          | —  | —                                 | —  | —  | —  | $10^{10}$ atoms/cm $^2$ |
| RCA with no H $_2$ O $_2$ in SC-2: spray | —  | —                                 | —  | —  | —  |                         |
| wet bench                                | —  | —                                 | —  | —  | —  |                         |

## CONCLUSIONS

We evaluated the particle and metallic removal efficiency and gate oxide integrity effects of various reduced chemistry / reduced sequence cleaning techniques using wet bench and spray acid tools. Based on particle measurements, TXRF, and gate oxide yield, we conclude that there is a wide cleaning process window in which  $\sim 100\text{\AA}$  gate oxides can be grown with no significant differences in particles, metallics, and gate oxide quality. This allows manufacturing operations to use criteria such as cost of ownership and other fab-specific constraints to optimize their wafer cleaning procedures.

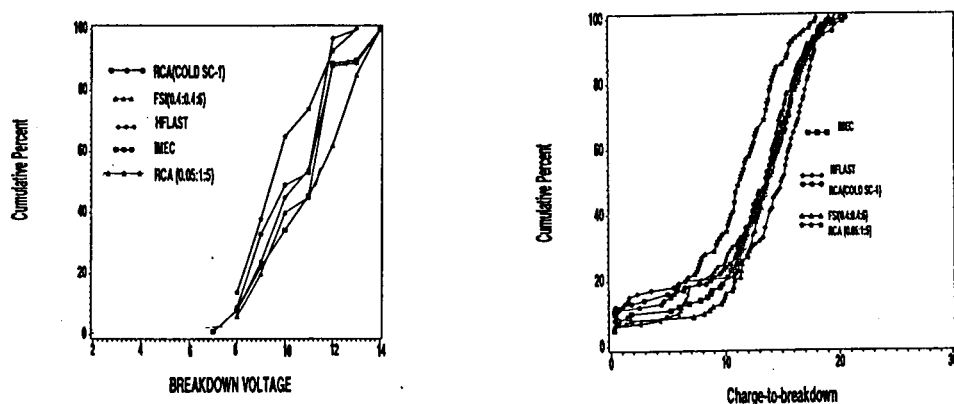


Fig. 2 Cumulative plot of (a) breakdown voltage, and (b) charge-to-breakdown for various pre-gate cleans.

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## HOT WATER ETCHING OF SILICON SURFACES: COMPARISON OF IMMERSION AND SPRAY TECHNOLOGIES

J.Q. Liu, J.M. Rosamilia\*, T. Boone\*, J. Sapjeta\*, C. Oberdorfer, G.S. Higashi

Bell Laboratories, Lucent Technologies  
9333 S. John Young Parkway  
Orlando, FL 32819

\*Bell Laboratories, Lucent Technologies  
600 Mountain Avenue  
Murray Hill, NJ 07974

### 1. INTRODUCTION

Controlling silicon surface topography in the cleaning processes of integrated circuits is crucial to device performance, reliability, and yield. In the RCA cleaning technique, water rinsing after HF processes may change surface topography since bare Si surfaces are exposed. It has been found that hot water rinsing following HF immersion can cause Si etching. Etch steps were seen near the field oxide isolation edges in gate oxide test structures. This etching consequently degrades Fowler-Nordheim tunneling voltages (FNV) and increases defect density [1]. The degradation was found to be eliminated by controlling the concentration of dissolved oxygen in the hot water. Higashi et al. [2] proposed a sequential back-bond attack mechanism, and implicated this phenomenon to OH<sup>-</sup> and dissolved oxygen. Recent studies of HF cleaned Si(100) surfaces in hot water by L. Li et al. [3] showed that the etching reaction was effectively suppressed by adding HCl to control the OH<sup>-</sup> concentration, confirming the role of OH<sup>-</sup>.

Increases in gate-oxide defect density have also been found in spray processing tools as a result of elevated temperature spray rinses. The objective of this study is to further investigate hot water etching using both immersion and spray techniques. We focus on the etching mechanism and the dependence on the water rinsing temperature, rinsing time, and the concentration of the dissolved oxygen.

### 2. EXPERIMENTAL AND RESULTS

With the immersion technique, 6-inch diameter Si(100) monitor wafers were immersed in a dilute HF bath, followed by a rinse with different times and dissolved oxygen concentrations. Surface roughness of these monitor wafers determined from AFM is illustrated in Fig. 1. With 10 min rinses at 70°C surface rms roughness increases from 1.9 Å to 2.8 Å, when the concentration of oxygen varies from 18.4 ppb to 5.5 ppm. With 99 min rinses at 65°C, rms roughness decreases from 19 Å to 12 Å, when the concentration of oxygen varies from 860 ppb to 7.6ppm. Therefore, with long time rinses higher concentration of oxygen results less rough surface. This may be due to suppression on silicon etching resulting from the reoxidation of the silicon surface during the long time rinses. Fixing the dissolved oxygen concentration and temperature at 500

ppb and 65°C, respectively, it is observed that surface roughness increases with rinsing time (shown in Figure 2).

Gate oxide zone testers were also dipped in a dilute HF bath, followed by rinses with different temperatures and concentrations of dissolved oxygen. The rinse water temperatures used were 21°C, 30°C, and 65°C. The concentrations of dissolved oxygen used were 6 ppb and 5 ppm. All the rinse times were set at 99 min. Etch steps of the testers were determined by TEM. Fig. 3 illustrates that increases in temperature is the most significant factor influencing etch depth. At 65°C, the etch rate is 1.49 Å/min for 6 ppb, and 0.91 Å/min for 5 ppm oxygen. At 30°C, the etch rate is 0.37 Å/min.

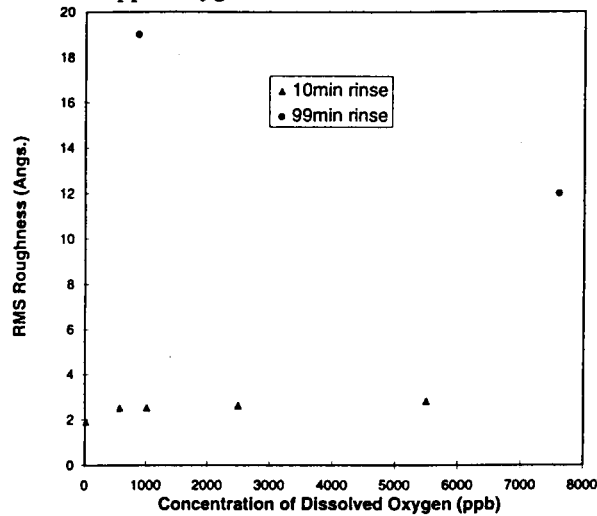


Figure1. Surface roughness with different dissolved oxygen concentration with 10 min water rinse.

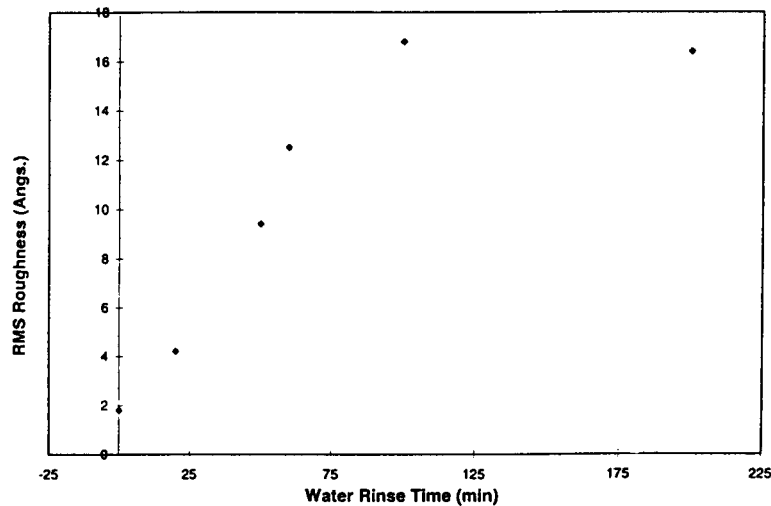


Figure 2. Surface roughness with different water rinse time with 500 ppb oxygen.

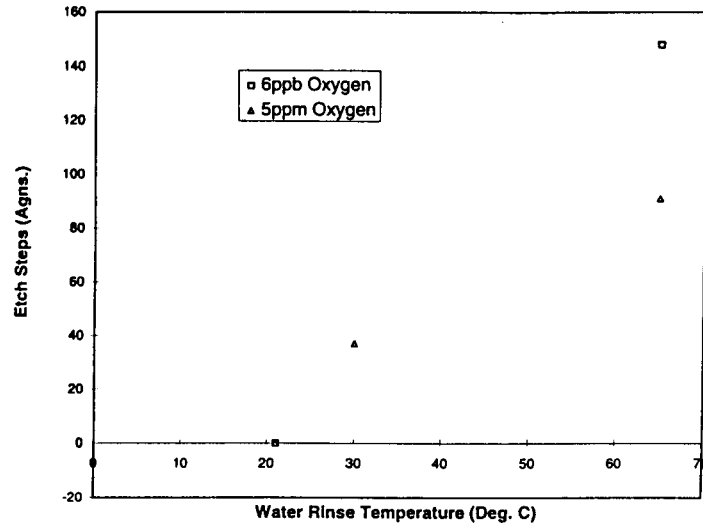


Figure 3. Etch steps of GOX zone testers with different rinse water temperature and dissolved oxygen concentration. (Rinse time: 99min)

With a spray processor, 6-inch diameter Si(100) monitor wafers were cleaned using an RCA cleaning sequence as follows:  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ --Hot DI rinse--Cold DI rinse--dilute HF--Cold DI rinse--Hot DI rinse-- $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ --Hot rinse-- $\text{HCl}/\text{H}_2\text{O}_2$ --Hot rinse--Dry. The temperature of the hot DI following HF process is  $78^\circ\text{C}$ . The concentrations of dissolved oxygen are 17 ppb, 3.5 ppm, 10 ppm. The rinse times vary from 3 min, 15 min, and 45 min. After the cleaning, the wafers were brushed scrubbed. The surface rms roughness determined by AFM is shown in Figure 4. We observed that surfaces get smoother with longer rinse times, independent of the dissolved oxygen concentration. Light Point Defects (LPDs) were measured before the cleaning, after the cleaning, and after the brush scrub on a Tencor 6400 for LPD sizes of  $\geq 0.2\ \mu\text{m}$  and  $\geq 0.15\ \mu\text{m}$ . In contrast to the decrease in AFM surface roughness, LPD counts at  $\geq 0.15\ \mu\text{m}$  were observed to increase after 45 min hot water spray rinses. This indicates significant surface damage on the wafers with 45 min hot rinses.

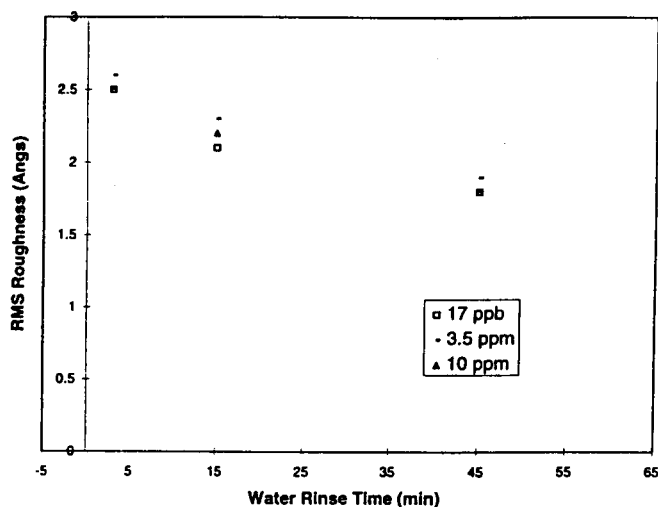


Figure 4. RMS roughness vs dissolved oxygen concentration and rinse time for spray technique

### 3. DISCUSSIONS AND CONCLUSIONS

With the immersion technique many factors influence the surface roughness. Both  $\text{OH}^-$  and oxygen play important roles in the etching. Surface roughness increases with the concentration of oxygen for short time rinses, but decreases with the concentration for long time rinses. This is because at high concentration of oxygen and long time hot rinse, silicon surface reoxidation occurs and suppresses the etching. The temperature of the water is the main factor influencing surface roughness and silicon etching. This may be due to that  $\text{OH}^-$  concentration increases at high temperatures, thus enhances the attacking of Si-Si back bond with oxygen or even without oxygen help.

On the other hand, the etching mechanism for the spray technique may be different. The concentrations of oxygen in the hot DI does not affect the surface roughness. Longer hot water rinses result in smoother surfaces, but cause tiny surface defects. Details are still under investigation. Finally, caution must be used in relying on AFM measurements alone since LPD counts increased while AFM surface roughness decreased.

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## Determination of Rinse Limiting Factors in Carryover Fluid Removal for Overflow Rinse Tanks<sup>\*\*\*</sup>

T. J. O'Hern<sup>\*</sup>, T. W. Grasser<sup>\*</sup>, A. S. Geller<sup>\*</sup>, P. G. Lindquist<sup>\*\*</sup>, and J. Throngard<sup>\*\*</sup>

The single most frequently used step in manufacturing integrated circuits is wafer cleans, accounting for about 30% of all manufacturing steps. The wafer cleaning process typically consists of cleaning and etching the wafer surface in a liquid chemical bath and then removing the remaining chemical residue layer (carryover) using ultrapure deionized (DI) water. A new wafer fabrication facility today consumes up to 1 billion gallons of water per year, most of it (approximately 70%) in the generation of ultrapure DI water for wafer processing and rinsing. At present wafer diameters, ultrapure water usage per wafer is estimated to be in excess of 2000 gallons (Chase, 1995). The larger wafer diameters forecast for future production are expected to require even more water per wafer as the number of processing steps increases. With more fabs being located in the U. S. Southwest, where pure water is a scarce resource, conservation of water is taking on increasing importance, as are purification and disposal costs. Beyond water conservation, optimization of the flow in rinse tanks is needed to optimize the rinse process, leading to better uniformity of rinsing of each wafer and from wafer to wafer. We report the results of an experimental study on the factors that control the removal of carryover liquid from wafers in an overflow rinse tank.

An ideal rinse tank would satisfy each of the following rinsing objectives:

- Desired levels of rinsing would be achieved using as little water as possible, in as little time as possible.
- Uniform rinsing of each wafer surface, i.e., no regions of significantly different contamination level would be present (uniformity across each wafer).
- Each wafer would rinse the same as all of the others, i.e., no wafers with significantly different contamination level would be present (uniformity across the tank).

The wafers entering the rinse tank are coated with a thin liquid chemical "carryover" layer from the previous wafer processing step. Typical carryover layer thicknesses are estimated to be 50-100  $\mu\text{m}$  (Rosato *et al.*, 1993). Ultrapure DI water is used to remove the chemical layer. Kempka *et al.* (1995) have shown, through computational simulation, that fluid flow controls the carryover removal. The goal of this work was to experimentally identify rinse limiting factors, allowing optimization of rinse tank performance in order to increase rinse efficiency and minimize DI water usage.

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\* Engineering Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, USA

\*\* Ultra Clean Research and Development, SCP Global Technologies, Boise, ID 83704, USA

## EXPERIMENTAL

A prototype test tank was designed to provide a flexible testbed, allowing control of the inlet and internal tank geometry, tank volume, and outflow wall height and geometry. In addition, this Plexiglas rinse tank provides good optical access for flow diagnostics. Either tap water or deionized water (18 gallons per minute (GPM) of 18 M $\Omega$ -cm) can be supplied. In the rinse tank, as many as fifty 200 mm silicon wafers are held vertically in two 25-wafer carriers (boats) placed in a large T-bar rack. The water inlet geometry, tank volume, and wall configurations are all adjustable.

Measurement of the fluid resistivity in the gap between two wafers was made using a wafer gap conductivity cell (Lindquist *et al.*, 1995), comprised of two specially prepared wafers which replace two of the standard wafers in the rinse tank. The conductivity of the liquid volume between these two wafers is measured. This allows a measurement more localized to the wafer region of interest, as well as wafer-gap to wafer-gap comparison to determine rinse uniformity across the tank. For the tests run here, rinsing of a carryover 1000 ppm NaCl standard solution was examined. Six standard gaps of interest were chosen, at the ends and center of each of the two wafer boats (gaps 1-2, 12-13, 24-25, 26-27, 37-38, and 49-50). Ion concentration was calculated from the raw resistivity data (Thornton and Light, 1989). From the concentration plot, the characteristic time  $\tau$  (the exponential decay constant) can be calculated from the slope of the linear portion of the concentration-time log-linear plot.

The primary visualization technique was particle image velocimetry (PIV), in which images of flow-tracing seed particles are captured on video or directly into computer memory. A time sequence of images (movie) of the flow tracing particles is recorded, and velocities are determined by cross-correlation of the particle motion between frames. The seed particles have a mean diameter of 14  $\mu$ m and a specific gravity of approximately 1.4. Using PIV, we can correlate the flow between wafers to the removal of carryover fluid, that is, to the rinse efficiency.

In order to determine the rinse limiting factors, an experiment design was created to test a number of rinse tank parameters effect on rinse behavior. The variables were:

|                  |                                              |
|------------------|----------------------------------------------|
| Flowrate         | 5 and 10 GPM (18.92 and 37.84 liters/min)    |
| Tank Volume      | Standard (39.52 liters) and reduced (35.72)  |
| Wall Outflow     | Normal or slotted                            |
| Side jets        | In addition to floor jets. Absent or present |
| Floor Injection  | Arrays of holes or slots                     |
| Floor Screen     | 80% open area nylon mesh. Absent or          |
| Slight Agitation | Absent or present                            |

The standard operating setup for this tank includes upward-directed flow from a series of 156 holes (2 mm diameter), normal wall height, no side wall injection, and standard tank volume. The floor inlet geometry of this tank provides a very uniform upflow velocity in the wafer gaps, with a PIV-measured magnitude of approximately 6 cm/s for a 10 GPM flowrate. All conductivity data for this designed experiment were acquired in wafer gap 12-13 (middle of 25 wafer cassette).



## RESULTS AND DISCUSSION

The results showed that the only factors that significantly affected the removal of carryover fluid from the wafers were tank volume and flow rate. The outflow geometry had negligible effect, except that the tank rinsed faster due to reduced volume. Addition of side jets to the upward flow through the floor had only a very minor effect. The effect of changing from holes to slots for floor injection was confined to certain gaps, with the array of small holes giving better uniformity. The negligible effect of the floor screen may be due to the fact that the injection jets are fully turbulent when they enter the wafer gaps, so a small additional turbulence component is negligible. For the 2 mm inlet holes, at 10 GPM, the jet Reynolds number is 2500 and average inlet velocity is 1.2 m/s.

The results of the parameter screening study were used to design an optimized rinse tank. Conductivity measurements were used to verify improvements. Several slight inlet modifications were made to provide a more uniform upflow over the wafer surfaces. In order to determine the gap-to-gap performance of the optimized configuration, resistivity measurements were made in the 6 standard gaps examined throughout this study. The results shown in Figure 1, the concentration of carryover solute plotted as a function of time for six interwafer gaps, demonstrate that the rinsing is relatively uniform across the tank, with a maximum variation of 2% between the best and worst gaps (Gaps 37-38 and 26-27, respectively). The exponential decay of concentration (see Figure 1) is indicative of removal from a perfectly stirred vessel (i.e., no concentration variation) and the slope of the decay is the time constant,  $\tau$ . The rinse performance of the optimized tank was 37% better than that of the baseline tank at the same flowrate.

The rinse data demonstrate an exponential decay of concentration with time, supporting the perfect mixing (CSTR) model proposed by Rosato *et al.*, 1993. In this model, convection dominates the contaminant removal process, and the carryover fluid is assumed to dissolve in the rinse tank instantaneously before removal by continuous steady dilution. The contaminant concentration decreases with time according to  $C(t) = C_0 e^{-t/\tau}$  where  $C(t)$  is the time-varying concentration,  $C_0$  is a constant related to the initial volume of carryover fluid,  $t$  is the time, and  $\tau$  is the exponential decay constant. The value of  $t$  has been shown to be reasonably estimated by a characteristic residence time (Rosato *et al.*, 1993). Concentration data from each gap support this model, with a fast rise in solute concentration as material is removed from the carryover layer into the bulk fluid, followed by a long decay as contaminated fluid is removed from the tank. However, the local value of  $\tau$  varies from one gap to another, and can be as much as 30% lower than that predicted by the full tank residence time.

## CONCLUSIONS

Experiments were performed to determine the rinse limiting factors in an overflow rinse tank. The results of the parameter sensitivity study indicate that the rinse tank acts in a CSTR fashion, with continual dilution of the carryover chemical. Flow visualization supports this, showing rapid mixing for all of the tank geometries

examined to date. Because of the CSTR nature of the flow, reducing tank volume is the key parameter for reducing rinse time. The results of the rinse limiting factors study were used to design an optimized rinse tank. The rinse performance of the optimized tank was 37% better than that of the baseline tank. The optimized rinse tank also demonstrated very good gap-to-gap uniformity, with a 2% difference in  $\tau$  between the 6 gaps examined.

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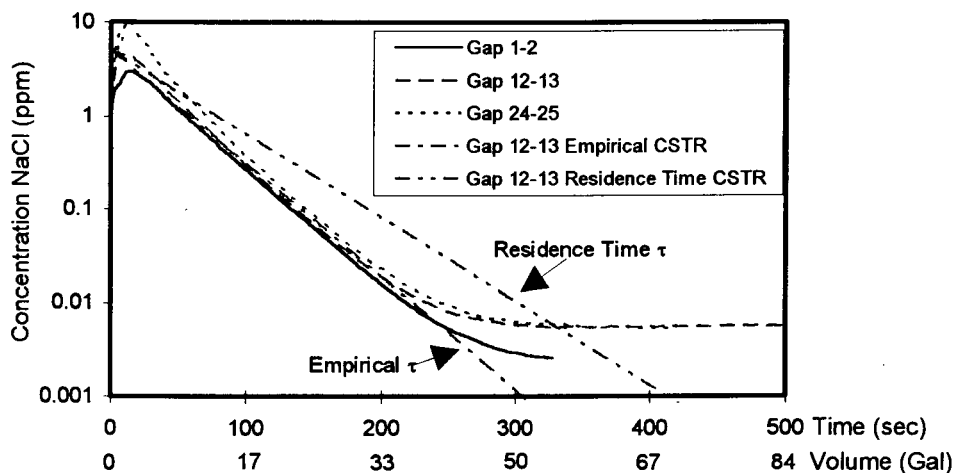


Figure 1. Concentration in six interwafer gaps as a function of rinse time. 10 GPM flowrate. Region of exponential decay (straight-line on log axis) is indicative of perfect mixing behavior. CSTR fits are to gap between wafers 12 and 13. Constant  $C_0$  was set at 5 for both CSTR fits, but the residence time  $\tau$  (48.54 sec) overestimated the best fit empirical  $\tau$  (35.84 sec).

## INTERACTION OF METAL CONTAMINANTS WITH THE SiO<sub>2</sub>/Si INTERFACE IN INSULATING LOCOS STRUCTURES

G. Franco<sup>\*</sup>, C.M. Camalleri<sup>\*</sup>, V. Raineri<sup>\*\*</sup>, D. Caruso<sup>\*</sup>.

In this paper the importance of gettering procedures is evidenced to demonstrate the possibility of autocleaning processes. In insulating LOCOS structures the Si/SiO<sub>2</sub> interface is studied controlling contamination and roughness. Contamination degrades the insulating characteristics while no influence was observed for interface roughness up to 1 nm. Metal impurities can be removed during device fabrication by segregation annealing on trapping centres.

### 1. INTRODUCTION

Understanding the interaction of contamination with silicon oxide growth is one of the main feature to improve the cleaning procedures adopted just in the involved steps and to obtain better device characteristics at a reasonable cost. To date, much attention was paid to surface roughness and wafer cleaning before thermal oxidation [1,2]. However, contaminants already present in the wafer or introduced during oxidation can diffuse through the wafer and segregate at the Si/SiO<sub>2</sub> interface. Two are the consequent effects: the increasing of the interface roughness and the formation of a metal precipitate network at the Si/SiO<sub>2</sub> interface [3,4]. In the past it was already shown that the metal precipitates and not crystal defects present at the Si/SiO<sub>2</sub> interface are responsible of oxide degradation [3]. In our work we demonstrate that for thick oxide ( $>0.5\ \mu\text{m}$ ) an increase in the interface roughness (up to 1 nm) does not influence its electrical behavior in insulating LOCOS (local oxide) structures, while the presence of small amounts of contaminants ( $>10^{11}\ \text{cm}^{-2}$ ) affects the sub threshold leakage current of the associated parasitic MOS (metal oxide semiconductor) devices. Indeed, these LOCOS structures in some cases can behave as parasitic MOS devices while they should always maintain the insulating characteristics.

### 2. EXPERIMENTAL PROCEDURE

Very large scale integrated (VLSI) logic circuits were fabricated controlling the surface roughness (0.03 nm) before the LOCOS thermal growth. In some wafers metal contaminations were appropriately introduced before the oxidation process

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<sup>\*</sup>SGS-Thomson microelectronics - Stradale Primosole, 50 - I95121 Catania, Italy.

<sup>\*\*</sup>CNR-IMETEM - Stradale Primosole, 50 - I95121 Catania, Italy.

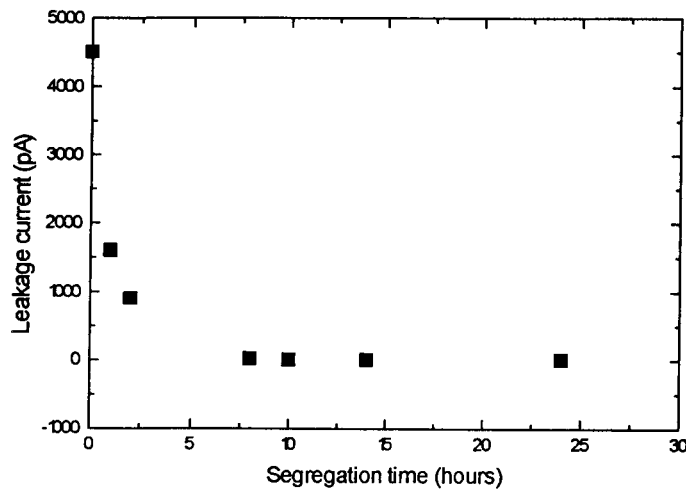


Figure 4. Leakage current versus the segregation annealing time.

#### 4. CONCLUSIONS

The importance to control the metal contamination position in the wafer by gettering procedures was demonstrated. Metal precipitation at the  $\text{SiO}_2/\text{Si}$  interface in LOCOS structures can dramatically reduce their insulating properties increasing the interface roughness. When metals are removed from the interface by a gettering procedure, the insulating properties are recovered even if the interface remain quite rough. Gettering can be used as an "in situ" cleaning method directly integrated in the silicon wafer. Heavy metals can be introduced immediately before the oxidation treatment or can be already present in the wafer. For this reason in ultra clean wafer processing the presence of a gettering process improve the cleaning of interface better than only cleaning before oxidation.

#### ACKNOWLEDGMENTS

We knowledge M. Furnari for the technical assistance.

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## Mechanistic Studies of SC-1 Particle Removal and Post Piranha Rinsing\*

P. Resnick<sup>+</sup>, C. Adkins<sup>+</sup>, D. Kittelson<sup>++</sup>, T. Kuehn<sup>++</sup>, R. Gouk<sup>++</sup>,  
Y. Wu<sup>++</sup>, P. Clews<sup>+</sup>, C. Matlock<sup>+</sup>

<sup>+</sup>Sandia National Laboratories, Albuquerque, NM USA 87185

<sup>++</sup>University of Minnesota, Minneapolis, MN USA 55455

### 1.0 INTRODUCTION

SC-1 ( $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ ) and piranha ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) cleans have been used for many years to remove particulate and organic contamination. Although the SC-1 clean, often used with applied megasonic power, is known to be highly effective for particle removal [1,2], the removal mechanism remains unclear. For the removal of heavy organic contamination, the piranha cleaning chemistry is an effective process; however, post-piranha residue adheres tenaciously to the wafer surface, causing a particle growth phenomenon [3]. A series of experiments have been performed to help understand the interaction of these processes with silicon surfaces.

### 2.0 EXPERIMENTAL

#### 2.1 SC-1/Megasonic

Two surface sensitive techniques, open circuit potential (OCP) and optical haze measurements, were used to study the etching/passivation of silicon surfaces with SC-1 chemistry under various process conditions. All wafers were pre-cleaned in a dilute SC-1 chemistry, giving rise to a hydrophilic surface. OCP measurements were performed in a single-wafer electrochemical cell, using a saturated calomel reference electrode. Detailed OCP data have been presented elsewhere [4]. Haze measurements were performed using the haze channel on a Tencor Surfscan<sup>®</sup> 6200. To evaluate the role of surface activity on cleaning performance, these results were then compared to silicon nitride particle removal efficacy ( $> 0.15 \mu\text{m}$   $\text{Si}_3\text{N}_4$  deposited from an aerosol). In addition to studying the effects of SC-1 chemistries, computational and experimental modeling is also being performed to understand the physical component of particle removal in acoustically assisted cleaning. The effect of the acoustic pressure field, as well as the effect of cavitation intensity and distribution are being studied.

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## 2.2 Sulfuric Peroxide (Piranha) Rinsing

To evaluate the amount of sulfur remaining on a wafer after a piranha clean, 150 mm n-type bare silicon and thermally oxidized wafers were processed through either 5:1 or 10:1 ( $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$ ) piranha at 95°C for 10 minutes. Following various modifications to the rinse process, time-of-flight secondary ion mass spectrometry (TOF-SIMS) and total reflection X-ray fluorescence spectrometry (TXRF) were used to measure residual sulfur. Light point defects (LPDs) were also measured as a function of time after wafers were rinsed and dried, as post piranha processed wafers have been shown to exhibit a particle growth phenomenon. The data from these analytical techniques were used to assess the efficacy of various rinsing techniques.

## 3.0 RESULTS AND DISCUSSION

### 3.1 SC-1/Megasonic

In the study of SC-1 chemistries, no correlation between the cleaning efficacy and either the measured open circuit potential or the haze delta was evident when dilute SC-1 chemistries were used. LPD removal efficiency, based on the removal of  $\text{Si}_3\text{N}_4$  particles is shown in Figure 1. These experiments were performed under conditions known to effect silicon etching (both n and p-type Si<100>, with and without illumination). The box plot of Figure 2 shows haze delta data for the same process conditions. Haze values can be related to surface roughness [5], which is caused by preferential Si{100} etching in basic media. It can be seen that conditions conducive to increased haze, and thus etching, do not correlate with increased particle removal efficiencies (see Figure 1). When sufficiently dilute aqueous ammonia solutions with no  $\text{H}_2\text{O}_2$  are used on hydrophilic wafers, alkaline attack and roughening of the silicon is minimal, yet effective particle removal is still

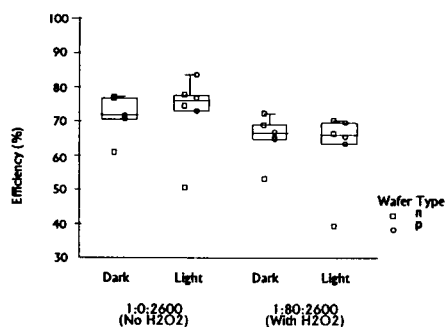


Figure 1. LPD removal as a function of wafer type and lighting conditions.

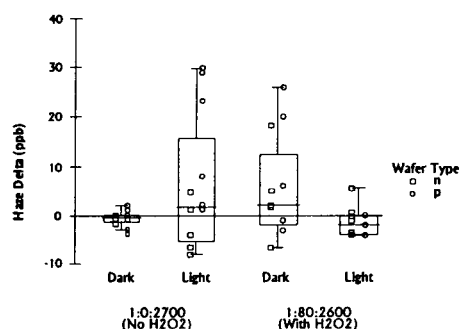


Figure 2. Delta haze as a function of wafer type and lighting conditions.

obtained. A measurable increase in haze was noted when hydrophobic bare silicon wafers were processed through the dilute aqueous ammonia solutions. It appears

that the thin chemical oxide resulting from an SC-1 preclean step is sufficient to suppress alkaline etching of the silicon surface in very dilute aqueous ammonia. These data suggest that etching of silicon is not requisite to an effective clean.

In order to understand the physical mechanism of megasonics in particle removal, a predictive model of the acoustic pressure field in the cleaning bath is required. Using a ray-trace method, calculated one-dimensional pressure fields were compared to measured values, as shown in Figure 3. In order to obtain pressure measurements free of reflections, the experimental transducer was operated in pulsed mode using a pulse duration of about 50 microseconds. This modeling method, which shows good agreement with measured values, can be used to predict pressure fields in various bath geometries, and ultimately may be used to optimize cleaning bath geometries in future generation tools.

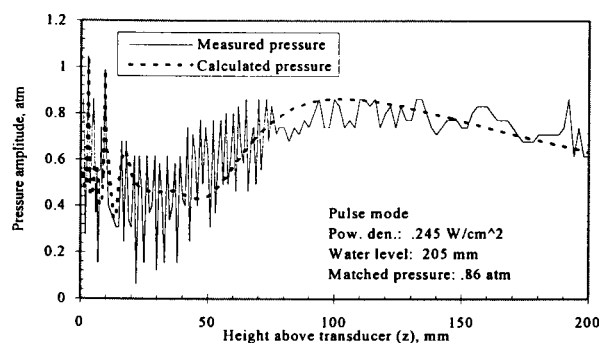


Figure 3. Predicted and measured pressure field. Pressure distribution along center axis above transducer midway between two wafers spaced 2 cm apart.

### 3.2 Sulfuric Peroxide (Piranha) Rinsing

Following a piranha clean, the residual sulfur contamination left on the wafer after rinsing adheres tenaciously to the silicon surface. This residual sulfur generates particle contamination with time when the wafers are exposed to cleanroom air. Indeed, the extent of the particle growth is indicative of the level of residual sulfur contamination on the wafer surface [6]. TOF-SIMS negative and positive ion image maps of the piranha-cleaned wafers shown in Figure 4 indicate that the particles are comprised of  $\text{SO}_x^-$  and  $\text{NH}_4^+$ . The addition of small amounts of ammonium hydroxide (*e.g.*, sufficient to achieve  $\text{pH} = 10$ ) to the post-piranha rinse bath has been found to be effective in reducing the surface concentration of sulfur, as well as mitigating the piranha induced particle growth. Sulfur concentration, measured by total reflectance x-ray fluorescence (TXRF), is shown in Figure 5 for both basic rinsing and rinsing in deionized water. The addition of ammonium salts to the rinse bath did not reduce the surface sulfur concentration, while the addition of other bases such as potassium hydroxide were effective. The hydroxyl ion is clearly the active species with respect to sulfur removal.

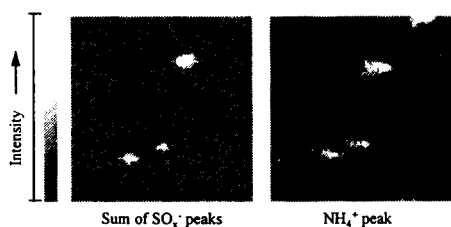


Figure 4. TOF-SIMS negative (left) and positive (right) ion maps.

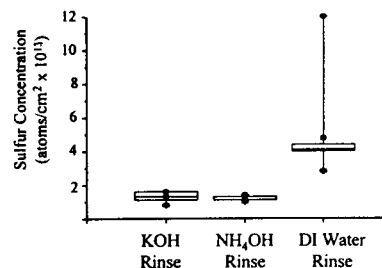


Figure 5. Surface sulfur concentration following basic and DI water rinsing.

#### 4.0 CONCLUSIONS

Surface sensitive techniques were used to study SC-1 chemical effects on silicon wafers. Particle removal efficacy does not necessarily depend on surface modification phenomena such as etching or passivation. To study the physical effects of megasonic cleaning, computational and experimental models are being developed. Such models will allow bath manufacturers to calculate cleaning performance based on first principles.

Sulfur residue remains on silicon wafer surfaces following a piranha clean and rinse sequence. This residue forms particulate matter when the wafers are stored in a cleanroom environment. TOF-SIMS was used to identify these particles as ammonium sulfate. The use of an alkaline rinse (*e.g.*, pH = 10) following piranha is effective in reducing the residual sulfur concentration, and thereby suppressing the time dependent particle formation.

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## Comparison of RCA and IMEC Clean (HF last) type cleaning sequences in full production environment

K. Wolke, M. Schenkl, P. Silvestre (STEAG MicroTech Pliezhausen, Germany)  
E. Bellandi, M. Alessandri (SGS Thomson)  
Ingrid Cornelissen, Marc Meuris (IMEC, Leuven, Belgium)

### ABSTRACT

The RCA sequence which is commonly used for critical cleaning steps in FEOL processing is compared to the alternative TWIN-IMEC type sequence, using optimized HF last for removal of contamination on the wafer. Experiments characterizing the single process steps as well as direct comparisons of cleaning capability were carried out on split lot basis at three different S/C manufacturing locations. Surface properties, particle and metallic removal efficiency are discussed, showing that the TWIN-IMEC type cleaning sequence shows absolutely equivalent results for cleaning and even better performance on surface roughness, while cost of ownership is reduced up to a factor of two compared to RCA processing.

### 1. INTRODUCTION

For critical cleaning steps in FEOL processing most S/C manufacturers rely on the use of ammonia - peroxide and HCl - peroxide mixtures commonly known as RCA Cleaning. This concept [1], which was published first in 1970 has been continuously improved with the introduction of diluted chemicals and megasonics and is considered the most effective cleaning for nearly all front end wafer applications. However this process is not fully satisfactory since the tremendous cost of chemicals and water and the substrate roughening by  $\text{NH}_4\text{OH}$  could not be successfully eliminated. As a high efficient, low cost alternative HF last processes like the IMEC Clean<sup>TM</sup> have been proposed [2]. Whereas laboratory investigations have shown that the IMEC clean concept using Marangoni drying [3,4] is absolutely equivalent to the RCA sequence with regard to cleanliness and particle or metallic removal, this paper will focus on a comparison of both processes in full production environment at CMOS manufacturers using  $0.5\ \mu$  technology. Experiments were done to determine the characteristics of the single process steps as well as the performance of the the whole sequence with respect to cleaning and intrinsic particle performance. In order to set up a production data base split lots were performed at a DRAM as well as Flash EEPROM manufacturer in which both sequences were compared on  $0.5\ \mu$  structures in pre-oxidation steps.

### 2. EXPERIMENTAL SETUP

The evaluation of both process sequences at the DRAM manufacturer was performed on two separate fully automated wet benches (STEAG AWP Gen.III), one consisting of the typical modules for the RCA sequence (SOM, HF, SC1, SC2, MgDry), and the other one designed for the IMEC type sequence with SOM - HF/HCl - QDR/HCl/O<sub>3</sub> - MgDry baths. At the Flash EEPROM manufacturing facility a hybrid tool (STEAG AWP Gen.

III) was used in order to reduce the differences in processing to the sequence only. The hybrid module sequence was

SOM - QDR - HF- OFR - SC1 - QDR - SC2 - QDR - HF/HCL - QDR/HCl/O<sub>3</sub> - MgDry.

For additional data verification some experiments have been repeated on a similar hybrid tool at IMEC, Leuven. All tools are operating 6 inch wafers and are equipped with VERTEQ Sunburst TURBO megasonics in the SC1 module. Standard 6 inch particle monitors were used for characterization of the single process steps, the testing of particle performance on clean wafers, as well as the particle removal efficiency with Si<sub>3</sub>N<sub>4</sub> particles with particle sizes of 0.16  $\mu$  and larger with a Tencor 6X00. For testing the metallic contamination after both processes TXRF was applied on virgin monitor wafers. For oxide thickness measurements an auto-ellipsometer was used.

To characterize the impact of the cleaning processes on current S/C technologies splitlots were run on 4 Mbit DRAM wafers run at pre gate and pre poly clean giving both parametric and functional yield data, as well as split lots on 0.5  $\mu$  Flash EEPROM wafers prior to tunnel and LV oxidation for defectivity and QBD and EBD data.

### 3. PROCESS CHARACTERIZATION

#### 3.1. Oxidation step

In order to characterize the first process step (which is common for RCA and IMEC<sup>TM</sup> Clean) comparative experiments were performed to characterize the sulphuric ozone mixture at different temperatures and an ambient temp. ozonated water process. A summary is shown in Table 1, indicating that the oxidation is achieved within less than three minutes of process time for both the hot sulphuric ozone mixture as well as the ambient ozonated water process. Particle performance on hydrophilic as well as hydrophobic wafers incoming is comparable if no bubbles occur in the bath itself. Tests of organic removal efficiency on medium doped resist (1.0  $\mu$ ) and HMDS layers showed quicker removal with SOM, however within a five minute process time the organic was also removed with ozonated water.

Table 1: Characteristics of oxidation step

| Chemistry                  | Oxidation speed | surface layer thickness | particle perf. (hydrophilic) | particle perf. hydrophobic) | organic removal time |
|----------------------------|-----------------|-------------------------|------------------------------|-----------------------------|----------------------|
| SOM 80 deg                 | 1 min           | 1.38 nm                 | <5 add. (.2 $\mu$ )          | < 10 adders                 | < 1 min              |
| SOM 110 deg                | 30 sec          | 1.37 nm                 | <5 add. (.2 $\mu$ )          | < 5 adders                  | < 1 min              |
| Ozone / DiH <sub>2</sub> O | 3 min           | 1.31 nm                 | neutral                      | < 10 adders                 | < 5 min              |
| SC1 (10:1:1)               | 5 min           | 1.24 nm                 | neutral                      | neutral                     | > 10 min             |

#### 3.2. HF step

In order to accomplish the necessary accuracy in etching especially for very thin oxides the bath to bath repeatability, within wafer and batch to batch uniformity and time

dependency has been evaluated for HF and HF/HCl mixtures. For this measurement a HORIBA HF monitoring system with an intrinsic accuracy of 0.005 % has been used. The results show repeatability of etch rates and concentration from bath to bath within less than 1 % for a 10 nm etch, which is slightly (appr. 10%) decreased when 0.1 mol/l HCl is added. Batch and wafer uniformity improved with the use of HCl by a factor of 1.8 to 1.8 % ( $3\sigma$ , within wafer) and 0.9 % ( $3\sigma$ , within batch) respectively. Nonuniformity becomes worse again with higher concentration of HCl added, which is correlating to the decrease of etch rate. For the HF concentration a timely drop of appr. 1,5 % per hour asymptotically slowing down was found indicating some influence of dissolved gases to the mixture. This was found to be independent of the adding of HCl.

### 3.3. HCl rinse with and without ozone

Although metallic contamination is already removed by the the HF cleaning step the removal efficiency was evaluated for HF/HCl mixtures as well as the use of HCl in the rinse after HF in comparison to the SC1 /SC2 sequence using Elymat diffusion lengths measurements in Fe contaminated Di water. The Elymat results (see table 2) revealed diffusion lengths of 450  $\mu\text{m}$  for the RCA sequence, whereas with HF only 1100  $\mu\text{m}$ , and HF with HCl/O<sub>3</sub> rinse even 1300  $\mu\text{m}$  could be achieved. Metallic removal thus is much more efficient with the IMEC clean sequence.

Table 2: Elymat results for metallic removal (Diff. lengths in  $\mu\text{m}$ )

| incoming | RCA | SC2 only | HF only | HF / HCl | O3 rinse | O3/HCl rinse |
|----------|-----|----------|---------|----------|----------|--------------|
| 350      | 450 | 700      | 1100    | 1250     | 700      | 1300         |

In order to obtain data on the hydrophobic (without adding ozone into FR) and hydrophilic path (with ozone) in the IMEC-TWIN Clean particle performance was evaluated for different process recipes and best results have been seen with simultaneously using of ozone and HCl with data equivalent to standard rinsing. However even without the use of ozone a particle neutral behaviour was found after HF processing, indicating that both process paths of the TWIN Clean are capable for critical cleaning.

## 4. SPLIT LOT RESULTS

In order to obtain the best process for the IMEC Clean particle performance and metal contamination testing was done prior to running the production splitlots for various recipes with and without HCl addition to the HF as well as with and without ozone injection into the final rinse. For comparison the standard production RCA process of the manufacturing sites was also tested. The results are summarized in fig. 1 and 2. For particle performance the hydrophobic path (i.e. without O<sub>3</sub> spiking in the final rinse) show slightly higher particle addition than the RCA process, but still excellent performance, whereas no difference was found for hydrophilic wafers. Particle removal efficiency tested with Si<sub>3</sub>N<sub>4</sub> contaminated wafers showed different results for the course of experiments done at the different production sites. While the RCA was performing at 98 % particle removal compared to 96 % for the IMEC sequence at on a contamination level of appr. 800 part., the results of the other manufacturer showed better results for the HF last process (99 % vs. 95 % RCA for appr. 1500 particles). On this high level of

performance and with the existing data base above differences are not significant in either direction, thus both sequence have to be considered equivalent.

Fig.1: Particle performance of different cleaning sequences

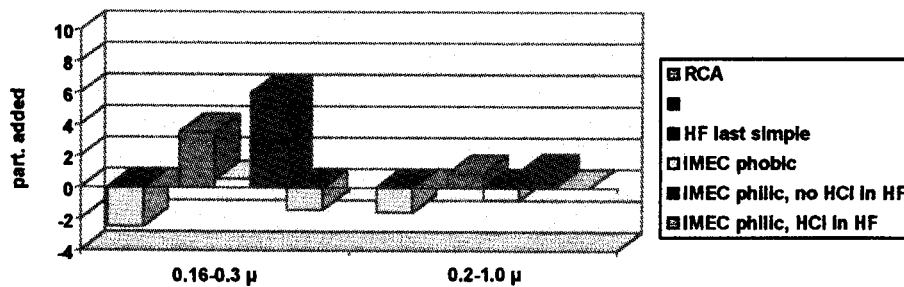
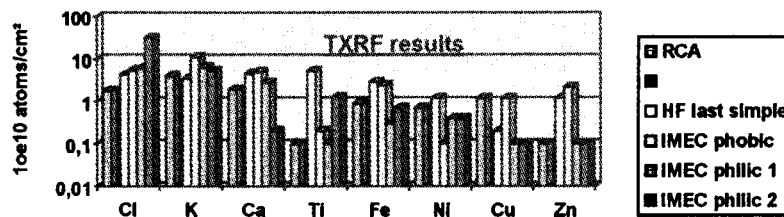


Fig 2: Metal contamination results of TXRF measurement( Det. limit 1e09/cm<sup>2</sup>)

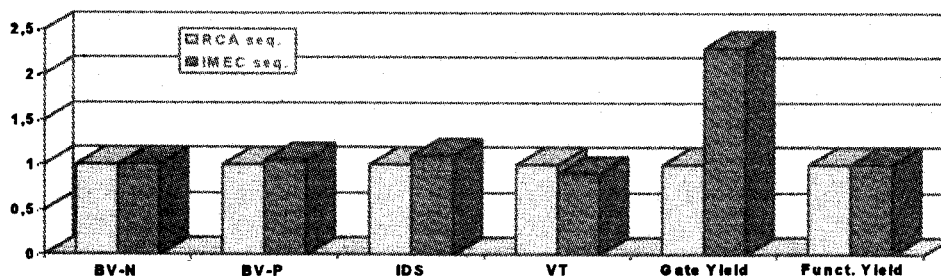


With respect to removal of most metallics the IMEC clean showed significantly better performance than the RCA sequence, with no difference for the two paths of the Twin-IMEC clean. Hydrophobic and hydrophilic wafers behave the same within the statistics. While the native oxide regrowth behaviour was equivalent with both processes, the GOI data were worse with the RCA sequence due to the substrate attacking characteristics of the SC1 solution.

Excellent results for electrical data on the production splitlots of the 4 Mbit DRAMs for both types of cleaning were found. The results for Breakdown Voltages,  $I_{ds}$ ,  $V_{t,s}$  and also the functional yield were comparable within the statistics of the experiments. However a big difference was found on Gate Yield between the HF last process compared to the RCA, indicating the advantage of the ammonia free processing for the gate dielectric. A summary of the normalized data is shown in Fig. 3.

The impact of the cleaning sequence on Flash EEPROM technology was evaluated with several splitlots at the cleaning prior to tunnel oxidation. The RCA sequence was compared to the hydrophobic and hydrophilic path of the TWIN-IMEC clean. Results of defectivity and QBD at tunnel oxidation on various size ( $9.8e-5$  to  $0.7$  cm<sup>2</sup>) capacitor and transistor arrays were obtained. No significant difference for either split part was found, however the IMEC clean with ozone in the final rinse turned out to have the smallest number of intrinsic defects.

Fig 3: Comparison of split lot data (4 Mbit DRAM, normalized to RCA sequence)



Another split experiment was performed at LV oxidation, where the use of HF is critical due to possible recess of open bird's beak structures. For this step a modified RCA clean without the HF step is standard. Using dilute HF mixtures (1:120) for the IMEC Clean sequence the QBD and EBD data did not differ for the split parts, although on one of the test structures the intrinsic defectivity was found to be slightly higher for the wafers that had been cleaned with HF. The experiments have shown that the higher sensitivity of HF last cleaning to oxide surfaces could be compensated by tight HF control.

#### 4. CONCLUSIONS

The experiments have shown that the process results of both types of cleaning were found to be equivalent, both for monitor and production wafer experiments. Slightly worse particle performance of the HF last sequence without Ozone spiking in final rinse even with Marangoni drying was compensated by the better surface conditions and in higher gate yield performance in the IMEC sequence due to the lack of SC1. Even though final optimizations especially on the oxidation step and the use of ozone after the HF treatment have not been finished, the results indicate that with regard to process performance the commonly used RCA cleaning has no advantage in state of the art S/C manufacturing. Thus the significant benefits in cost of ownership (smaller footprint, lower cost for equipment, chemicals and water) and environmental compatability for the TWIN-IMEC clean concept will gate the decision for the best process in critical cleaning.

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## Wet Metal Strip After $\text{TiSi}_2$ Formation

Sean O'Brien, Ivan Goldwasser, & Doug Prinslow

Semiconductor Process and Device Center

Texas Instruments, Dallas TX 75265

### Abstract

The process window for wet etching of TiN after self-aligned  $\text{TiSi}_2$  formation has been investigated leading to a more selective process for the wet strip. This new chemistry, named "Low pH SC1" ( $55^\circ\text{C}$  1:200:600  $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ), has a much lower pH (9.0) than the traditional SC1 chemistry (10.4). A process model has been generated with a quadratic experimental design on concentration and temperature. The DOE results show that the  $\text{H}_2\text{O}_2$  determines the TiN etchrate, and the  $\text{NH}_4\text{OH}$  determines the  $\text{TiSi}_2$  etchrate. This data shows that etching of TiN is electrochemical and etching of  $\text{TiSi}_2$  is not. This reaction chemistry has a sharp temperature dependence, the etchrates increase an order of magnitude from  $25$  to  $70^\circ\text{C}$ . Above  $0.1$  moles/liter the ammonia does not change the TiN etch rate (in 30%  $\text{H}_2\text{O}_2$ ). Ti reacts with  $\text{H}_2\text{O}_2$  to form an orange peroxy-titanate coordination complex, this prevents decomposition of the peroxide.

### TiN and $\text{TiSi}_2$ Wet Metal Etching

The selective wet chemical strip of unreacted Ti/TiN after self-aligned silicide formation (salicide) must remove all bulk metal which shorts out adjacent circuitry, it must remove  $\text{TiSi}_2$  filaments which degrade device performance, yet it must have very high selectivity to the  $\text{TiSi}_2$  which was formed on the polysilicon lines and substrate silicon. This work describes the testing required to define the process window of the wet metal strip for titanium silicide processing, independent of device technology.

The primary etchant used for the strip is SC1. In any study of electrochemical etching it is important to understand the pH as a function of concentration. Even though  $\text{H}_2\text{O}_2$  is an extremely weak acid ( $K_a = 2.7 \times 10^{-12}$ ) as compared with  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) when the ratio of  $\text{H}_2\text{O}_2/\text{NH}_3$  is high the pH strongly depends on  $[\text{H}_2\text{O}_2]$ . Aqueous  $\text{NH}_3$  and  $\text{NH}_4\text{OH}$  are exactly the same, the dissociation into  $\text{NH}_4^+$  and  $\text{OH}^-$  results from an ammonia molecule surrounded by several solvent  $\text{H}_2\text{O}$  molecules. At pH 9 there is 99%  $\text{NH}_4\text{OH}$  dissociation, at 10.4 only 1% is dissociated. Figure 1 shows the theoretical calculation of pH in the relevant ranges of SC1 concentration. The regions around 1:1:5 and 1:200:600 are highlighted with circles. A key point is that this graph only applies to  $25^\circ\text{C}$  solutions. The dissociation constants for ammonia, peroxide, and water increase significantly with higher temperature. This calculation does not take into account solvation by peroxide at large  $[\text{H}_2\text{O}_2]$ .  $K_a$ ,  $K_b$ , and  $K_w$  are only known for solvation by water, there is no reason they would be the same for the  $\text{H}_2\text{O}_2$  solvent cage.

For this study 150mm wafers were used with non-recirculated heated quartz baths. 30% by weight  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$  were manually poured, with a volumetric accuracy of  $\pm 5\%$ . Metal films were sputtered onto either bare Si or  $\text{SiO}_2$ , followed by a  $720^\circ\text{C}$  RTP formation. Sheet resistance was measured by 4-point probe, and the bulk resistivity was used to calculate the metal film thickness using  $140 \mu\text{ohm-cm}$  for TiN and 60 for  $\text{TiSi}_2$ .

Various salicide references in the literature refer to a heated SC1 bath, but none of them have ever shown the dependence of etch rates or selectivity on any process parameter. The temperature dependence of this reaction is shown in Figure 2. Two data points per temperature were run. A plot of  $\log(\text{etchrate})$  versus  $1/T$  gives a good fit which gives an activation energy of  $0.51$  (TiN) and  $0.48$  eV ( $\text{TiSi}_2$ ). The similarity of the values is not proof of identical chemical reactions. In fact, considering the remainder of this paper, the similarity is surprising.

Calculation of the etchrate of  $\text{TiSi}_2$  is complicated by the presence of a thin layer of TiN and unreacted Ti on the surface of the film. The thickness and resistivity of this film are not well characterized, and only by analyzing the change in sheet resistance as a function of immersion time in the strip chemistry can the true  $\text{TiSi}_2$  thickness be determined. As seen in Figure 3, the thickness drops quickly (sheet resistance rises quickly) upon immersion, then a more linear time dependence develops. Calculation of the  $\text{TiSi}_2$  etchrate requires this type of analysis on a case by case basis since the etchrate of the surface layer will not necessarily have the same process window as the  $\text{TiSi}_2$ .

Assuming for a moment that there are no filaments to be etched, the process goal is to strip TiN with infinite selectivity to TiSi<sub>2</sub>. By varying the temperature and concentration of the solution, and the ratio of H<sub>2</sub>O<sub>2</sub> to NH<sub>4</sub>OH it is possible to vary the selectivity by a wide margin as seen in Table 1.

**Table I** TiN/TiSi<sub>2</sub> Selectivity and Etch rates versus SC1 Concentration

| SC1 Process Ratio<br>NH <sub>4</sub> OH:H <sub>2</sub> O <sub>2</sub> :H <sub>2</sub> O | [NH <sub>3</sub> ]<br>(mol/l) | [H <sub>2</sub> O <sub>2</sub> ]<br>(mol/l) | Temp<br>(°C) | TiN ER<br>(Å/min) | TiSi <sub>2</sub> ER<br>(Å/min) | Selectivity |
|-----------------------------------------------------------------------------------------|-------------------------------|---------------------------------------------|--------------|-------------------|---------------------------------|-------------|
| 1:1:6                                                                                   | 1.023                         | 1.264                                       | 27           | 57                | 11.8                            | 4.8         |
| 1:200:600                                                                               | 0.01021                       | 2.522                                       | 27           | 35                | 1.0                             | 35          |
| 1:200:600                                                                               | 0.01021                       | 2.522                                       | 55           | 180               | 2.5                             | 72          |
| 1:200:0                                                                                 | 0.0407                        | 10.05                                       | 40           | 67                | 1.0                             | 67          |
| 1:200:0                                                                                 | 0.0407                        | 10.05                                       | 55           | 170               | 1.3                             | 131         |

The concentration dependence of the TiN etch rate is shown in Figures 4 & 5. It is important to use true chemical concentration in moles/liter instead of volumetric ratios. In Fig. 4 the data over an extremely large range is shown at 55 °C. Both peroxide and ammonia strongly impact the etch rate of TiN. The data at the far left hand side is actually zero added NH<sub>3</sub>. While the etch rate curves are not exactly linear with log[NH<sub>3</sub>] they certainly do not increase 4 orders of magnitude. This strongly indicates that etching of TiN is through electrochemical oxidation-reduction reactions. This does not in anyway require the presence of oxygen atoms, the oxidation of zero-valent Ti metal to Ti cations is probably the rate limiting step in this process.

The curve for pure (30w%) H<sub>2</sub>O<sub>2</sub> is interesting, the etch rate hits a maximum near 0.1 M NH<sub>3</sub>. Although not shown in Fig. 4, the etch rate is constant with any subsequent addition of NH<sub>3</sub>. This test needs to be carefully studied since [H<sub>2</sub>O<sub>2</sub>] is changing with the large ammonia addition. Only by use of H<sub>2</sub>O<sub>2</sub> above 30% can the final mixture have high [NH<sub>3</sub>] and still be 30% H<sub>2</sub>O<sub>2</sub>. It is possible that the peroxide is dropping just enough to compensate the increased ammonia. But more likely is that at high concentrations the solvent H<sub>2</sub>O<sub>2</sub> molecules interfere with traditional aqueous chemistry by perturbing the acid-base equilibria. This behavior is not seen for more dilute peroxide solutions as shown in Fig 5.

In Figure 5 the contour plot for the TiN etch rate as a function of [H<sub>2</sub>O<sub>2</sub>] and [NH<sub>3</sub>] is given. Similar to results in Fig. 4 both chemicals significantly impact the etch rate. However, in Figure 6 it is obvious that the TiSi<sub>2</sub> etch rate does not depend on [H<sub>2</sub>O<sub>2</sub>] in the range of 1-3.5 moles/liter. This strongly indicates that the ammonia moiety is directly involved as a reactant in etching TiSi<sub>2</sub>. At 0.01 M [NH<sub>3</sub>] the concentration of [OH<sup>-</sup>] doubles as [H<sub>2</sub>O<sub>2</sub>] decreases from 3 to 1 (see Fig. 1). The TiN/TiSi<sub>2</sub> selectivity contour plot is shown in Fig. 7.

It is extremely interesting to note that, as seen in Fig. 8 for undiluted H<sub>2</sub>O<sub>2</sub>, the etch rate of TiN shows no change with time even after 5 hours at 55 °C and massive levels of Ti. This is accompanied by the change of color of the peroxide to a deep yellow/orange. The reaction between Ti metal and H<sub>2</sub>O<sub>2</sub> is well known, it has been used as a standard titration method for most of the 20th century. What is interesting is the reason for the yellow color, a coordination complex involving the peroxide anion O<sub>2</sub><sup>2-</sup> and Ti cations readily forms. This is definitely not TiO<sub>2</sub> despite the similar chemical formula. TiO<sub>2</sub> does not involve a stable peroxide anion.

Heated SC1 solutions degrade with time, due to the decomposition of H<sub>2</sub>O<sub>2</sub> and evaporation of NH<sub>3</sub>. Using a fixed process time for all lots the loss of concentration of SC1 with bath age will change the etch process. This is an excellent application for either automated process control (APC) or insitu concentration control (ISCC). Using an insitu sensor for H<sub>2</sub>O<sub>2</sub> and NH<sub>4</sub>OH the control software will determine a different process time for each individual lot in an APC scenario. Alternatively the control software can spike in precise amounts of concentrated chemical to maintain the target concentrations.

## Conclusions

The process window for the TiN wet etch process following TiSi<sub>2</sub> formation has been characterized. The "low pH SC1" process with a chemical ratio of 1:200:600 (NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O) at 55°C has been characterized for TiN/TiSi<sub>2</sub> selectivity. The 99% reduction in NH<sub>4</sub>OH concentration and elevated temperature results in a much faster process, thus reducing cycletime and increasing equipment throughput. The etching of



TiSi<sub>2</sub> appears to be a true chemical reaction involving the ammonium species, while the etching of TiN is an electrochemical oxidation-reduction.

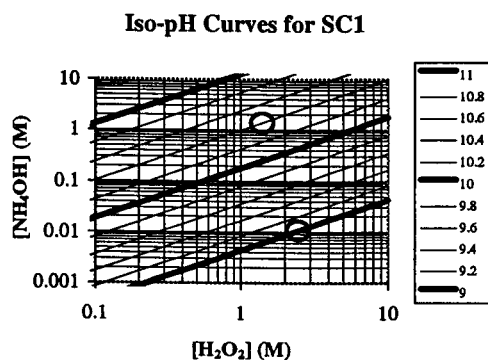


Figure 1 The pH of SC1 as a function of H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub> concentration in moles/liter. The acidity of H<sub>2</sub>O<sub>2</sub> is important for very low levels of NH<sub>3</sub>. The 1:1:5 and 1:200:600 regions are shown with circles.

#### TiSi<sub>2</sub> Etch Rate in 1:1:5 SC1

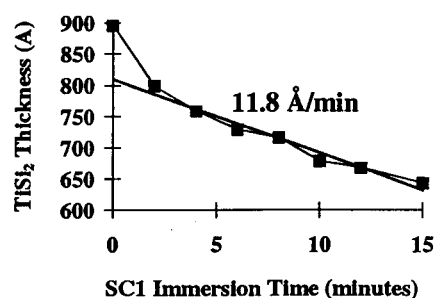


Figure 3 Time dependence of TiSi<sub>2</sub> etch in 27 °C 1:1:5 SC1 strip chemistry. The initial fast decline is due to a thin layer of unreacted metal on top of the silicide.

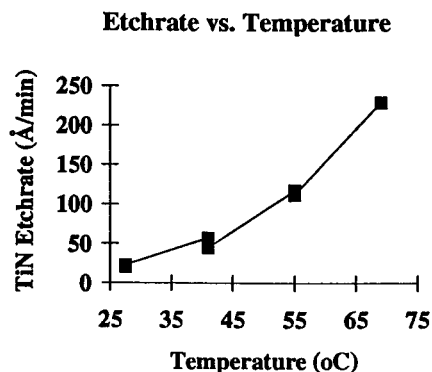


Figure 2 The temperature dependence of the TiN etchrate for the low-pH SC1 strip chemistry (1:200:600). The data (2 points per temp.) are fit to an exponential with an activation energy of 0.51 eV. A similar study gives 0.48 eV for TiSi<sub>2</sub>.

#### TiN ER vs. NH<sub>3</sub> Concentration 55 °C

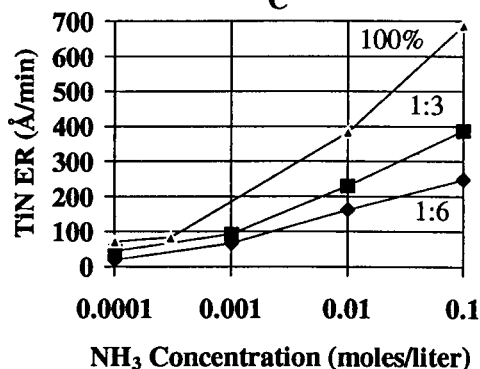


Figure 4 TiN etchrate as a function of H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O and NH<sub>4</sub>OH concentration at 55 °C. The ammonia concentration at 0.0001 is really zero. Not shown is that in 30% H<sub>2</sub>O<sub>2</sub> for [NH<sub>3</sub>] > 0.1 M the etch rate is constant.

$\text{H}_2\text{O}_2$  was added to the bath manually as needed to keep the pH of the solution constant. The actual solution concentrations were established using an ion-selective electrode for the  $[\text{NH}_4\text{OH}]$  and permanganate titrations for the  $[\text{H}_2\text{O}_2]$ . Trace chemical reactions between the  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  were monitored using ion-chromatography.

### 3. EQUILIBRIUM CALCULATIONS

$\text{NH}_4\text{OH}$  is a weak base. Whereas, a strong base such as  $\text{KOH}$  would be 100% dissociated into  $\text{K}^+$  and  $\text{OH}^-$  in aqueous solutions,  $\text{NH}_4\text{OH}$  is only partially dissociated. The amount of dissociation is governed by chemical equilibrium and is related to the concentration of reactants by the law of mass-action (depicted in equation (1) for  $\text{NH}_4\text{OH}$ ).

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = k_1 \sim 10^{-5} \quad (1)$$

The bracketed ( $[*]$ ) quantities represent the concentration of the species indicated in moles/liter and  $k_1$  is the dissociation constant of the reaction.  $\text{H}_2\text{O}_2$  is a weak acid whose equilibrium reaction is depicted in equation (2).

$$\frac{[\text{H}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]} = k_2 \sim 10^{-12} \quad (2)$$

At this point, all one needs to understand for the mixtures of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  is that all acid/base reactions are mediated by the dissociation of water (equation (3)).

$$[\text{H}^+][\text{OH}^-] = k_3 \sim 10^{-14} \quad (3)$$

Combining equation (2) with equation (3) and rewriting equation (1) gives equations (4) and (5), respectively.

$$[\text{H}_2\text{O}_2] = \frac{k_3}{k_2} \frac{[\text{HO}_2^-]}{[\text{OH}^-]} \quad (4)$$

$$[\text{NH}_4\text{OH}] = \frac{1}{k_1} [\text{OH}^-][\text{NH}_4^+] \quad (5)$$

Evaluation of equations (4) and (5) for commonly used  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  concentrations shows that the negative ion concentration in these solutions are dominated by  $\text{HO}_2^-$ . Since these solutions are basic (low  $\text{H}^+$  concentration), charge conservation demands that the concentrations of  $\text{HO}_2^-$  and  $\text{NH}_4^+$  be approximately equal. The  $\text{HO}_2^-$  and  $\text{NH}_4^+$  ions together, therefore, must dominate the conductivity

of these solutions. Thus, the conductivity ( $\sigma$ ) of the solution is proportional to  $[\text{HO}_2^-]$  which is equal to  $[\text{NH}_4^+]$ . Since  $[\text{OH}^-]$  can be determined from the solution pH,  $\sigma$  and the pH uniquely determine  $[\text{H}_2\text{O}_2]$  and  $[\text{NH}_4\text{OH}]$  from equations (4) and (5), respectively.

#### 4. CONTROL SCHEME

Substituting  $[\text{HO}_2^-]$  for  $[\text{NH}_4^+]$  in equation (5), new expressions can be written for the conductivity and pH (shown in equations (6) and (7)).

$$\sigma \leftrightarrow [\text{HO}_2^-] = \sqrt{\frac{k_1 k_2}{k_3} [\text{H}_2\text{O}_2] [\text{NH}_4\text{OH}]} \quad (6)$$

$$\text{pH} \leftrightarrow [\text{OH}^-] = \sqrt{\frac{k_1 k_3}{k_2} \frac{[\text{NH}_4\text{OH}]}{[\text{H}_2\text{O}_2]}} \quad (7)$$

Note that  $\sigma$  varies as the square-root of the product of the  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{OH}$  concentrations. The result of plotting  $\sigma$  vs.  $\sqrt{[\text{NH}_4\text{OH}]}$  at fixed  $[\text{H}_2\text{O}_2]$  is shown in Fig. 1.

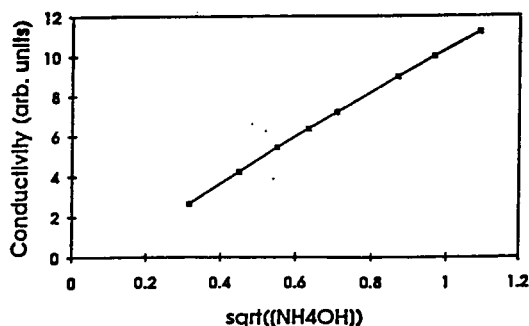


Fig. 1 SC1 solution conductivity ( $\sigma$ ) vs. the square-root of the number of liters of  $\text{NH}_4\text{OH}$  added at fixed  $[\text{H}_2\text{O}_2]$  (4 L  $\text{H}_2\text{O}_2$ , 32 L total).

The observed linear relationship gives one confidence that a proper understanding of the chemistry has been obtained. The  $[\text{OH}^-]$ , on the other hand, varies as the square-root of the ratio of the  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  concentrations. The control scheme chosen for this study is described in the following.  $\sigma$  is used to control the addition of ammonia. Thus, when  $\sigma$  goes low, ammonia is added. The pH is used to control  $[\text{H}_2\text{O}_2]$ . As the hydrogen-peroxide concentration goes low, the pH goes high and peroxide must be added to the solution to bring the pH down. Using the control scheme described above SC1 concentration control is possible over extended periods of time. Data taken over an 8 hr period is shown in Fig. 2.

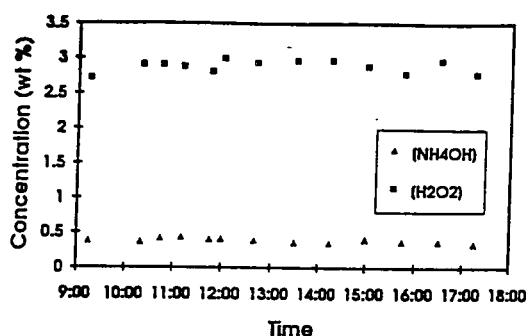


Fig. 2  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{OH}$  concentrations for an SC1 bath at  $70^\circ\text{C}$  as a function of time, determined by titration and using an ion-specific probe, respectively.

Good concentration control is clearly evident during the entire duration of the experiment. It should be noted that wafers were being run continuously through the bench during this experiment in order to simulate a production environment. This data should be contrast to the degradation of a normal SC1 bath. At  $70^\circ$  half the  $\text{NH}_4\text{OH}$  concentration would be lost in approximately 30 min. with the  $\text{H}_2\text{O}_2$  lasting for a few hrs. Reaction byproducts were characterized ( $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) and found to be insignificant in concentration ( $\leq 100$  ppm).

## 5. SUMMARY

Understanding the chemical equilibrium between  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}_2$  has led to the discovery that SC1 solution concentrations can be controlled using a technique which monitors the solution conductivity and pH. Composition control has been achieved for a period as long as 8 hrs.

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## Liquid Phase Processing of Features on a Wafer

Moshe Olim  
FSI International  
322 Lake Hazeltine Drive  
Chaska, MN 55318, USA

### 1 Introduction

The four stages of silicon wafer processing which are relevant to features such as trenches, vias, and topology are: (1) feature wetting, (2) chemical transport into and (3) out of the feature, and (4) feature drying. The investigation is focused on hydrophilic surfaces. The dominating mechanisms and their time scales are established. In addition to that, the drying stage is analyzed under "worst case scenario".

### 2 Wetting

Hydrophilic walls of a feature create a concave air/water interface thus increasing the pressure in the air trapped in the feature. This situation is schematically depicted in Figure 1. The pressurized air dissolves into the

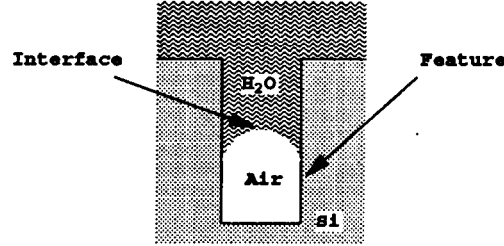


Figure 1: Air and water in a hydrophilic feature.

water allowing the water to fill the feature. While it is accepted (e.g. [1], [2]) that the time required for the water to fill the feature is short, it is instructive to estimate that time interval. Analysis of the process yields an upper limit on the time required to fill the feature (see [3]),  $\Delta t_{fill}$ :

$$\Delta t_{fill} = \frac{k}{D R T} \left( 1 + \frac{P_h}{\Delta P} \right) h^2 \quad (1)$$

where  $k$ ,  $D$ ,  $R$ ,  $T$ , and  $h$  are, respectively, a proportionality constant, vapor/air diffusion coefficient, universal gas constant, temperature, and feature depth,  $P_h$  is the atmospheric pressure, and  $\Delta P$  is the capillary pressure difference across the interface. The value of  $\Delta t_{fill}$  was calculated from Equation (1) for feature widths  $\leq 1.0 \mu m$ , several  $w/h$  ratios, and a contact angle

of  $53^\circ$  (the largest angle given in [4]). The results are shown in Figure 2. For example, a feature  $0.5 \times 4 \mu m^2$  fills up in approximately 1.5 seconds.

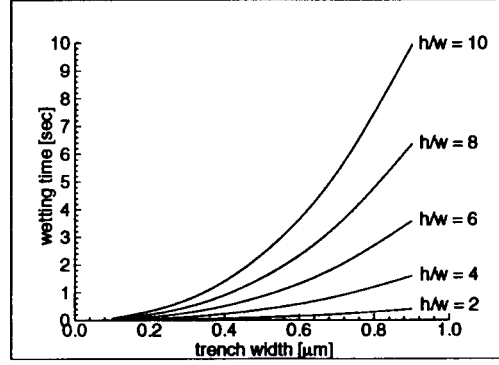


Figure 2: Trench wetting time *vs.* feature width for a contact angle of  $53^\circ$ .

### 3 Chemical transport

A chemical reagent must quickly be transported into the feature, and it is imperative to identify the dominant transport mechanism. This question was addressed in [2] by numerically solving the convection/diffusion equation

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = D \nabla^2 C. \quad (2)$$

To add to the information presented in [2], the transport of a reagent into a  $0.5 \mu m \times 4 \mu m$  feature is investigated for three cases:

1.  $u_h = 0.01 \text{ m/s}$  and  $D = 10^{-9} \text{ m}^2/\text{s}$ ;
2.  $u_h = 1.0 \text{ m/s}$  and  $D = 10^{-9} \text{ m}^2/\text{s}$ , and
3.  $u_h = 0.01 \text{ m/s}$  and  $D = 10^{-10} \text{ m}^2/\text{s}$

where  $u_h$  is the horizontal velocity of the liquid at the top of the feature and  $D$  is the diffusion coefficient. The initial and boundary conditions were those of a feature filled with pure water ( $C = 0$ ) covered with water containing a reagent ( $C = 1$ ):  $C(t, x, z = h) = 1$ ,  $C_z(t, x, z = 0) = 0$ , and  $C(t = 0, x, z < h) = 0$ . The results are presented by displaying the minimum concentration of the reagent (which occurs at the bottom of the feature, i.e.  $z = 0$ ) as a function of time in Figure 3. It clearly indicates that increase of the velocity has a negligible effect on the transport whereas decrease of the diffusivity has a significant impact on same. Since the diffusion coefficient used in cases 1 and 2 is of realistic value, it may be concluded that diffusion is the dominant

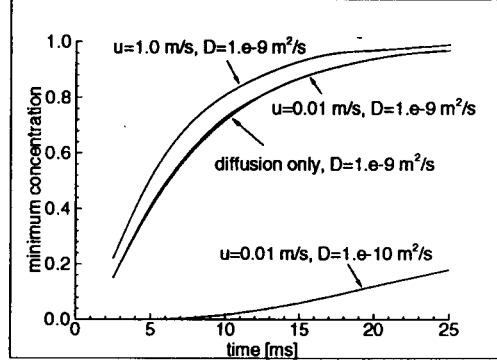


Figure 3: Minimum concentration *vs.* time for the three convection-diffusion cases and for the diffusion only case.

mechanism and that the time required for a chemical to uniformly occupy the feature is of the order of ten milliseconds.

It is instructive to solve the one-dimensional diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (3)$$

with  $D = 10^{-9} \text{ m}^2/\text{s}$  and subject to  $C(t, z = h) = 1$ ,  $C_z(t, z = 0) = 0$ , and  $C(t = 0, z < h) = 0$ . The minimum concentration obtained from this equation is also presented in Figure 3, and it closely matches the data obtained from the two-dimensional simulation of case 1.

The transport of the reagent *out* of the feature is described by the same equations used to model the transport *into* the feature with the appropriate boundary and initial conditions. Equation (3) was therefore solved subject to  $C(t, z = h) = 0$ ,  $C_z(t, z = 0) = 0$ , and  $C(t = 0, z < h) = 1$ . These conditions describe a feature filled with water containing a reagent covered with pure water. The maximum concentration, which occurs at the bottom, is presented as a function of time in Table 1 showing that within 100 *ms* the chemical concentration is reduced by seven orders of magnitude.

| time [ms] | 10     | 20     | 50     | 100    | 200     |
|-----------|--------|--------|--------|--------|---------|
| $C_{max}$ | 2.7e-1 | 5.8e-2 | 5.7e-4 | 2.5e-7 | 5.1e-14 |

Table 1: Maximum concentration *vs.* time.

## 4 Drying

Transport of chemicals out of the features constitutes the rinse step upon completion of which the surface must be dried. To estimate the amount

of residual that remains on the wafer after the dry step the worst possible scenario is analyzed. In this scenario all the water in the feature evaporates. The typical concentration of dissolved silica in rinse water is of the order of 1 *ppb* by volume. Thus, water in a feature whose width, depth, and length are, respectively, 0.5  $\mu m$ , 4  $\mu m$ , and 10  $\mu m$  contains  $20 \times 10^{-9} \mu m^3$  of dissolved silica. Upon complete evaporation of the water this silica solidifies into a particle whose diameter is of the order of  $3 \times 10^{-3} \mu m$  which is orders of magnitude smaller than a particle that may have a detrimental effect.

To estimate the time required to evaporate the water out of a feature one may express the molar flux of the water evaporating at the interface in terms of known parameters thus yielding a differential equation for the water depth. Solution of this equation provides an upper limit on the time required to completely evaporate the water in the feature (see [3]):

$$\Delta t_{evap} = \frac{h \rho_{H_2O}}{N_{H_2O} M_{H_2O}} \quad \text{where } N_{H_2O} = \frac{P D}{R T h} \ln \left( \frac{P_{gas,t}}{P_{gas,b}} \right) \quad (4)$$

where  $\rho_{H_2O}$  and  $M_{H_2O}$  are, respectively, the water density and molecular weight,  $P$  is the total pressure,  $P_{gas}$  is the partial pressure of gas, and the  $b$  and  $t$  subscripts indicate bottom and top of the feature. Using typical values for the physical parameters and  $h = 4 \mu m$  one obtains  $\Delta t_{evap} \approx 0.25 \text{ sec}$ .

## 5 Summary

It has been shown that the size of a silica particle left by water evaporating in a feature is orders of magnitude smaller than a particle that may have a detrimental effect on the device. It has also been shown that, while the time scales on which the dominant mechanisms occur are different, they are nevertheless very short compared to the process time scale. Therefore, spray technology possesses a significant advantage over wet benches because it allows for rapid exchange of chemicals on the wafer surface.

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## The optimization of SC-1 cleaning

Michimasa Funabashi\* and Curtis W. Frank  
Department of Chemical Engineering, Stanford University  
Stanford, California 94305 USA

### Introduction

Wet chemical processing has been widely used as a major cleaning process in ULSI manufacturing and the current wet cleaning process for silicon wafers is based on the RCA cleaning method introduced by W. Kern and D. A. Poutien in 1970 [1].

One of the RCA cleaning techniques known as SC-1 cleaning, which involves a mixture of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and water, is the best for removal of particles and has become the most important cleaning technique in the manufacture of sub-micron devices. On the other hand, SC-1 cleaning is associated with the degradation of surface smoothness. An increase of silicon surface micro-roughness result in a reduction in the breakdown of electric field intensity ( $E_{bd}$ ) and the time dependent dielectric breakdown ( $Q_{bd}$ ) [2]. Ohmi et al. evaluated the micro-roughness of silicon and silicon dioxide surfaces by atomic force microscopy (AFM) [3], and proposed that the  $\text{NH}_4\text{OH}$  mixing ratio to water should be decreased from 1/5 to 1/100.

Although the relationship between SC-1 composition and maintenance of surface smoothness and particle removal has been studied[4][5], a method to optimize the composition has not been reported. This report will describe a method for optimization of SC-1 based upon a technique to determine the concentrations of ionic species.

### Experimental

SC-1 solutions were prepared by mixing deionized water with an  $\text{NH}_4\text{OH}$  solution (28%) and a  $\text{H}_2\text{O}_2$  solution (30%). The water was heated to a temperature such that the addition of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  resulted in 80°C solutions. The pH of the solutions was measured by a pH meter, Beckman 44.

Silicon wafers were thermally oxidized to a depth of 50nm and 1 mm line&space photoresist patterns were formed. The masked wafers were then treated in buffered hydrofluoric acid ( $\text{HF}=2.3\%$ ,  $\text{NH}_4\text{F}=38\%$ ) for 5 minutes to remove the thermal oxide. The silicon wafers were treated in the solutions after removal of the photoresist. The oxidized layer was removed by the buffered hydrofluoric acid and the etched depth was measured by an AFM, Digital Instruments Nano-Scope 3.

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\* Semiconductor & Integrated Circuits Div, Hitachi, Ltd. 20-1, Josuichon-cho Schome, Kodaira-shi, Tokyo 187, Japan

## Results and discussion

Fig. 1 shows the pH values of the SC-1 solutions at three concentrations of ammonium hydroxide (data points). As expected, adding  $H_2O_2$  lowers the pH, and reducing the  $NH_4OH$  lowers the pH. The broken lines are the pH that would result from a neutralization reaction based on the dissociation constants of  $H_2O_2$  ( $K_{H_2O_2} = 2.4E-12$ ) and  $NH_4OH$  ( $K_{NH_3} = 1.78E-5$ ). According to Debye-Huckel theory, the equilibrium constant is given by activity coefficient defined as "r" and dissociation constants defined as " $K_1, K_2$ " of  $NH_4OH$  and  $H_2O_2$  as in (1). The mean activity coefficient is expressed by (4) where I is ionic strength as in (5).

$$K_{neut} = r^2 * K_1 * K_2 / K_{water} \quad (1)$$

$$K_1 = K_{H_2O_2} \quad (2)$$

$$K_2 = K_{NH_3} \quad (3)$$

$$\text{Log}(r) = -0.51 * (\text{SQRT}(I) / (1 + \text{SQRT}(I)) - 0.3 * I) \quad (4)$$

$$I = ([NH_4^+] + [HO_2^-] + [OH^-] + [H^+]) / 2 \quad (5)$$

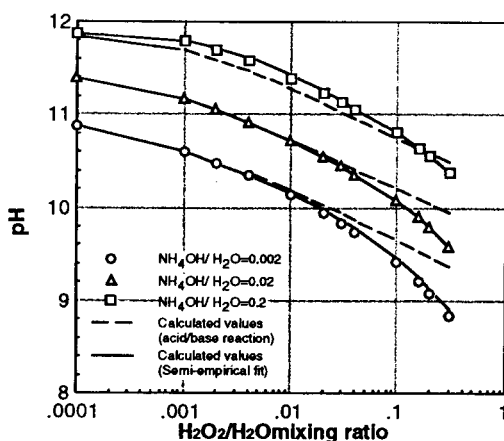


Fig. 1 The comparison of pH between measured and calculated values

At low  $H_2O_2$  concentrations ( $<0.01$ ), the calculated values and measured values agreed. As the  $H_2O_2$  concentration was increased, the measured values deviated from the calculated values in a dose-dependent manner. The equilibrium constant increased with  $H_2O_2$  concentration, allowing the calculation of a factor to correct this,  $f_1$  in (1'). At the highest  $NH_4OH$  concentration in Fig.1, the discrepancy between the measured (data points) and theoretical values (broken line) is different than at lower  $NH_4OH$  concentrations. pH

measurements of  $NH_4OH / H_2O$  solutions demonstrated that the dissociation constant required correction as shown in (7) and (3').

$$K_{neut} = r^2 * f_1 * K_1 * K_2 / K_{water} \quad (1')$$

$$\text{Log}(f_1) = 0.294 * [H_2O_2] \quad (6)$$

$$f_2 = 1 + 0.17 * [NH_3] \quad (7)$$

$$K_2 = f_2 * K_{NH_3} \quad (3')$$

The reasons for this deviation and the effect of concentration on the neutralization constant are currently being studied. Solid lines in Fig.1 show the comparison between measured values and the calculated values which are obtained by solving these equations with empirical factors. Use of empirical factors allows one to calculate the pH with an error of less than 0.05 of pH for each solution.

Comparison of pH at 23°C and 80°C showed a linear relation as in (8), with the slope and intercept varying with the mixing ratio of  $H_2O_2 / H_2O$ . They were

proportional to the logarithm of  $H_2O_2/H_2O$  mixing ratio and they were expressed by (9) and (10) respectively. Thus pH values of the solutions at  $80^\circ C$  could be calculated even though (1') contains empirical factors.

$$pH@80^\circ C = b + a * pH@23^\circ C \quad (8)$$

$$a = 1.02 - 0.14 * LOG(x) \quad (9)$$

$$b = -0.61 + 1.66 * LOG(x) \quad (10)$$

$$x = H_2O_2 / H_2O$$

Fig. 2 shows the pH dependence of the etching rate. Increasing pH enhances the etching rate gradually up to a critical point. Beyond this point, the etching rate increased drastically because the surface oxidation by  $H_2O_2$  is not fast enough to protect the silicon surface from etching [6]. Between pH 8.6 and 10.4, the etching rate (nm/min) is proportional to pH or  $[OH^-]$ , and can be expressed by (11). The etching rate as measured in this study was independent of  $H_2O_2$  concentration in the pH 8.6 - 10.4 range. With (11), it is possible to determine the optimal pH of the solution.

$$\text{Etching rate} = 25 * [OH^-]^{1/10} \quad (11)$$

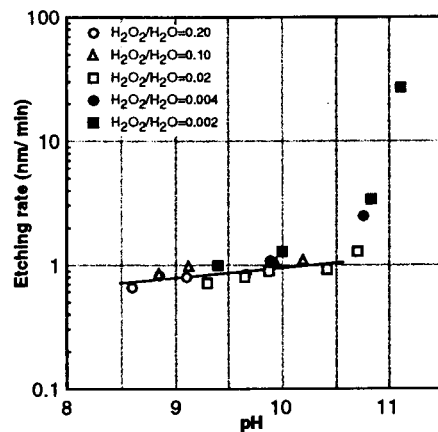


Fig. 2 The pH dependence of etching rate

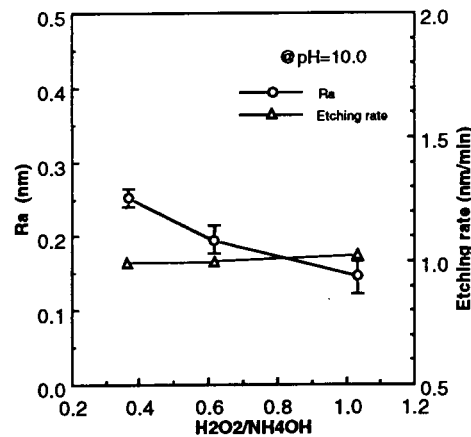


Fig. 3 The effect of  $H_2O_2/NH_4OH$  mixing ratio on etching rate and Ra

Fig. 3 shows the relationship between surface roughness and the  $H_2O_2/NH_4OH$  mixing ratio at pH 10.0. The surface roughening is reduced by increasing the  $H_2O_2/NH_4OH$  mixing ratio even though the etching rate is constant. Since surface oxidation efficiency controls the surface roughness, thus, the  $H_2O_2/NH_4OH$  mixing ratio should be as great as possible.

The literature reports that particle removal is dependent upon maintenance of a high rate of etching [4][7]. A solution of 0.05:1:5 ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ) has been reported to remove particles without inducing surface roughening [2]. Our results demonstrate that pH can define the optimum mixing ratio, therefore, we determined the maximal  $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$  at the pH produced by a 0.05:1:5 ratio (Fig.4). The optimal solution based on these condition is 0.034:0.65:5.

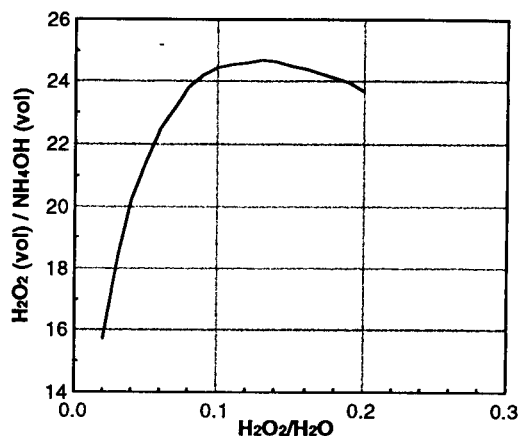


Fig. 4 The combinations of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$  mixing ratios that show the same pH as 0.05:1:5 ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ )

### Conclusion

The pH value can be calculated by the equations with empirical factors and dissociation constants of  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}_2$ . The etching rate of silicon is determined by pH and is proportional to  $25 * [\text{OH}]^{1/10}$ . The surface roughness is influenced by the  $\text{H}_2\text{O}_2$  to  $\text{NH}_4\text{OH}$  mixing ratio; higher  $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$  ratios yield a smoother surface. From these results, the best mixing ratio is calculated to be 0.034:0.65:5 ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ ).

### Acknowledgments

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# THE EFFECT OF MEGASONIC IRRADIATION ON ULTRA PURE WATER

M. Toda\*, M. Kato\* and T. Ohmi\*\*

## 1. INTRODUCTION

To keep wafer surface ultra clean, items such as (1)particle free, (2)metal free, (3)organic contamination free, (4)moisture free, (5)surface micro-roughness free, (6)native oxide free, (7)perfect hydrogen termination and (8)charge up free should be realized[1-3]. In the present time, RCA cleaning method developed by Werner Kern [4] has been utilized in wafer cleaning process. In this cleaning process, cleaning solutions such as hydrogen peroxide, sulfuric acid, ammonia, hydrochloric acid and hydrofluoric acid have been used. In this process, high temperature operation, which generates the vapor of chemicals, is claimed by some process steps. Thus, the following problems might be arisen. Namely, the ambience of clean room might be contaminated by these chemical vapor, and the air volume exhausted from clean bench will be increased extremely. Therefore, to realize the economical wafer cleaning it is necessary to reduce the cleaning steps and to decrease the consumption volume of ultra pure water and chemicals as much as possible. From this point of view, T. Ohmi et al.[5-6] have proposed a new wet cleaning process. Figure 1 shows a new wet cleaning process.

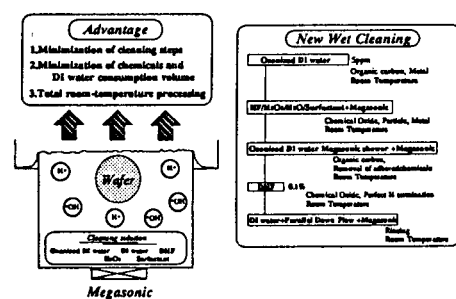


Fig. 1 The new wet cleaning process

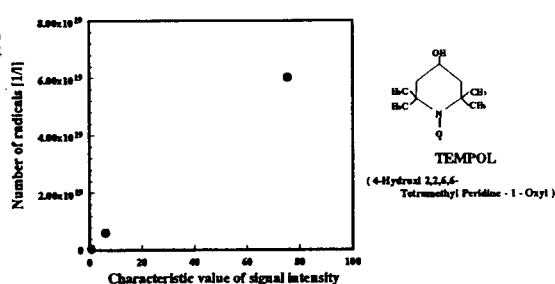


Fig. 2 Calibration line of DMPO adduct

In this new process, ultra pure water is a main cleaning agent and the concentration of chemicals will be controlled perfectly. The megasonic is also introduced to decrease the consumption volume of ultra pure water and chemicals. Therefore, the effect of megasonic irradiation on ultra pure water should be clarified to make this cleaning process most suitable. And for the effective operation of this process a right under-

\* Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, 3 - 16, Jonan 4-Chome, Yonezawa, Yamagata, 992, Japan

\*\* Department of Electronics, Faculty of Engineering, Tohoku University, Aoba, Aza, Aramaki, Sendai, 992, Japan

standing of the relations between megasonic irradiation and chemical reaction, and/or radicals formation in ultra pure water and in the cleaning solution is also necessary.

In this paper, the radicals formed by megasonic irradiation in ultra pure water were measured and evaluated by ESR(Electron Spin Resonance) spectrometer. The effect of dissolved gas in ultra pure water on radical formation was examined. The measurement of ions formed by megasonic irradiation was also carried out to know the chemical reaction process in ultra pure water and the change of physical and chemical properties of ultra pure water by megasonic irradiation was studied.

## 2. EXPERIMENTAL APPARATUS AND PROCEDURES

The frequency of megasonic is 0.95 MHz and the output of maximum power is 1200 Watt. After ultra pure water was filled in the quartz glass cell, DMPO was added to adduct the generated free radicals by spin-trap method. The generated free radicals were evaluated by X-band ESR spectrometer and the formed ions were evaluated by ion-chromatography.

For the quantitative analysis of generated radicals, the stable radicals should be necessary for standard materials. In general, TEMPOL(4-hydroxyl 2,2,6,6-tetramethyl peridine-1-oxyl), of which structure is shown in Fig.2, was used as the standard chemical materials of radicals. The calibration line obtained by TEMPOL was also shown in Fig.2. It is clearly known that the number of radical is directly propotional to the characteristic value of ESR signal intensity.

The trace amount of hydrocarbon contaminants on silicon wafer surface was evaluated by FT-IR-ATR method.

## 3. RESULTS AND DISCUSSIONS

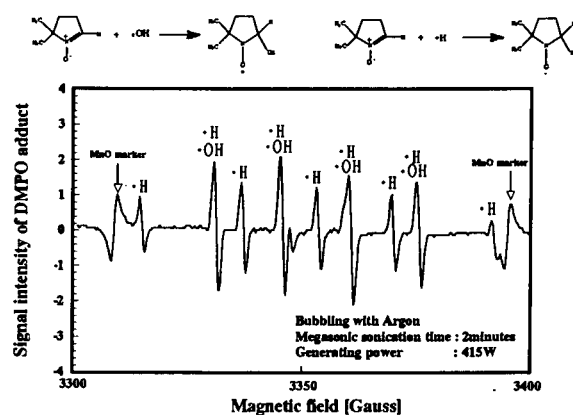


*Fig. 3 Effect of Ar gas on radical formation in ultrapure water excited by megasonic*

Figure 3 shows ESR spectra of DMPO-H and DMPO-OH formed by megasonic irradiation in ultra pure water saturated with nitrogen gas. The structure of DMPO, DMPO-H and DMPO-OH were shown in Fig.3. The nitron spin traps used in this

work react with short-lived free radicals generated by megasonic to produce longer-lived spin adducts as shown in the figure. The spin adducts of this spin trap always have one  $\beta$ -hydrogen except for the H adducts which have two hydrogen atoms in  $\beta$ -positions. Therefore, a secondary doublet due to the  $\beta$ -hydrogen is always observed in the ESR spectra while a secondary triplet is obtained in the case of the H adducts. In order to determine the concentration of H radical, the product of the peak to peak height of the ESR intensity and the square of the half-height width of the third signal on the left-hand (excluding the signal of MnO) was calculated at first. Then the six times the product above mentioned was compared with the calibration line shown in Fig.2 to determine H radical concentration. In case of the determination of OH radical concentration, the characteristic value of OH radical after subtracting the six times the product for H radical from total characteristic value of signals concerning to H and OH radicals was compared with the calibration line shown in Fig.2 to obtain the concentration of OH radical.

Figure 4 illustrates the effect of dissolved gas on H and OH radicals formation. OH radical was extremely formed with megasonic irradiation in ultra pure water containing oxygen gas. It can be considered that OH radical was produced by the reaction of oxygen atom O from  $O_2$  on H radical from  $H_2O$  in addition to OH radical generation from ultra pure water. Thus, H radical in ultra pure water dissolving oxygen gas was not confirmed. In comparison of H and OH radicals formation in ultra pure water containing argon gas with those in ultra pure water dissolving helium gas, the concentrations of H and OH radicals in ultra pure water dissolving argon gas were always higher than those in ultra pure water containing helium gas. According to the previous paper[7], H and OH radicals were considered to be formed by the cavitation effect with sonication in water. The details of radical formation mechanism, however, has not been clarified yet satisfactory. In Fig.4, the production of H radical in ultra pure water having argon gas was found to be higher than that in ultra pure water dissolving nitrogen gas. The generation of OH radical in ultra pure water having nitrogen gas was also found to be much higher than that in ultra pure water dissolving argon gas. It is assumed that the reaction course of radicals generation can be differed by the sort of dissolved gases.

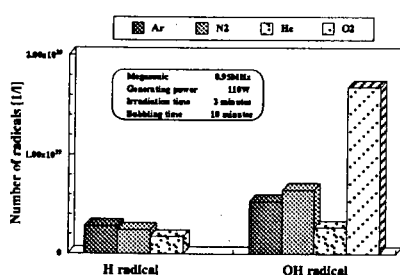


Fig. 4 Effect of dissolved gas on H and OH radicals formation

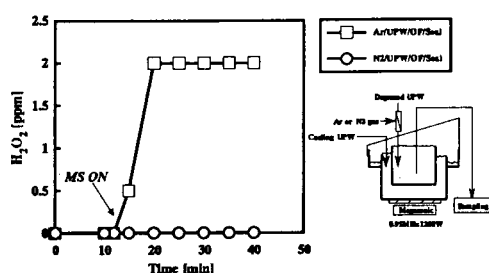


Fig. 5 Formation of hydrogen peroxide in ultra pure water by megasonic irradiation

Figure 5 illustrates the formation of hydrogen peroxide in ultra pure water by megasonic irradiation. In the case of argon gas, hydrogen peroxide was immediately formed as megasonic irradiation was begun. The production of hydrogen peroxide was

much higher than that in ultra pure water containing nitrogen gas. The hydrogen peroxide can be formed by recombination of OH radicals. Thus the amount of OH radical formation is considered to be higher than that in ultra pure water containing nitrogen gas. At the same time, the hydrogen peroxide was decomposed to oxygen atom O and H<sub>2</sub>O. This decomposition reaction was occurred in the presence of the catalyst of H<sup>+</sup> and metal ions such as Fe<sup>2+</sup> and Cu<sup>2+</sup> containing in ultra pure water.

The effect of dissolved gas in ultra pure water on the production of ions was shown in Fig.6. In this figure, argon gas was utilized to discharge the dissolved nitrogen gas from ultra pure water. In spite of lower concentration of nitrogen gas in ultra pure water, the concentration of NH<sub>4</sub><sup>+</sup> was recognized to be much higher compared with that in ultra pure water saturated with nitrogen gas. This is because in ultra pure water containing argonj gas, a lot of H radical is generated by megasonic irradiation. From this result, the concentration of ions formation was found to increase with increasing in H and OH radicals formation. And it was found that oxygen atom O formed from hydrogen peroxide reacts on NH<sub>4</sub><sup>+</sup> and finally NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were formed in ultra pure water.

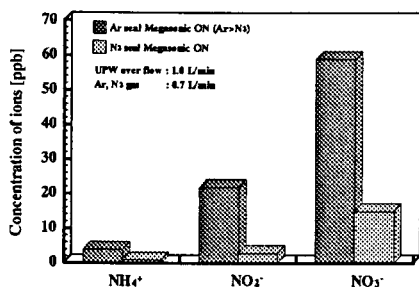


Fig. 6 Effect of dissolved gas in ultra pure water on production of ions

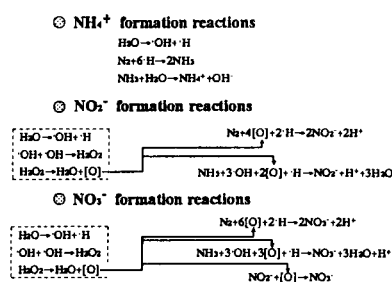


Fig.7 The reactions process in ultra pure water containing Ar or N<sub>2</sub> with megasonic irradiation

Figure 7 shows the reaction paths which will be occurred by megasonic irradiation in ultra pure water containing nitrogen gas.

In case of NH<sub>4</sub><sup>+</sup> formation, H radical formed from ultra pure water by megasonic irradiation reacts on N<sub>2</sub> to produce NH<sub>3</sub>.

In case of NO<sub>2</sub><sup>-</sup> formation, two reaction courses can be assumed. In the first reaction course, H<sub>2</sub>O<sub>2</sub> was generated by recombination of OH radicals formed by megasonic irradiation from H<sub>2</sub>O. And H<sub>2</sub>O<sub>2</sub> was decomposed to oxygen atom O and H<sub>2</sub>O. Oxygen atom O formed from H<sub>2</sub>O<sub>2</sub> and H radical react on N<sub>2</sub> to produce NO<sub>2</sub><sup>-</sup> and H<sup>+</sup>. In the second reaction course, OH and H radicals which were formed from H<sub>2</sub>O by megasonic irradiation and oxygen atom formed from H<sub>2</sub>O<sub>2</sub> react on NH<sub>3</sub> to produce NO<sub>2</sub><sup>-</sup>, H<sup>+</sup> and H<sub>2</sub>O.

In case of NO<sub>3</sub><sup>-</sup> formation, three reaction courses can be assumed. In the first reaction course, H<sub>2</sub>O<sub>2</sub> was generated by recombination of OH radical formed from H<sub>2</sub>O by megasonic irradiation. And H<sub>2</sub>O<sub>2</sub> was decomposed to oxygen atom O and H<sub>2</sub>O. Oxygen atom formed from H<sub>2</sub>O<sub>2</sub> and H radical react on N<sub>2</sub> to produce NO<sub>3</sub><sup>-</sup> and H<sup>+</sup>. In the second reaction course, OH and H radicals which were formed from H<sub>2</sub>O by megasonic irradiation and oxygen atom O formed from H<sub>2</sub>O<sub>2</sub> react on NH<sub>3</sub> to produce NO<sub>3</sub><sup>-</sup>, H<sup>+</sup> and H<sub>2</sub>O. In the third reaction course, oxygen atom O formed from



$\text{H}_2\text{O}_2$  reacts on  $\text{NO}_2^-$  to produce  $\text{NO}_3^-$ .

Figure 8 shows the dependence of resistivity of degassed ultra pure water on megasonic irradiation time. From this figure, the megasonic irradiation into ultra pure water dissolving argon gas was found to make resistivity much lower. This is because the amount of ions formation was increased gradually by megasonic irradiation.

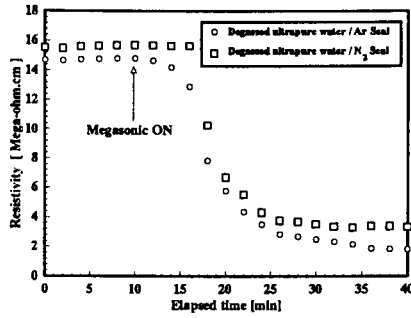


Fig.8 Variation of resistivity of degassed ultra pure water with elapsed time

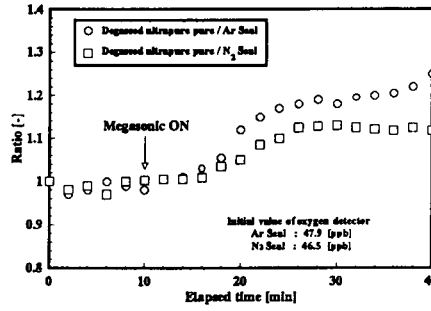


Fig.9 Formation of oxygen molecules in degassed ultrapure water with megasonic irradiation

Figures 9 and 10 show the formation of oxygen and hydrogen molecules by megasonic irradiation in degassed ultra pure water. After megasonic irradiation, the amount of oxygen and hydrogen molecules increased with increasing in the elapsed time. In general, the formation of H and OH radicals from  $\text{H}_2\text{O}$  by megasonic irradiation was considered to be caused by cavitation effect in water. From figures 9 and 10, however, it is assumed that the decomposition of  $\text{H}_2\text{O}$  by megasonic irradiation is caused by the another factors. The space in original structure of water can be considered to be used to decompose  $\text{H}_2\text{O}$ .

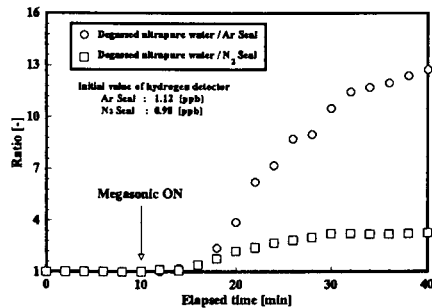


Fig.10 Formation of hydrogen molecules in degassed ultrapure water with megasonic irradiation

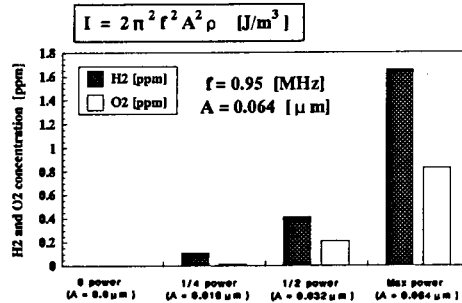


Fig.11 Estimated concentration of  $\text{H}_2$  and  $\text{O}_2$  formed by H and OH radicals respectively in ultra pure water

Figure 11 indicates the estimated concentration of  $\text{H}_2$  and  $\text{O}_2$  formed by H and OH radicals in ultra pure water, respectively. In this figure, the calculation of radical concentration was based on the intensity of energy of harmonic vibration given by the following equation. In this equation, A is amplitude, f is frequency and  $\rho$  is density of ultra pure water.

$$I = 2\pi^2 f^2 A^2 \rho \quad [\text{J/m}^3]$$

In the estimation of radical production, it was assumed that the calculated intensity of energy was consumed to generate  $\text{H}_2$  and  $\text{O}_2$  perfectly. It is noted from figure that the estimated values of  $\text{H}_2$  and  $\text{O}_2$  formed by megasonic irradiation in ultra pure water

were the order of ppm. Observed concentration of  $H_2$  and  $O_2$  generated by megasonic in ultra pure water was the order of ppb. Therefore, if the estimation values were compared with observed ones, it can be considered that almost all intensity of energy given by megasonic was consumed to rise the bulk temperature of ultra pure water.

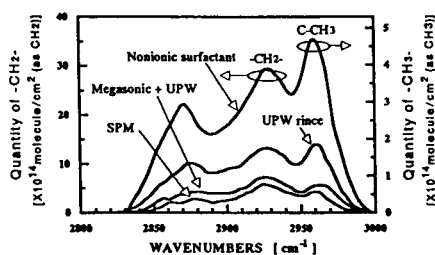


Fig.12 Removal of organic contamination by UPW rinse, UPW excited with megasonic and SPM

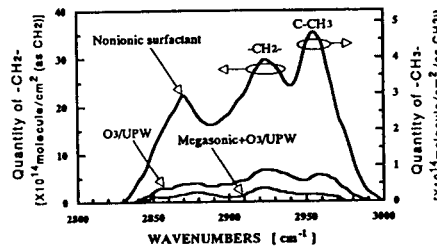


Fig.13 Removal of organic contamination by ozonized UPW and ozonized UPW excited with megasonic

Figures 12 and 13 show the removal of organic contamination on wafer surface by each cleaning solutions. Silicon wafers on which surface the nonionic surfactant was adsorbed were used to measure the removal of organic contamination. It is observed from Fig. 12 that the rinsing by ultra pure water can remove the organic contamination on wafer surface. And the ultra pure water irradiated by megasonic was also found to be very effective for removal of organic contamination as same as that obtained by SPM( $H_2SO_4/H_2O_2$ ) cleaning solution. In Fig.13, it is seen that ultra pure water in which ozone simply dissolved can remove the organic contamination on wafer surface sufficiently. On the other hand, megasonic irradiation to ozonized ultra pure water was recognized to be very effective to remove organic contamination as shown in Fig.13. Because the observed FT-IR-ATR signal in Fig.13 was the detection limit values of measurement apparatus.

#### 4. CONCLUSION

The results of this study are summarized as follows;

- (1) H and OH radicals were confirmed to be formed from the ultra pure water by megasonic irradiation. The amounts of H and OH radicals' formation were affected by the sorts of dissolved gases and its quantity.
- (2) The amounts of H and OH radicals' formation was confirmed to be decreased by  $N_2$  gas dissolved in ultra pure water.
- (3) Oxygen atom formed from hydrogen peroxide which was produced by the recombination of OH radicals reacts on  $NH_4^+$  and  $NO_2^-$  and  $NO_3^-$  was produced.
- (4) The most part of supplied power in megasonic irradiation was found to be used to rise the temperature of the bulk water.
- (5) In the removal of organic contaminations on wafer surface, the ozonized ultra pure water with megasonic irradiation was better than the other cleaning solutions.

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## PARTICLE AND METALLIC INTERACTIONS WITH MEGASONIC ENERGY IN WAFER CLEANING

R.M. Hall, L. Li\*, R.C. Hawthorne\*, T. Jarvis

Santa Clara Plastics, 400 Benjamin Lane, Boise, ID 83704

\*Micron Technology, Inc. 8000 S. Federal Way, Boise, ID 83707

### 1. Introduction

The application of megasonic processing to wafer cleaning has recently attracted a lot of research focus. Megasonic energy in wafer cleaning solutions has been shown to be extremely useful for the removal of submicron particles and surface residue that would otherwise be difficult to remove<sup>1-3</sup>. The effects of acoustic streaming and cavitation induced by sonic processing are generally thought to be beneficial in the contamination removal process. It has also been proposed that the same mechanisms responsible for particle removal in megasonic cleaning applications may, under certain circumstances, promote particle deposition<sup>4</sup>. With megasonic excitation, particles can be accelerated to high velocities which increase the probability of collisions between a particle and the wafer surface. When a particle is sufficiently close to the wafer surface, Van Der Waals forces of adhesion become the dominant mechanism for particle adhesion<sup>5</sup>. In this study we examine the effects of particle deposition in various cleaning media under the influence of megasonic excitation. From this work we will identify different cleaning regimes where the use of megasonic energy can either degrade or improve cleaning efficiency.

### 2. Experimental

To investigate the effects of particle deposition with megasonic excitation, a PSL particle source was chosen for a solution contaminant. The size of the particles were 0.205  $\mu\text{m}$ , and the concentration in each cleaning solution was 10K PSL/ml. The effect of solution pH was examined with HF (50:1), DI water, and SC-1 (0.1:1:5) bath chemistries. Table 1 contains a summary of the bath conditions for each of the experimental trials. In each case wafers were first processed in the chemical tank (10 min.), rinsed in DI water (6 min.), and dried in an IPA Vapor Jet Dryer. The Megasonic transducer in the process tank had a curved lens for radial power distribution (0 or 400 watts) and no moving parts were required for effective distribution of energy. All processing was carried out with a reduced process cassette in a Santa Clara Plastics 9400 automated surface preparation system. Particles on the wafer surface were measured with a Tencor 6200 surfscan in the range of 0.18 - 0.22  $\mu\text{m}$ . All wafers used in the experiment were p-type 200 mm wafers.

### 3. Results and Discussion

The influence of megasonic excitation on particle deposition was examined in several common process chemistries containing PSL contaminant as shown in Figure 1. In each

case particle deposition on the wafer surface was greater for wafers processed with megasonic excitation as opposed to those processed without. It is interesting to note that even when a repulsive electrical zeta potential is present in the process chemistry, significant particle deposition can occur when particles are sufficiently close to the wafer surface. In order to understand these effects more clearly, wafers with different initial particle contamination levels were processed through DI water solutions containing 10K PSL/mL. This data is shown in Figure 2. In this data we can observe the effects of both particle removal and particle deposition as a function of the initial surface and bath contamination level. Wafers with initial particle counts less than 2000 particles/wafer showed particle addition, while wafers with greater than 3000 particles/wafer showed a net reduction in surface particle counts. This data suggests that an equilibrium is reached when the surface contamination level matches that which would result from exposure to the solution. Wafers with surface contamination below the equilibrium value show particle addition, while wafers with surface contamination above the equilibrium value show particle removal. In each case, megasonic energy accelerates the process as shown in Figure 3. This is modeled by a simple regression analysis:

$$P_{\text{adder}}(\text{Meg}) = -0.927 \cdot P_i + 2258 \quad [2]$$

$$P_{\text{adder}}(\text{NoMeg}) = -0.507 \cdot P_i + 967 \quad [3]$$

Where  $P_{\text{adder}}$  is the contamination removed/added to the wafer surface, and  $P_i$  is the initial contamination present on the wafer surface. In these models, the slope of curve can be regarded as the particle deposition/removal efficiency, and the intercept as the contamination that would be added to the surface for a wafer with no initial contamination. From these models it can be seen that the efficiency at which particles are added to (removed from) the wafer surface under megasonic excitation is approximately 2x that of the non-megasonic case. Note that when the surface contamination level approaches the liquid contamination level, there is no significant particle addition or removal regardless of megasonic conditions.

In addition to examining the effects of particle deposition under the influence of megasonic excitation, metallic deposition was also considered. Figure 4 shows the surface metallic contamination levels for wafers processed with and without megasonic energy in an SC-1 solution containing < 1ppb of Fe. In this data both process temperature and megasonic energy act to increase the Fe surface contamination levels. As with the particle data, it is believed that the addition of megasonic energy to bath chemistry shifts the equilibrium constants such that Fe deposition is promoted<sup>6-7</sup>.

#### 4. Conclusions

The influence of megasonic energy on particle and metallic deposition has been considered. In this work we have identified different cleaning regimes where megasonic processing can produce dramatically different results depending on the wafer and liquid contamination levels. In general, we have shown that when wafer surface contamination levels are below those in solution, megasonic processing promotes particle deposition

above that which would be found on wafers processed without megasonic excitation. This result was shown to be independent of the solution chemistry and wafer surface condition (hydrophilic, hydrophobic). By contrast when the contamination level on the wafer surface is greater than that found in solution, megasonic processing is highly beneficial for increasing particle removal efficiency.

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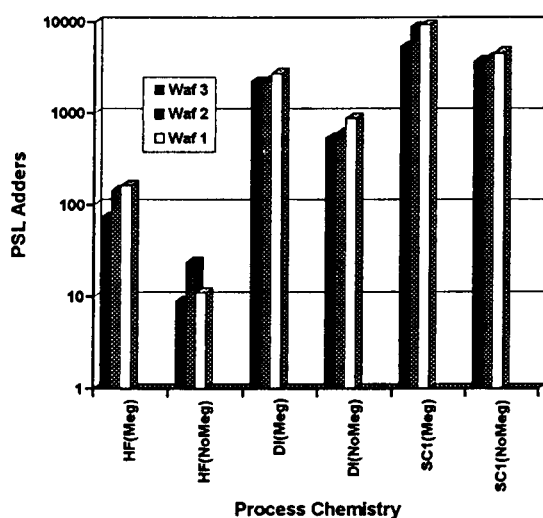
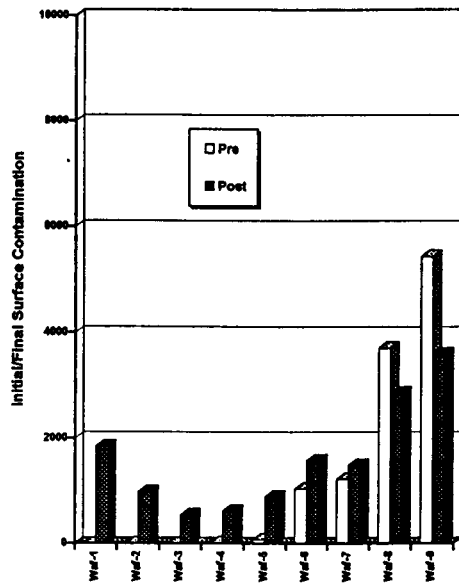


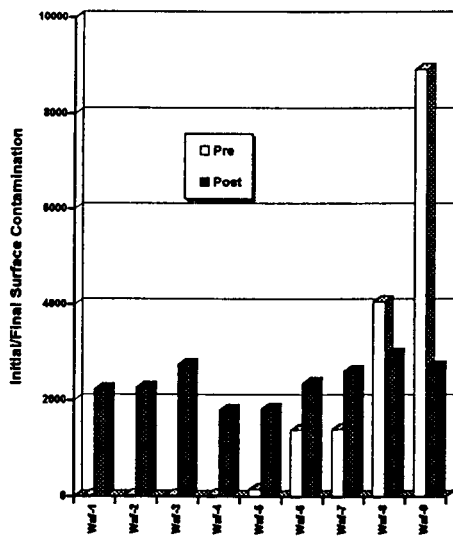
Figure 1: Surface contamination levels for wafers processed in HF, DI water, and SC-1 chemistries.

Table 1: Bath Process Conditions

| Chemistry       | Ratio       | Temp. | Time    | PSL/mL |
|-----------------|-------------|-------|---------|--------|
| DI Water        |             | 20 °C | 10 min. | 10K    |
| HF              | 50:1        | 22 °C | 10 min. | 10K    |
| SC-1            | 0.1:1:5     | 50 °C | 10 min. | 10K    |
| Megasonic Power | 0/400 Watts |       |         |        |
| Chemical Grade  | PPB         |       |         |        |



(a) Non-Megasonic



(b) Megasonic

Figure 2: Contamination added/removed from wafer surface as a function of initial particle count (DI water).

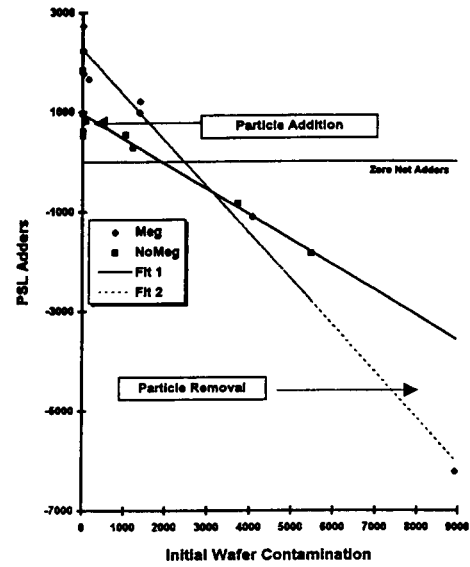


Figure 3: Effect of megasonic energy (dashed line) on particle removal/addition (DI water).

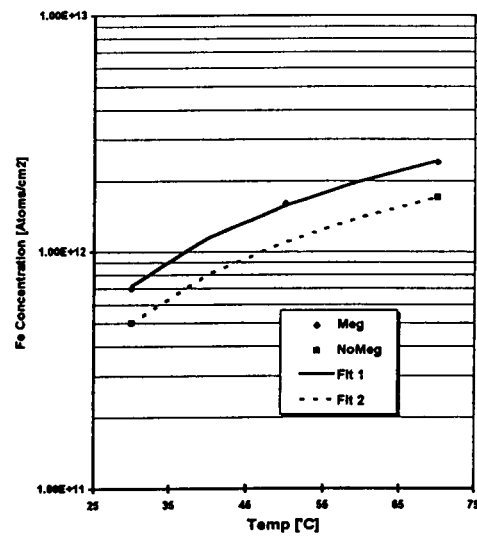


Figure 4: Fe deposition from an SC-1 solution as a function of megasonic energy (solid line) and temperature.



## The particle cleaning for FPMS with megasonic irradiation combined with spin cleaning

T.Kujime, Y.Nishiyama, S.Okano and T.Ohmi  
Tohoku University  
Department of Electronics, Faculty of Engineering

### Abstract

The removal mechanism for particles on silicon wafer surface is as follows:

- 1: Detach from substrate.
- 2: Prevent readhesion to wafer surface.

At the present time, the APM cleaning method (SC-1) is applied for particle cleaning on silicon wafer surface. Particle removal mechanism of SC-1 cleaning is: (1) etching of silicon substrate, (2) electrostatic repulsion between particle and substrate in alkaline solution.

In this study, we propose the particle cleaning method using the FPMS (HF+H<sub>2</sub>O<sub>2</sub>+surfactant) solution excited by megasonic irradiation. The etching of silicon substrate by HF and megasonic vibration promotes the detachment of the particles from silicon surface. Besides surfactant addition to cleaning solution is effective to prevent readhesion to wafer surface. It is because the zeta potentials of particles and wafer surface in cleaning solution could be controlled by the surfactant addition.

By FPMS with megasonic irradiation at room temperature, we obtained nearly the same efficiency as the SC-1 cleaning at elevated temperature.

This cleaning method is possible to remove particles and metallic impurities simultaneously without increasing the surface microroughness.[1]-[2]

Furthermore, the spin cleaning method combined with FPMS+megasonic can decrease the cleaning time drastically.

### Introduction

Recent studies have revealed the mechanism of contamination and cleaning Si wafer surface.[3]-[4] The cleaning contaminants on Si wafer surface is following:

- To remove metallic impurities and organic contaminants from the Si wafer surface, it is necessary to use a solution featuring high redox potential. This solution captures electron from contaminants to oxidize them. In this cleaning process, metallic impurities are ionized to be dissolved into the solution while organic impurities are decomposed to CO<sub>2</sub>, H<sub>2</sub>O etc.
- To remove particles, it is need to get slightly etching rate and use megasonic irradiation which makes particles detach from the substrate surface. Additionally necessary that particles and surface feature the same polarity of zeta potential.

The elucidation of these cleaning mechanism realize the total room temperature cleaning process, decreasing

of the number of process step and decreasing of large amount of chemicals and UPW.

Figure 1(a) shows the new proposed Si surface cleaning process in every step is performed at room temperature.

Figure 1(b) shows the conventional RCA cleaning process. The new wet cleaning process is following:

- 1: The  $O_3$  injected UPW is to remove the metallic impurities and organic contaminants from surface.
- 2: The Surfactant added HF and  $H_2O_2$  mixture (FPMS) with irradiating megasonic (MS) is to remove particles and metallic impurities. This metallic impurities are captured in the chemical oxide at process 1.
- 3: The  $O_3$  injected UPW is to cleaning the organic contamination. This contaminants are surfactant adsorbed on the surface at process 2
- 4: The DHF is etching the chemical oxide and making a surface H-terminated.
- 5: UPW is final rinse.

In this report , we propose the particle cleaning method using FPMS solution exited by megasonic vibration.

### Experimental

Cz Si(100) wafer were used for evaluations. The component and composition of chemicals used in this experiment are shown as follow.

DHF : 0.5wt% aq. (at 25°C)

SPM :  $H_2SO_4$ (98t%)/ $H_2O_2$ (30wt%)=4:1(volume ratio),(at 120~150°C)

APM :  $NH_4OH$ (28wt%)/ $H_2O_2$ (30wt%)/UPW=0.05:1:5(volume ratio),(80~90°C)

FPM : HF/ $H_2O_2$ /UPW (at 25°C)

FPMS : FPM + surfactant (at 25°C)

Using surfactant is normary injected 50ppm

Fig.2 shows the schematic diagram of batch type experimental equipment. And 0.95MHz megasonic was used as the vibration source in this experiment.

Fig.3 shows the schematic diagram of spin cleaning equipment. The densely cleaning solution is supplied separately from ultrapure water and mixed on spinning wafer surface.

Particle counts on wafers were evaluated using a Laser scanning type particle inspection system. Particles were used Polystyrene latex(PSL) and  $\alpha-Al_2O_3$ (alumina) Fig.4 shows the relationship between the zeta potential of various materials and pH.

### Results and Discussion.

Fig.5 shows the removal efficiency of various cleaning method. DHF, FPM and FPMS are found hardly effective in removing particles. Particle removal efficiency of high-temperature APM cleaning is exceeded at room temperature only when megasonic was applied to FPMS at room temperature. Slightly etching and megasonic vibration can detach the PSL from substrate. The PSL and Si surface have the same polarity of zeta potential due to the existence of the surfactant.

Fig.6 shows the particle removal by FPMS with megasonic irradiation dependence on dipping time. The contamination of particles was removed in 5 min.

Fig.7 shows the particle removal by FPMS with megasonic irradiation combined with spin cleaning method. To perform completely removal of the particles down to the before contamination level by spin cleaning, it requires 30 sec. It is considered that the particle is taken away from wafer surface by high speed liquid flow in short time.

### Conclusion

We have evaluated the new cleaning method of silicon surface. The solution is surfactant added diluted HF and  $H_2O_2$  mixture. We use this solution with megasonic vibration, it become to possible to remove particles simultaneously without the increasing of the surface microroughness.

The spinning method is found more effective than the dipping method in the cleaning of particles from Si wafer surface. The spinning method requires less time and a smaller chemical volume to remove contaminants from substrate.

We have established a novel wet cleaning process. This process is performed entirely at room temperature. We are confident that this new process will make a significant contribution to efficient semiconductor manufacturing.

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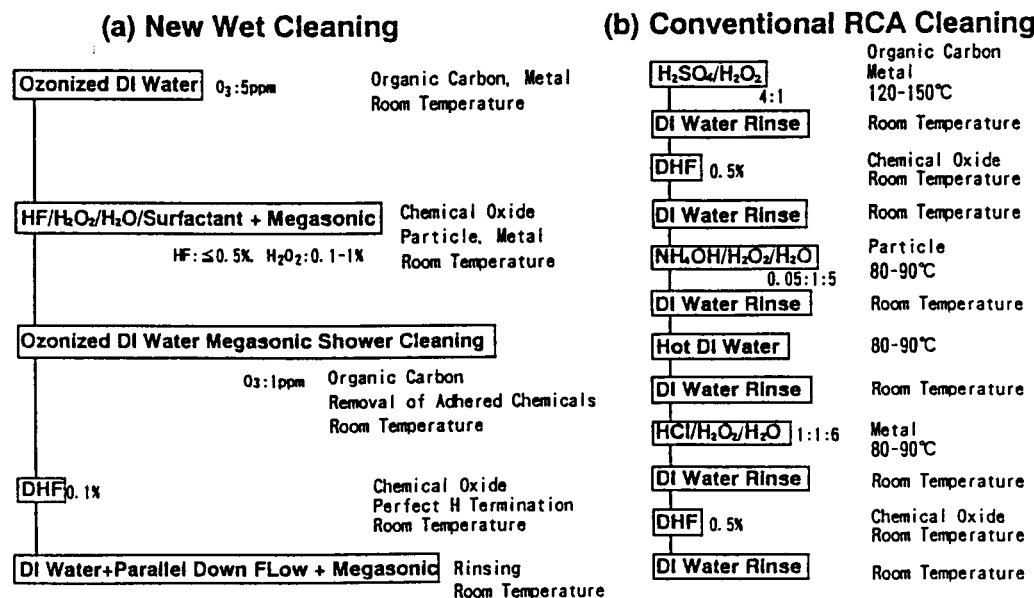


Fig.1 New and conventional wet cleaning process.

## Experimental Apparatus - Batch type

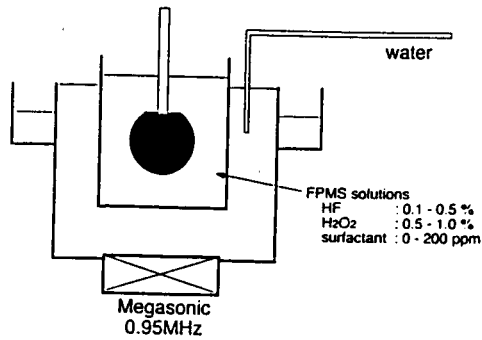


Fig.2 The schematic diagram of batch type experimental equipment.

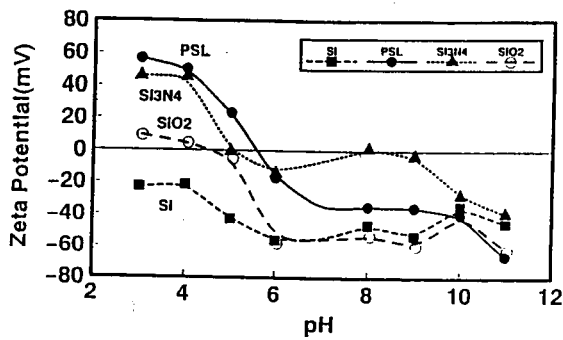


Fig.4 Zeta potential of various material as a function of solution pH.

## Spin Cleaning by FPMS with Megasonic

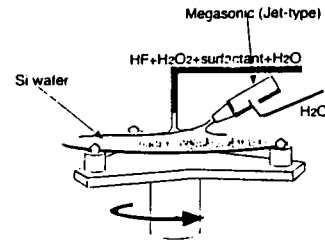


Fig.3 The schematic diagram of spin cleaning equipment.

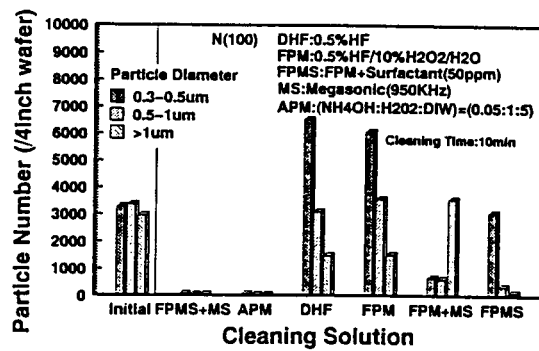


Fig.5 Particle removal efficiency of various cleaning method.

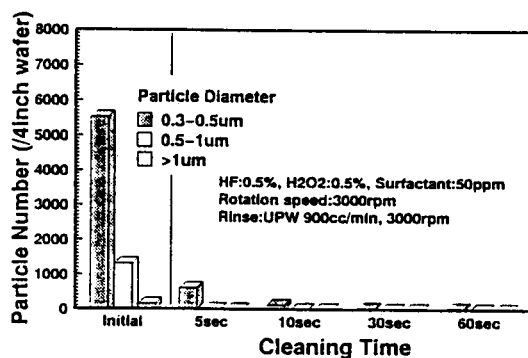


Fig.6 Particle removal efficiency of FPMS+megasonic dependence on dipping time.

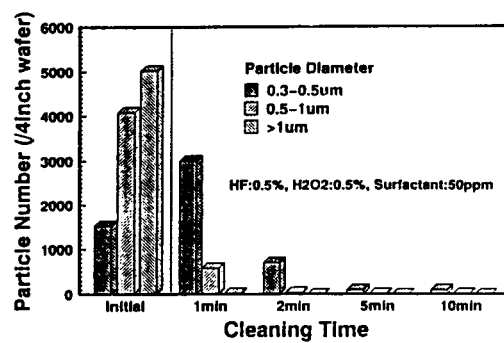


Fig.7 Particle removal efficiency of FPMS+megasonic combined spin cleaning method.

## THE ROLE OF POWER IN EFFECTIVE MEGASONIC CLEANING USING DI WATER

Ahmed A. Busnaina

*Clarkson University, USA*

Glenn W. Gale

*IBM Microelectronics, USA*

Ismail I. Kashkoush

*SubMicron Systems, Inc., USA*

### 1. INTRODUCTION

Though wafer cleaning in tanks may appear to be one of the simpler processes in a semiconductor fab, the megasonics technique actually produces a range of complex interrelated effects which have traditionally been poorly understood. This paper concentrates on the effects of power on particle removal efficiency.

### 2. THEORY

In megasonics, a pressure wave (near 1 MHz) produced by a piezoelectric transducer in the tank bottom is transmitted through the process liquid. Pressure and point velocity are sinusoidal functions of position and time. Pressure waves result in a "pulling apart" of liquids, known as cavitation. The collapse of cavitation bubbles releases enough energy to effect particle detachment from a surface. Cavitation can be stable (entailing small oscillations about an equilibrium bubble radius) or transient (involving large bubble size variations and eventual violent collapse). Stable cavitation is associated with mainly gaseous cavities, while transient cavitation is associated with mainly vaporous cavities [1].

Since the threshold pressure amplitude for cavitation increases with increasing frequency, and cavitation bubbles are not visible at MHz frequencies, it has been thought that cavitation does not occur at those frequencies with commonly used power densities [2]. However, some methods of detecting cavitation are more sensitive than others, and in many cases cavitation may exist on a scale too small to be sensed by certain techniques.

Cavities begin as small nuclei (trapped or stabilized gas pockets) on the order of a micron in scale [3, 4]. These grow in size via a rectified diffusion process as ultrasonic power is increased. Eventually gaseous (stable) cavitation develops if the liquid is gas saturated. At still higher powers vaporous (transient) cavitation may occur. It has been demonstrated theoretically [3], that at 1 MHz the resonance radius for a bubble is about 3 microns, and that a bubble of such size will grow by rectified diffusion at acoustic pressure amplitudes on the order of 0.1 MPa or greater (within the power density range of commonly used sonic cleaning equipment).

Sonoluminescence is the weak emission of light from a sound field in liquid

(believed to be caused by localized high temperatures resulting from cavitation). It is useful to use sonoluminescence to find out whether cavitation in megasonics can be detected. In a procedure similar to one previously described [5], sonoluminescence experiments were carried out at Clarkson University. Transducers of different frequencies were immersed separately in filtered, deionized water tanks. Sonoluminescence was observed at 40 kHz as expected. However, it was also observed at 360 kHz and 750 kHz, indicating that cavitation was present at all of these frequencies. The very faint light pattern was recorded using a 35mm camera with an exposure time of 25 minutes [3].

The light observed at the higher frequencies (360 and 750 kHz) is believed to be due to stable cavitation for several reasons. First, intensities were lower than the thresholds for transient cavitation predicted by theory and reported in the literature. Second, sonoluminescence was visible to the naked eye, whereas transient cavitation-induced luminescence is mostly UV (peak at approximately 270-290 nm [6]) and is visible only with the aid of wavelength shifting chemicals (as was the case with the 40 kHz transducer). Stable cavitation produces a violet light (peak at approximately 400 nm), which is consistent with what was observed. Also, no damage to aluminum foil exposed to the 360 and 750 kHz transducers was observed. Such damage, indicative of transient cavitation implosion, has been observed at <100 kHz frequencies [2].

Also present in all sonic cleaning is acoustic streaming, which refers to steady fluid flow patterns produced by a sound field due mainly to viscous attenuation but also related to wave interaction with solid boundaries. Acoustic streaming can occur outside the boundary layer (large scale vortices), or it can occur inside the boundary layer (small scale vortices). Large velocity gradients exist in the boundary layer, causing high viscous stresses which can aid in reaction acceleration and the removal of surface contaminants [7]. The acoustic boundary layer thickness is equal to  $(2\nu/\omega)^{1/2}$ , and thus becomes smaller as frequency increases. At 900 kHz it is only about 0.6  $\mu\text{m}$  [1].

An additional type of acoustic streaming is related to cavitation. Microstreaming occurs near bubbles of a compressible substance such as a gas in the irradiated liquid. In this powerful type of streaming, the bubbles scatter sound waves and generate remarkably swift localized currents which can also contribute to cleaning. The currents are most pronounced near bubbles undergoing volume resonance and located along solid boundaries [8].

### 3. PARTICLE REMOVAL EXPERIMENTS

Experiments were performed using a commercially available high-power megasonic tank integrated in a wet bench. Wafers were intentionally contaminated with submicron silica and silicon nitride particles as an aerosol using a nebulizer. The solutions used were water and SC1 ( $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ ). A statistically designed set of experiments was performed for each particle type; independent variables were megasonic power, and SC1 ratio R (where R is defined as the volume ratio of  $\text{NH}_4\text{OH}$  divided by the volume ratio of  $\text{H}_2\text{O}_2$  such

that a standard SC1 solution of 5:1:1 has an R value equal to 1.0).

Figures 1 and 2 show the removal efficiency of silica particles in DI water and SC1 (5:1:1), respectively, as a function of power and temperature. Power clearly has a greater effect than temperature. Removal efficiencies were low at all temperatures when power was near zero. When power is tuned properly (about 500-600 W), however, highly efficient removal can be obtained over a wide range of temperatures. As expected, silicon nitride was harder to remove than silica due to zeta potential interactions.

The following model for cleaning of wafer surfaces by megasonics is proposed. Particles are adhered to the wafer surface by van der Waals and sometimes chemical bonds which must be overcome in order for the particles to be detached from the wafer. Once particles are detached a favorable electrical charge interaction between particle and wafer prevents redeposition. Furthermore, fluid flow is important in transporting detached particles from the wafer surface region (boundary layer) to the main flow and away from the wafers to a drain or filter recirculation. It is concluded from the present work that forces due to stable cavitation and associated microstreaming aid in the detachment of particles from the wafer, while acoustic streaming provides efficient transfer of detached particles away from the wafer surface due to strong currents and boundary layer thinning.

An explanation for the decrease in removal efficiency at high powers is as follows. It has been reported in the literature that as power applied to transducers is increased, the actual intensity in the liquid increases linearly to a maximum, after which it *decreases* [9]. The decrease occurs when so many gas bubbles are created that these bubbles scatter the sound waves to the vessel walls or back toward the transducer. Additionally, the absorption of sound energy in a gas is substantially larger than in a liquid (absorption coefficient four orders of magnitude larger). Thus, ultrasonic efficiency and therefore the actual intensity in the tank are lowered. It is possible that at such high powers the cavitation begins to transform from stable to transient.

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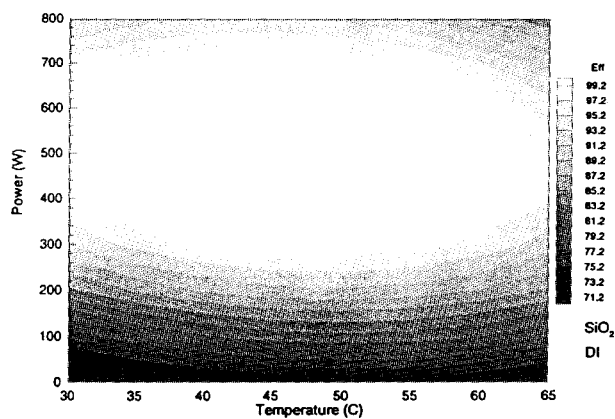


Figure 1. Contour plot showing removal efficiency of silica particles in DI water as a function of temperature and power.

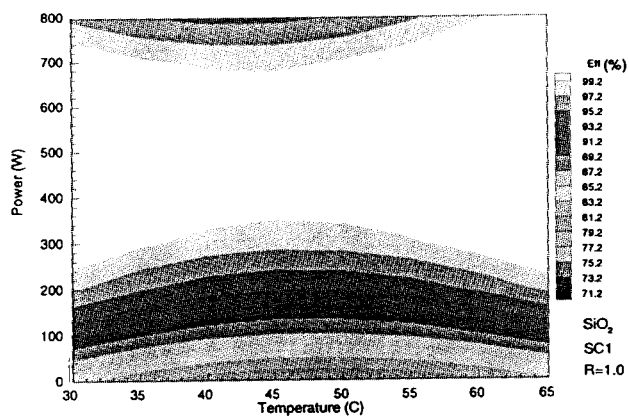


Figure 2. Removal efficiency of silica particles in SC1 as a function of power and temperature (5:1:1 SC1)



## A Theoretical Evaluation of Megasonics Performance For Sub-Micron Particles

Moshe Olim  
FSI International  
322 Lake Hazeltine Drive  
Chaska, MN 55318, USA

### 1 Introduction

There is a great deal of confusion in the literature regarding the physics of Megasonic particle removal. Cavitation effects are generally believed (see [1]) to play no role in Megasonic cleaning. In addition to that, they are uncontrollable and, while having the potential to enhance the cleaning, may also severely damage the surface (see [2]). Acoustic streaming forces were shown in [3] to be two orders of magnitude below the van der Waals force for a  $1\mu m$  particle. Thus, the mechanism by which the Megasonic energy is converted to force on a particle has never been clarified.

In this report the physics of particle removal by Megasonic waves is analyzed, and the relevant quantities are evaluated. It is shown that the removal force scales as the cube of the particle diameter, and that the technology should not be expected to work for particles of the order of 0.1 micron and smaller.

The megasonic particle removal effects are produced by generating sonic waves in the frequency range of 0.7 to 1.5  $MHz$ . These waves emanate from piezoelectric transducers mounted on the bottom or the sides of the tank. Vibration of these transducers generates compression and expansion waves which propagate into the tank. A vibrating transducer and a one-dimensional sonic wave are depicted in Figure 1. When a sonic wave passes over a particle, the pressure gradient in that wave exerts a force acting on the particle. This mechanism is schematically depicted

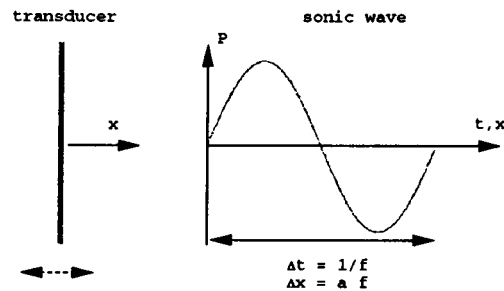


Figure 1: Oscillating transducer and sonic waves.

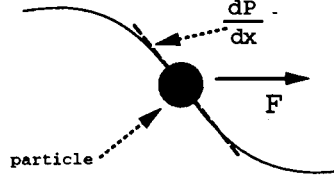


Figure 2: Pressure gradient exerting a force.

in Figure 2. While an extensive literature search revealed no satisfactory attempt to quantify the force exerted by the sonic waves, it is generally believed (e.g. [4], p.421) that if this force exceeds the adhesion force between the particle and the wafer then the particle will be dislodged.

The analysis presented herein is carried out assuming that the sonic waves propagate in one dimension only. In reality the waves propagate in three dimensions and their energy is dispersed. Thus, the analysis presented herein is that of a “best case scenario”, i.e. the real limits of the process are more stringent than those resulting from this analysis.

## 2 Analysis

The pressure gradients in the sonic wave exert a force acting to dislodge an adhered particle. This force can be calculated by integrating the pressure over the particle surface. Since the acoustic wave length is  $O(1mm)$  which is orders of magnitude larger than the particle diameter, the pressure gradient may be treated as constant yielding an absolute value of the force exerted on the particle:

$$F_{meg} = \frac{dP}{dx} \frac{\pi}{6} D^3 \quad (1)$$

where  $P$  is the pressure,  $x$  is the spatial coordinate, and  $D$  is the particle diameter. Equation (1) clearly shows that the removal force of the Megasonic process scales as the cube of the particle diameter (while adhesion scales as  $D$ ). If this force is larger than the adhesion force between the particle and the wafer,  $F_{ad}$ , the particle will be dislodged. To evaluate the dislodging force  $F_{meg}$  one must calculate the pressure gradient in the sonic wave.

The pressure gradient may be estimated by utilizing methodology from the field of compressible fluid dynamics. When the transducer starts moving it generates a sound wave which propagates into the liquid. The wave propagation in this process is schematically depicted in Figure 3 on an  $x, t$  diagram. In this figure the transducer is initially located at  $x = 0$ , and at  $t = 0$  it starts moving to the right at a speed  $v$ . The sound wave generated by the transducer also moves to the right at the speed of sound,  $a$ . During a time  $\Delta t$  this sound wave travels over the distance  $\Delta t \times a$ .

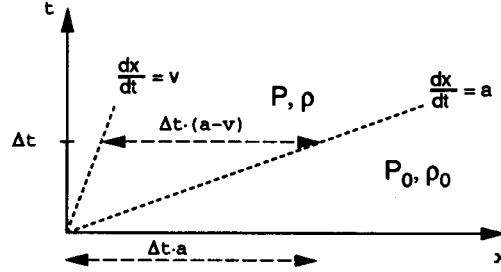


Figure 3: Waves in the system.

The distance the transducer moves during the same time interval is  $\Delta t \times v$ . Thus, the liquid that occupied the space  $\Delta t \times a$  now occupies the space  $\Delta t \times (a - v)$  and, consequentially, is compressed from its original density,  $\rho_0$ , to a density  $\rho$ . The average density of the compressed liquid is given by

$$\rho = \rho_0 \frac{a}{a - v} \quad (2)$$

leading to the following density increase

$$\Delta \rho = \rho - \rho_0 = \rho_0 \frac{v}{a - v} \quad (3)$$

From the definition of the speed of sound the pressure increase is

$$\Delta P = a^2 \Delta \rho \quad (4)$$

from which the pressure gradient required in Equation (1) may be estimated:

$$\frac{dP}{dx} \approx \frac{\Delta P}{\Delta x} \approx \frac{a^2 \rho_0}{\Delta x} \frac{v}{a - v} \quad (5)$$

where  $\Delta x = a/f$  is the acoustic wave length,  $f$  being the transducer frequency. The velocity of the transducer may be estimated from

$$v \approx 2 A f \quad (6)$$

where  $A$  and  $f$  are, respectively, the amplitude and the frequency of the transducer.

By substituting the appropriate variables into Equation (1) and given that  $a \gg v$  this force may now be represented as

$$F_{meg} \approx \rho_0 A f^2 D^3 \quad (7)$$

Based on the quantities presented in the Ultrasonic and Megasonic sections of [4], the vibration amplitude of a transducer is of the order of a micron. Substitution of  $\rho_0 = 1000 \text{ kg m}^{-3}$  and  $f = 1 \text{ MHz} = 10^6 \text{ s}^{-1}$  into Equation (7) yields

$$F_{meg} \approx 1 \times 10^9 D^3 \quad (8)$$

where force is given in Newtons and the particle diameter,  $D$ , is given in meters. Thus, for a  $1\mu m$  particle, the megasonic force is of the order of  $1 \times 10^{-9} N$ . According to [5], the adhesion force between a  $1\mu m$  silica particle and a bare silicon surface in water is of the same order thus enabling removal of the particle.

Given that the above analysis is Order of Magnitude analysis and that the performance of Megasonic cleaning is improved by using SC-1 and/or SC-2 chemistry (see [6] in which particles larger than  $0.1\mu m$  were removed) it is reasonable to extend the range of applicability of the analysis by another order of magnitude. Thus, it is possible that the actual particle size where megasonic force is approximately equal to the adhesion force is closer to  $0.1\mu m$  than to  $1\mu m$ . As shown by Equation (1), the force exerted on the particle scales as the cube of the particle diameter. Thus, since the adhesion force scales approximately as the particle diameter, Megasonic cleaning cannot be expected to perform for particles smaller than  $0.1\mu m$ .

### 3 Conclusions

In this report the physics of particle removal by a Megasonic wave is analyzed, and the relevant quantities are evaluated. It is shown that the removal force scales as the cube of the particle diameter, and that Megasonics technology should not be expected to work for particles of the order of 0.1 micron and smaller.

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## CRYOGENIC AEROSOL CLEAN: A NOVEL APPROACH TO WAFER CLEANING

Raj Shah, IBM assignee to SEMATECH  
J.J. Wu, Chien Yu, Chi Hua Yang, Donna Miura,  
Nancy Greco, George Gifford  
Advanced Semiconductor Technology Center  
IBM Microelectronics, East Fiskill, New York  
Gerald Smolinsky, SEMATECH

### 1.0 INTRODUCTION:

A new enabling technology has been developed in IBM. Cryogenic Aerosol Clean has been shown to be very effective for removing particulate contaminants from wafer surfaces (1-3). When the high velocity aerosol spray is directed toward a surface, the collision of the frozen particles in the stream with surface contaminants imparts sufficient energy to dislodge them. To dislodge debris on the sidewalls of etched structures, the size of cryogenic particles within the jet must be properly controlled so that they can penetrate into the restricted geometries associated with semiconductor devices. The orientation of the cryogenic stream relative to that of the etched structures must be optimized to result in an efficient process. The pressure and temperature conditions of the gas liquid mixture typically fall within 20-180 psi and 80-110 Kelvin, respectively.

This paper reports the feasibility study of cryogenic aerosol cleaning as a dry-cleaning method for removing particles and post-etch residues following the etching and ashing process on 0.35  $\mu\text{m}$  device structures. Split-lot evaluations were used to compare the cryogenic cleaning process to standard wet cleaning methods. Specifically, cryogenic aerosol cleaning was compared to N-methyl-2-pyrrolidone (NMP), sulfuric acid plus hydrogen peroxide (SP), and the IBM-standard wet clean for removing particles and residues remaining on wafers after oxide, polysilicon, and metal etching processes. Cryogenic aerosol cleaning is an environmentally friendly process; no hazardous chemicals; no waste treatment and no disposal problems. The gases used are benign, the gas pressures modest and the power consumption relatively small. Preliminary cost-of-ownership calculation indicate significant savings by cryogenic aerosol cleaning process per wafer pass.

## **2.0 POST-OXIDE ETCH EVALUATION:**

### **2.1 Experimental Methods and Procedures:**

Short-loop defect monitor wafers containing electrical test structures were fabricated. Each wafer contained 96 test sites, and each test site consisted of five defect mazes with two serpentine patterns and two finger patterns of various array sizes. Each of the five mazes is designated A, B, C, D, or E and represents the 1, 2, 4, 8, and 16 Mbit-equivalent array size, respectively. The minimum ground rule for the comb and serpentine structures was 0.4  $\mu\text{m}$ . A minimum of four wafers from each cleaning slit were selected and 40 test sites on each wafer were electrically tested. Open defects were distinguished from short defects and yields associated with each are reported. Residue removal by the cryogenic aerosols at the center and edge of the wafers were verified by SEM analysis. Electrical testing was made by applying five volts across the metal lines.

The oxide patterns consisted of 0.4  $\mu\text{m}$  lines and 0.475  $\mu\text{m}$  spaces that were etched, using a  $\text{CF}_4/\text{CHF}_3$  plasma after a deep ultraviolet (DUV) lithographic process performed on a Micrascan 92. Following etching and stripping, the patterned wafers (split-lot) were subjected to either a cryogenic aerosol clean or NMP solvent clean. A conductance path was formed by filling the etched oxide structures with tungsten. Any excess metal was removed by chemical/mechanical polishing (CMP). Electrical opens and shorts testing was made by applying five volts across the metal lines.

Test wafers were examined by a KLA 2130 patterned-wafer defect inspection system. The resulting defect maps were used in an optical microscope inspection to characterize and identify the sources of the defects. SEM examinations were made both before and after aerosol cleaning. For these, center and edge portions of the wafer were cross-sectioned to reveal the distribution and quantity of residue. The differences observed between the before and after cleaning were quantitatively related to the effectiveness of the aerosol cleaning process.

### **2.2 Results and Analysis**

#### **2.2.1 Defect Types**

To gain an understanding of defect development, their number and evolution were followed on some wafers by KLA mapping and optical inspection. These analyses were carried out throughout wafer fabrication, after lithography, etching and stripping, cleaning, and electrical testing. Using this technique, 0.3  $\mu\text{m}$  defects could be identified. Results showed that a majority of the defects were developed during the lithography process; a small fraction existed as electrical opens. Other types of defects included stains, charred resist, and streaks. Recurring defects were examined by SEM to reveal their nature and potential mechanism of formation; for example, a streak found after lithography. Although the streak did

not develop into an open defect, its formation and nature deserves further investigation.

### 2.2.2 Aerosol Cleaning Performance

To uncover any processing residues, some wafers were cross-sectioned before and after aerosol cleaning and subjected to a SEM analysis. It was found that the bulk of the photoresist was removed by the stripping process. However, any small amount of residual resist can reduce the conductance of the metal lines and result in an open circuit and/or a reliability problem. A residue with a physical size of  $\geq 0.16 \mu\text{m}$  (one-third of line spacing,  $0.475 \mu\text{m}$ ), inside an etched structure, can cause the electrical current to drop below the threshold (e.g.,  $0.0145 \mu\text{A}$ ) for the E maze (16-Mbit-array size) and register as an open. (On the other hand, shorts between metal lines are generally caused by incomplete metal polishing and/or by damage or pitting produced on the oxide. They are less likely to be related to etching residues.) Examination of the cleanliness inside etched structures on the center and on the edge of wafers, together with different orientations of these structures (Figure 1), shows the effectiveness of the aerosol-cleaning process.

### 2.2.3 Electrical Test Results

Forty of the 96 chips on each defect monitor were tested for open circuits. Measurement of electrical continuity was performed on each of the two serpentine patterns within each of the five mazes. The defect maps obtained in this way provided a means of identifying potential systematic problems. The composite yields of the NMP and aerosol-cleaning processes from four defect monitors of each group are summarized in Table 1 along with the results from second split test performed one month later. The defect density calculation assumed that all defects are random in distribution. Since the number of the defects is significantly lower than the number of test sites, the distribution of random defects approaches a Poisson distribution. The relationship between the testing yield and the defect density is expressed as [4]

$$Y = Y_0 \exp [-DA_{cr}]$$

where  $A_{cr}$  is the critical area defined as the area in which the center of a defect must fall to cause an electrical problem, and  $Y_0$  is the limiting yield at zero critical area

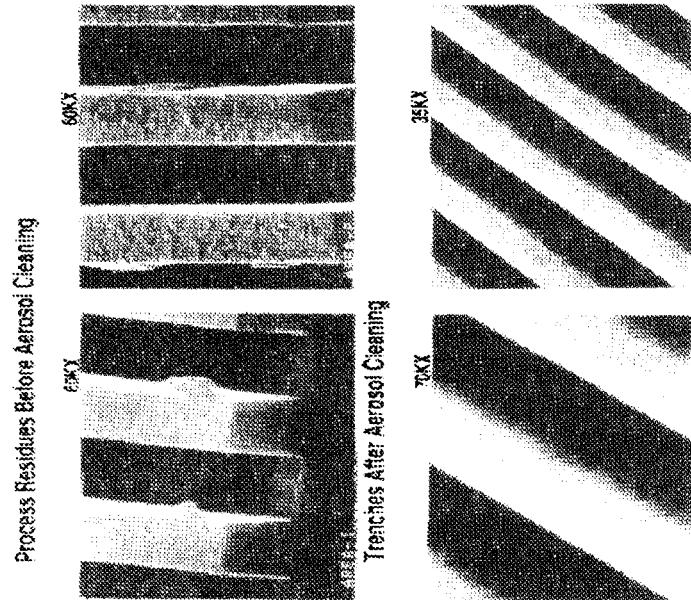


Figure 1 SEM Photomicrographs of Oxide Structures Before and After CAWC

Table 1: Open-Circuit Electrical Yields and Defect Densities:  
NMP Solvent Cleaning versus Cryogenic-Aerosol Cleaning

| Test<br>(Calc $Y_0$ ) | Percent Yield (Good) |             |             |             |              | Defect Density<br>(D, $\text{cm}^{-2}$ ) |
|-----------------------|----------------------|-------------|-------------|-------------|--------------|------------------------------------------|
|                       | 1 Mb<br>(A)          | 2 Mb<br>(B) | 4 Mb<br>(C) | 8 Mb<br>(D) | 16 Mb<br>(E) |                                          |
| #1                    |                      |             |             |             | 96.5         |                                          |
| NMP (98.9)            | 98.3                 | 98.3        | 99.5        | 97.3        | 99.5         | 0.014                                    |
| CAC (99.6)            | 100.0                | 99.0        | 99.5        | 100.0       |              | nil                                      |
| #2                    |                      |             |             |             | 95.2         |                                          |
| NMP (98.6)            | 100.0                | 98.8        | 100.0       | 92.8        | 95.2         | 0.034                                    |
| CAC (98.3)            | 98.3                 | 97.3        | 97.3        | 98.5        |              | 0.015                                    |

The theoretical value of  $Y_0$  is 100% if all defects are truly random. The calculated values of  $Y_0$  in Table 1 were obtained by a linear least-square fit of the data (i.e., the logarithmic value of the open yield,  $Y$ , versus the critical area,  $A_{cr}$ , of the tested mazes). In both Tests 1 and 2, the aerosol-cleaning splits possess a tighter fit than the NMP splits. The fact that all values of  $Y_0$  approach 100% validates the assumption of randomness. The defect densities of aerosol-cleaned wafers are slightly lower than the NMP cleaned wafers.



The test for electrical shorts is a measurement of the leakage current between two adjacent comb and serpentine patterns in the mazes. The yields from the shorts test provide additional insight into the adverse effect of the cleaning processes. The shorts can be a result of incomplete metal polishing. Any damage or pitting produced on the oxide during the cleaning processes potentially could cause shorts as well. Table 2 shows the composite shorts yields of the cleaning splits. The same fabrication and testing procedures were used as for the test wafers measured and reported in Table 1.

The defect densities calculated from the shorts yields and shown in Table 2 do not constitute a direct measure of cleaning performance following CMP processing. For example, some of the particles left behind from the post-polish cleaning process are dielectric and may not produce shorts. However, the consistent findings of yields and defect densities from both measurements, shorts and opens, suggest that any damage caused by the cryogenic-aerosol cleaning process is negligible.

**Table 2**      **Short-Circuit Electrical Yields and Defect Densities:  
NMP Solvent Cleaning Versus Cryogenic Aerosol Cleaning**

| Test<br>(Calc Y <sub>o</sub> ) | Percent Yield (Good) |             |             |             |              | Defect Density<br>(D, cm <sup>-2</sup> ) |
|--------------------------------|----------------------|-------------|-------------|-------------|--------------|------------------------------------------|
|                                | 1 Mb<br>(A)          | 2 Mb<br>(B) | 4 Mb<br>(C) | 8 Mb<br>(D) | 16 Mb<br>(E) |                                          |
| #1                             |                      |             |             | 96.3        |              |                                          |
| NMP (99.4)                     | 99.3                 | 99.3        | 99.3        | 99.5        | 96.8         | 0.019                                    |
| CAC (100.2)                    | 99.5                 | 100.0       | 99.5        |             | 97.0         | 0.017                                    |
| #2                             |                      |             |             |             |              |                                          |
| NMP (99.2)                     | 99.5                 | 98.0        | 99.0        | 97.0        | 98.0         | 0.020                                    |
| CAC (99.5)                     | 100.0                | 98.5        | 98.5        |             | 96.5         | 0.018                                    |

### 3                      Summary

Split-lot testing has demonstrated that cryogenic-aerosol cleaning can replace NMP solvent cleaning to remove particles and photoresist residues following plasma ashing. The demonstration was performed with wafers having features with submicron dimensions. Evaluations were made at those points in the fabrication sequence when the device was sensitive to contamination.

In this study, KLA defect inspection, followed by optical review, concluded that the majority of the defects  $\geq 0.3 \mu\text{m}$  identified by the inspection are not particles, but are mostly lithographic defects. A SEM examination, which revealed smaller processing residues than can be identified by a KLA/optical review, has shown cryogenic-aerosol cleaning completely removed resist residues on the sidewall of

etched structures. Films on wafers cleaned with a cryogenic aerosol withstood a peel test slightly better than films on wafers cleaned with an NMP solvent process. The minute amount of film peeled from the NMP cleaned wafers contained some fluorocarbon contaminant that was detected by XPS.

To verify the overall performance and integrity of the cleaning processes, short-loop structures were tested electrically. The test structures were designed to have a sensitivity to defect densities as low as  $0.009/\text{cm}^2$ . The nearly equal short-circuit yields observed with wafers cleaned by either method indicate that cryogenic aerosol clean did no damage to the structures. Particles and/or residues generated during the etching process affected the open-circuit yields measured in this evaluation. Both cleaning procedures resulted in a >95% yield for the 16-Mbit equivalent array maze. The aerosol cleaned group showed slightly better performance than the NMP solvent cleaned group.

Using the electrical-test results, the defect density attributed to residues on the aerosol-cleaned wafers was  $<0.015/\text{cm}^2$  (size  $\geq 0.16 \mu\text{m}$ ). These results demonstrate that the SEMATECH NMP process defect goal for 0.25  $\mu\text{m}$  technology (1997) is possible using cryogenic aerosol clean.

Cryogenic aerosol cleaning is an environmentally friendly process. There are no hazardous chemicals, no waste treatment, and no disposal problems. The gases used are benign, the gas pressures modest, and power consumption relatively small. Operators can be readily and completely shielded from the process.

Cryogenic aerosol cleaning is an alternative to wet chemical cleaning for the removal of particles and process residues. These tests show that a cryogenic aerosol clean is sometimes more but never less efficacious than a corresponding wet cleaning process. In addition, cryogenic aerosol processing was found to be safe to the product (i.e., no mechanical damage) and favorable in cost to state-of-the-art wet cleans.

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## REMOVAL OF FLUORINE AND CF<sub>x</sub> RESIDUE FROM Si (100) SURFACES BY REMOTE RF HYDROGEN PLASMA

J.P. Barnak, H. Ying, S. King, And R.J. Nemanich\*

A remote rf plasma was employed to remove fluorine and CF<sub>x</sub> residues using H<sub>2</sub> or H<sub>2</sub>/SiH<sub>4</sub> chemistries. The Si(100) surface was intentionally contaminated to approximate the residual fluorine concentration remaining after an HF last process. A H-plasma exposure reduced fluorine below the detection limit of XPS. Remote H<sub>2</sub> and H<sub>2</sub>/SiH<sub>4</sub> plasma processes were studied as potential dry cleaning methods following RIE. The RCA oxide on a Si(100) substrate was removed using a CHF<sub>3</sub>+Ar RIE. Auger electron spectroscopy (AES) and AFM were used to characterize the Si surface. A 400W remote plasma processes removed the CF<sub>x</sub> residue layer below the detection limits of AES in less than 1 minute. The results demonstrate the potential use of a remote H<sub>2</sub> and H<sub>2</sub>/SiH<sub>4</sub> plasma processes as an *in situ* cleaning module on a cluster tool prior to selective Si epitaxial growth or contact formation.

### 1. INTRODUCTION

#### 1.1 Fluorine Removal

Atomic and ionic hydrogen sources have been shown to be effective in removing impurities, such as carbon, oxygen, and halides, from semiconductor surfaces[1-2]. We intentionally placed contaminants on the Si surface that might occur after a HF dip or HF vapor phase clean and developed a cleaning process that removes those contaminants. A concentrated HF dip was chosen since the amount of residual F remaining on the Si surface increases as the HF concentration in solution increases[3]. By using an H-plasma after an HF last step the residual contaminants are removed and it leaves a hydrogen terminated surface. In this study a mechanism is proposed for fluorine removal by atomic hydrogen generated from a remote rf H-plasma.

#### 1.2 CF<sub>x</sub> Removal

Anisotropic SiO<sub>2</sub>/Si selective etching processes are employed prior to source-drain and contact formation[4-13]. It has been suggested that the deposition of a fluorocarbon (CF<sub>x</sub>) film on the Si Surface is crucial to achieve the SiO<sub>2</sub>/Si etch selectivity[8,9]. The CF<sub>x</sub> film must be removed prior to further processing. Processes that have demonstrated

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\* Center for Advanced Electronic Materials Processing  
North Carolina State University, Raleigh, NC 27695-8202

success in post RIE cleans include: (1) thermally grown sacrificial oxide[5], (2) O<sub>2</sub> plasma [6,9,10], and (3) UV/O<sub>3</sub>[11]. In each case, however, a wet etch step (HF dip) was involved. It would be advantageous to use a dry cleaning process after RIE. A cleaning procedure based on a hydrogen plasma process reduced a CF<sub>x</sub> polymer film from 5nm to 1nm[12]. Post RIE treatment in an NF<sub>3</sub>/Ar plasma completely removed the CF<sub>x</sub> polymer film as well as the subsurface defect zone, but increased surface roughness[13]. It has also been shown that the surface morphologies are dependent on substrate temperature and pressure during H-plasma cleaning[14,15]. H-plasma exposures at 350-550°C result in a smooth H-passivated surface and no subsurface damage[15]. In this study, a similar H-plasma process was utilized as a post RIE cleaning process.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Fluorine Removal

The one inch Si(100) wafers used in this study were p-type boron doped(0.8-1.2ohm-cm). The wafers were RCA cleaned then dipped in a 49% HF solution for 10s. The XPS and plasma chambers are connected through a UHVsample transfer mechanism; permitting the samples to be moved from chamber to chamber *in situ*. A schematic and the operation of the remote plasma cleaning system has been previously described[16]. The surface of each sample was characterized using XPS after each of the following steps: (1) 10s HF dip (as loaded condition for all samples), (2) 450°C vacuum anneal for 5min, and (3) 450°C H-plasma for 0.1min. For the H-plasma cleaning experiments, the H<sub>2</sub> flow was established prior to increasing the temperature. In the H-plasma cleaning experiments, the wafers were exposed to a rf (13.56MHz) excited remote H-plasma using the following conditions: (1) 50mTorr, (2) 20W rf, (3) 450°C, and (4) 141sccm H<sub>2</sub>. The pressure was controlled by the H<sub>2</sub> flow rate.

### 2.2 CF<sub>x</sub> Removal

The RCA oxide was removed down to the Si substrate using a CHF<sub>3</sub>+Ar RIE. The rf power was 85W (0.15W/cm<sup>2</sup>), and the gas flow rates were 40sccm CHF<sub>3</sub> and 10sccm Ar. The SiO<sub>2</sub> was etched at 60mTorr. The pressure was increased to 90mTorr for an additional 0.5min to deposit a 15nm conformal CF<sub>x</sub> polymer film as a capping layer on the Si surface. For the post RIE cleans three approaches were studied: (1) UV-O<sub>3</sub>/HF; 10min UV-O<sub>3</sub> exposure followed by a 1min HF dip(10:1) repeated twice, (2) remote H-plasma at 450°C, 85sccm H<sub>2</sub>, 15mTorr, 20W and 100W rf power, and (3) remote H<sub>2</sub>/SiH<sub>4</sub>-plasma at 450°C, 25mTorr, and 400W rf power. The H<sub>2</sub> and H<sub>2</sub>/1% SiH<sub>4</sub> flow rates were 86sccm and 10sccm, respectfully. The gases were mixed prior to entering the plasma chamber. Once the wafers were RIE etched the samples were transferred *in situ* between the H-plasma chamber and the AES and LEED surface analysis chambers[14]. The surface roughness of the wafers was characterized by atomic force microscopy(AFM).

### 3. RESULTS AND DISCUSSION

#### 3.1 Fluorine Removal

The residual surface concentration of F on a Si(100) wafer after dipping in concentrated HF was measured by XPS (Figure 1.). Following an HF dip the F 1s peak was centered at 685.9eV (Figure 1.a). This wafer was annealed at 450°C for 5min at  $10^{-10}$ Torr. The F 1s peak after annealing is shown in Figure 1.b and indicates that the majority of F remained on the silicon surface. However the position of the F 1s peak had shifted to a higher binding of 686.2eV. This is indicative of Si-F bonding and the value agrees with previously published results[17-18]. Since the Si 2p peak position did not shift either before or after annealing, the peak shift cannot be due to charging or spectrometer drift. It is argued that the F 1s peak in Figure 1.a is actually a convolution of two peaks. One belongs to a weakly bound physisorbed state of F, which forms the tail on the low energy side of the peak (Figure 1.a), and the other is due to a strongly bound chemisorbed state of F (i.e. Si-F bonds). Annealing at 450°C desorbs the more weakly bound physisorbed F leaving behind only the chemisorbed F. Figure 1.c shows the XPS spectrum of the F 1s peak after a 0.1min exposure to the remote H-plasma. The F was removed below the detection limits of XPS, and the surface was hydrogen terminated which was concluded from Angled Resolved UV Photoemission Spectroscopy (ARUPS) data[19]. The chemisorbed F reacts with H from the plasma to form HF which desorbs from the surface[20]. These Si dangling bonds react with atomic H to form a H passivated surface.

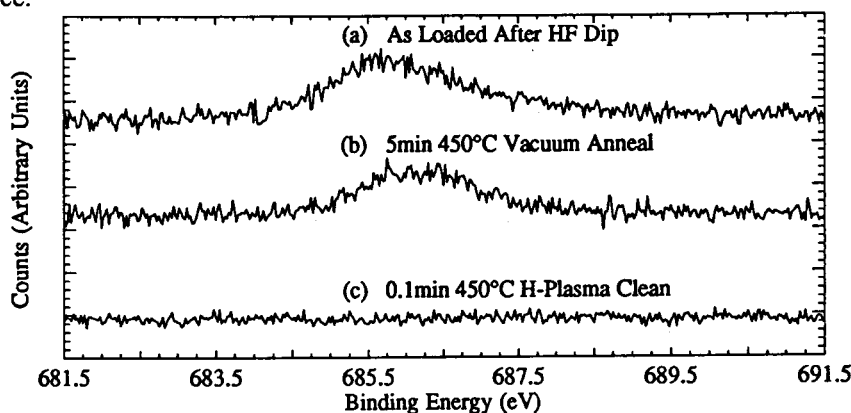


Figure 1. F 1s XPS spectra illustrating the effectiveness of the 0.1min 450°C hydrogen plasma clean in removing fluorine below the detection limit of XPS.

#### 3.2 CF<sub>x</sub> Removal

The AES spectra of the CF<sub>x</sub> film removal by remote H-plasma is shown in figure 2. By exposing the residue to 400W H-plasma at 15mTorr and 450°C, the CF<sub>x</sub> polymer film

was completely removed in less than 1min. Longer exposure leads to a decrease but not complete removal of the residual oxygen contamination. The oxide was apparently formed during the RIE process and might be buried in the defect sites at the near surface region. In each of the post RIE cleaning approaches the F was below the AES detection limit. This agrees with the experimental observation that F is more effectively removed from the contamination layer than C[12]. All three processes exhibit a significant reduction in surface contaminants with essentially submonolayer carbon and oxygen residuals. Both *in situ* techniques show no detectable C between 1 and 10min exposures, while the *ex situ* approach of UV-O<sub>3</sub> and HF dip showed some C that may be attributed to the wafer transfer into the AES system. Both plasma processes show slight increases of oxygen after the removal of the RIE CF<sub>x</sub> passivation layer. It is probable that this oxygen formed during the RIE process as the passivation layer was formed. With the addition of a small amount of SiH<sub>4</sub>, the remote H<sub>2</sub>/SiH<sub>4</sub> plasma was more effective for oxygen removal[21]. It was also shown that the very dilute H<sub>2</sub>/SiH<sub>4</sub> plasma results in SiO<sub>2</sub> etching with no Si deposition on any oxide surfaces[21]. Although there is a small increase in roughness observed by AFM, low energy electron diffraction (LEED) measurements display the expected 2x1 surface reconstruction indicating that the surface is crystalline and not amorphized by either the RIE or the H-plasma clean. Future studies will explore whether the epitaxial quality will be effected by the small increase in surface roughness.

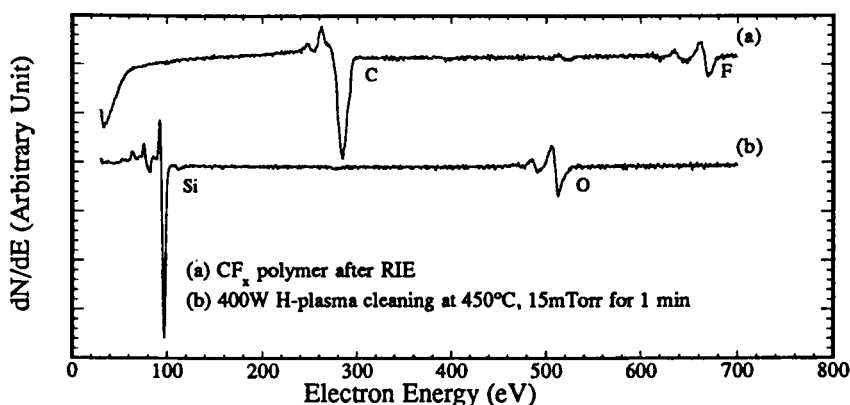


Figure 2. RIE passivation layer removal by remote H-plasma cleaning.

#### 4. CONCLUSIONS

The remote hydrogen plasma removes the residual fluorine and CF<sub>x</sub> polymer using either an H<sub>2</sub> or H<sub>2</sub>/SiH<sub>4</sub> plasma chemistry, respectively. Once the fluorine species were removed the Si surface was hydrogen terminated due to the flux of atomic hydrogen from the plasma. This hydrogen passivation layer prevents further recontamination of the Si surface. The plasma processes described here could prove useful as a cleaning module

for single wafer clustered systems. Future studies will focus on issues related to Si epitaxial growth and defect structures.

## 5. ACKNOWLEDGMENTS

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## CHEMICAL VAPOR CLEANING OF TRANSITION METALS FROM WAFER SURFACES

S.E. Beck, M.A. George, D.A. Bohling, D.A. Moniot, K.M. Young, and A.A. Badowski

Air Products and Chemicals, Inc., Allentown, PA, USA

### 1. INTRODUCTION

A novel vapor phase clean utilizing chelation compounds such as 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ( $H^+hfac$ ) and 1,1,1-trifluoro acetic acid ( $H^+tfaa$ ) has been suggested for the removal of transition metals from wafer surfaces [1].  $H^+hfac$  reacts with a variety of transition metal oxides [2-5]. The basis of these vapor phase cleans is the heterogeneous reaction of coordinating gas phase ligands with the surface contaminants forming volatile coordination compounds or organometallic compounds. This process is illustrated with the reaction of  $H^+hfac$  with copper (II) oxide



In this work we explore the effects of varying processing conditions on the removal of copper and iron initially present on wafer surfaces at near-monolayer levels. Previous work has shown that the  $H^+hfac$  molecule can decompose under certain processing conditions producing trifluoroacetate ( $C_2HF_3O_2$ ) [5,6]. In that work it was suggested that some removal of transition metals was in the form of a  $tfaa$ -based molecule such as  $Fe(hfac)_x(tfaa)_{3-x}$  where  $0 \leq x \leq 3$ . Due to this finding a portion of this work also explores the differences between the use of  $H^+hfac$  and  $H^+tfaa$  for transition metal removal.

### 2. EXPERIMENTAL

Copper and iron contaminated samples were prepared on thermally oxidized 150 mm diameter, {100} silicon wafers via evaporation. All wafers underwent SC1 and SC2 cleans before the intentional contamination step. Metals were deposited by evaporation with the wafers held at room temperature to ensure that the metals resided on the wafer surface. Three points on each wafer were analyzed by total reflection x-ray fluorescence (TXRF) before cutting them into  $1\text{cm} \times 1\text{cm}$  squares for processing. Typical initial contamination levels on these samples were  $1.1 \times 10^{15}$  Cu atoms/cm<sup>2</sup> and  $1.6 \times 10^{15}$  Fe atoms/cm<sup>2</sup>.

Exposures were done in a vertical furnace capable of handling wafers up to 3 inches in diameter. Two special pedestals were manufactured to hold the  $1\text{cm} \times 1\text{cm}$  samples either perpendicular to or 30° relative to the gas flow in the reactor. A syringe pump (ATI Orion Sage Model M365) was used to inject the chelation compounds into the process chamber through a 0.005 inch ID PEEK capillary at a rate of 0.1 ml/min. This produced an  $H^+hfac$  partial pressure of 0.6 torr. All exposures were performed in a dry air (79%  $N_2$ /21%  $O_2$ ) ambient at a total pressure of 7.6 torr and a temperature of 300 °C unless otherwise stated. Exposure times varied from 6 to 60 minutes. Surface SIMS was performed on samples cut from the original wafers and on the exposed samples to ensure consistency in the measurements [7].

### 3. RESULTS

Flow dynamics play an important role in the removal of surface metal contamination. We have found that the sample orientation within the reactor can dramatically affect the final surface metal concentration. By rotating the sample from an orientation 90° relative to the gas flow to 30° relative to the gas flow, final surface concentrations can be reduced by as much as one and one half orders of magnitude. This can be seen by comparing the 7.6 torr results in Figure 1 with the 6 min. H<sup>+</sup>hfac results in Figure 2. Further optimization of reactor flow dynamics was beyond the scope of this study, although pressure and temperature changes can have a dramatic effect on gas dynamics.

The removal of Cu and Fe from wafer surfaces as a function of processing conditions was examined. Sub-monolayer Cu and Fe contaminated samples were exposed to H<sup>+</sup>hfac for 6 minutes at various pressures while keeping the space velocity within the reactor constant at 34 cm/sec. Samples were held 30° relative to the gas flow and the sample temperature was maintained at 300°C. The initial Fe and Cu concentrations were  $3 \times 10^{14}$  cm<sup>-2</sup> and  $2 \times 10^{13}$  cm<sup>-2</sup>, respectively. Figure 1 depicts the result of these exposures. Experiments were also conducted varying the reactor temperature from room temperature to 300°C. After a 6 minute exposure at room temperature the Cu concentration was decreased by a half an order of magnitude, while there was no statistically significant change in the Fe concentration. Arrhenius plots of these data consisted of three regions: a surface diffusion rate limited region, a reaction rate region, and a desorption limited region. From these plots the activation energies for H<sup>+</sup>hfac reaction with sub-monolayer Cu and Fe contamination were determined to be  $2.6 \pm 0.3$  kcal/mol and  $11.8 \pm 2.1$  kcal/mol, respectively. Since it was found that trifluoroacetic acid was formed on Fe surfaces exposed to H<sup>+</sup>hfac [5,6], contaminated samples were also exposed to H<sup>+</sup>tfaa. During these exposures samples were held 90° relative to the gas flow. Results of these exposures are shown in Figure 2. For comparison, results for samples exposed to H<sup>+</sup>hfac held in the same orientation are also depicted in this figure.

### 4. DISCUSSION

A variety of mechanisms may be responsible for the differences in transition metal removal rates during cleaning with H<sup>+</sup>hfac. As can be seen in Figure 1 there is no discernible difference in Cu removal with changing pressure when the residence time is held constant. The final surface Cu concentration is a very low value (concentrations as low as  $6 \times 10^9$  cm<sup>-2</sup> have been achieved). This is most likely due to a rapid copper removal rate resulting in attainment of the low final Cu concentration before the end of the exposure. The extremely small activation energy reported here is indicative of this rapid removal. The reaction of H<sup>+</sup>hfac with sub-monolayers of Cu is most likely first order in H<sup>+</sup>hfac; being a nucleophilic substitution reaction.

The reaction of H<sup>+</sup>hfac with Fe contamination is much more complex. Fe removal is very dependent upon the reactor pressure, indicating the effect of the H<sup>+</sup>hfac delivery rate to the wafer surface (at higher pressures more H<sup>+</sup>hfac is delivered to the surface per unit time). This increases the probability of a reaction with the surface Fe which can decrease the effects of steric hindrance. Although tfaa can be formed on the surface during H<sup>+</sup>hfac exposure, the creation of Fe(tfaa)<sub>3</sub> cannot be entirely responsible for the Fe removal (see Figure 2). Several mechanisms are most likely responsible for the removal of Fe. These include a nucleophilic substitution reaction and a reaction leading to the decomposition of the H<sup>+</sup>hfac molecule resulting in a volatile mixed ligand system [5,8]. The activation energy for Fe removal is low and may be indicative of either a sorption

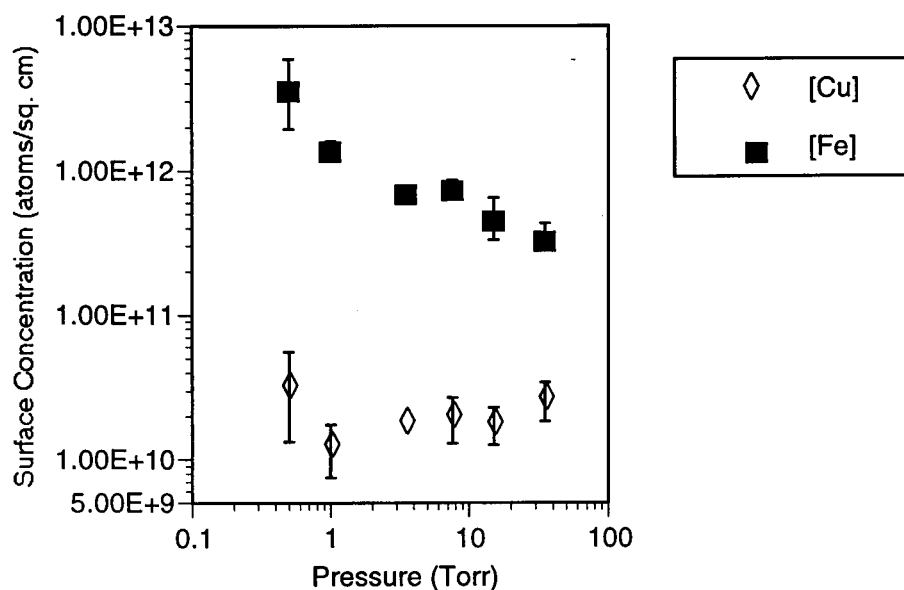


Figure 1. The Cu and Fe surface concentration after a 6 min. exposure to  $H^+hfac$  while varying pressure and maintaining a constant residence time. Samples were oriented at  $30^\circ$  relative to the gas flow.

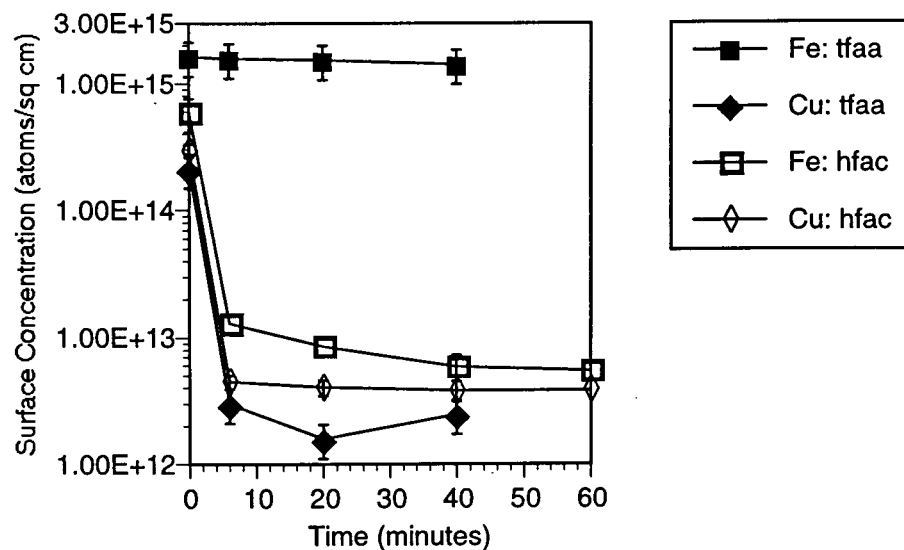


Figure 2. The resultant Fe and Cu surface concentrations after exposure to  $H^+hfac$  and  $H^+tfaa$ . Samples were oriented at  $90^\circ$  relative to the gas flow. Compare the 7.6 torr results in Figure 1 with the 6 min.  $H^+hfac$  results in this figure to see metal removal dependence on orientation.

process [9] or an isomerization reaction [10]. Isomerization reactions require the breakage of chelate oxygen bonds and proceed at activation energies between 13 kcal/mol and 30 kcal/mol. Due to the steric hindrance of accommodating three ligands to Fe on the wafer surface, it is reasonable to expect an intermediate surface species containing Fe bonding to two ligands and the surface. To accommodate the third ligand one can speculate that at least one ligand bond and the surface bond might be broken [11]. This potential mechanism allows for the creation of a volatile mixed ligand system, i.e.,  $\text{Fe}(\text{hfac})_x(\text{tfac})_{3-x}$ .

## 5. ACKNOWLEDGMENTS

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## THE EFFECT OF PRE-ETCH SURFACE HYDRATION ON THE SiO<sub>2</sub> GAS PHASE ETCH PROCESS

J. Staffa\* and J. Ruzyllo\*

### 1. INTRODUCTION

Among the differences between anhydrous HF:methanol gas-phase etching and conventional liquid-phase HF etching is the relative scarcity of moisture available during the gas-phase etch. During a wet etch the effect of the hydration of the oxide both at the surface and in the bulk is largely masked by the availability of water in solution. In contrast, the gas-phase oxide etch is largely limited by the availability of hydroxyl groups necessary to initiate the etch reaction.<sup>1</sup> During the course of the investigation of the AHF:methanol (AHF) gas-phase SiO<sub>2</sub> etching process, it was observed that thermal oxides, grown under the same process conditions, but having different histories between the thermal oxidation and AHF:methanol etch, display greatly differing etch rates when etched under identical process conditions. The object of this study was to explore the nature of these variations and to suggest methodologies for minimizing and monitoring them. In particular, the effect of pre-etch SiO<sub>2</sub> surface hydration on the anhydrous HF:methanol gas-phase etch process is examined through study of the etch rates of aged SiO<sub>2</sub>.

### 2. EXPERIMENTAL

P-type (100) prime silicon wafers with a resistivity of 2-5 ohm-cm were used for this experiment. The wafers were cleaned through a standard AMP clean and dilute HF process. The wafers were then thermally oxidized at 900 °C to the oxide thickness of 200 Å and set aside to allow the surface of the oxide to age. The change in the AHF:methanol etch rate produced by the aging of the SiO<sub>2</sub> surface was observed by etching different wafers in the commercial dry cleaning tool<sup>2</sup> over a period of days under identical etch conditions.

In order to determine the relative difference in the amount of moisture physisorbed and chemisorbed on the oxide surface, static SIMS measurements were carried out on wafers directly from the oxidation furnace, and wafers stored under various conditions for a week. Thermal anneals in nitrogen at the atmospheric pressure and UV irradiation of wafers in vacuum (10<sup>-4</sup> torr) were used to control the effect of surface hydration.

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\*Electronic Materials and Processing Research Laboratory  
Department of Electrical Engineering  
The Pennsylvania State University, University Park, PA 16802

### 3. RESULTS AND DISCUSSION

In the course of our research of AHF:methanol etching of oxides it was observed that oxide etch rates vary significantly depending on the time of exposure of the oxide to the ambient air prior to etching (Fig. 1). The accumulation of moisture on the oxide surface was presumed to be a reason for these variations. Surface hydration related to aging has manifested itself previously as an agent for roughening silicon oxides during thermal oxidation.<sup>3</sup> In an analogous fashion, hydration of the surface may also produce variations in AHF:methanol etching.

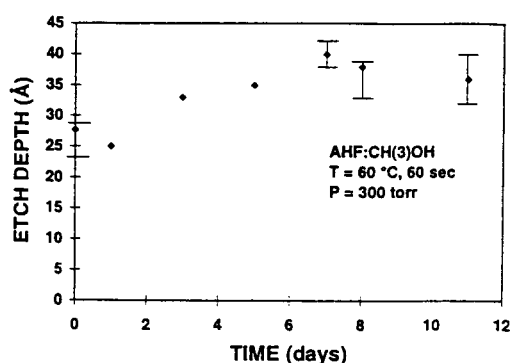


Figure 1 Effect of aging of SiO<sub>2</sub> on the etch rate of the AHF:methanol process

In order to limit the effect of surface hydration on the AHF:methanol etch rates, the wafers were annealed at several different temperatures in nitrogen ambient (Fig. 2).

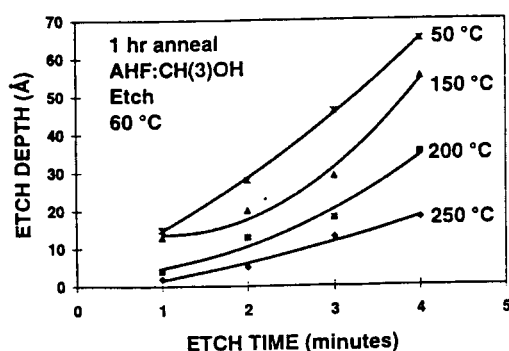


Figure 2 Effect of nitrogen anneal temperature on the gas-phase etch rate

That the change induced by the thermal treatments is in fact related to surface dehydration is indicated by the effect of methanol flow rate during the AHF:methanol process on annealed and unannealed wafers (Fig. 3). The difference between the etch rates of annealed and unannealed wafers is most pronounced at low methanol flow rate. This is an indication that the moisture pre-existing on the surface is acting as an etch initiator in the absence of methanol in the gas stream and that the thermal pre-treatment is removing the water from the oxide surface.

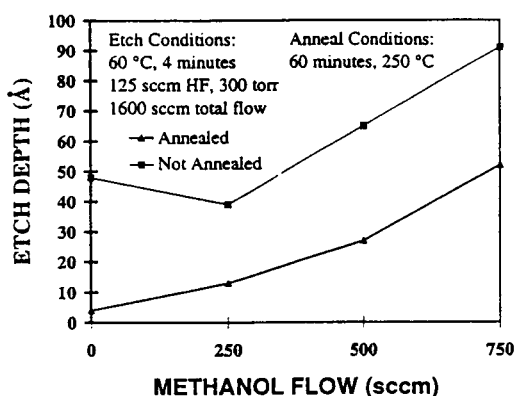


Figure 3 Etch rate vs. methanol flow for annealed and unannealed wafers

An elevated temperature process step immediately prior to the oxide etch is impractical because the temperature sensitive nature of the AHF:methanol etch process would necessitate an extended cooling period between the two process steps. An *in situ* UV irradiation has been found to produce the same effect without elevating the temperature above 60-70 °C. The etch rates for UV-treated oxides are comparable to those that received the thermal treatments (Fig. 4). It was determined that 30 seconds long UV exposure at  $10^{-4}$  torr was sufficient to dehydrate the surface.

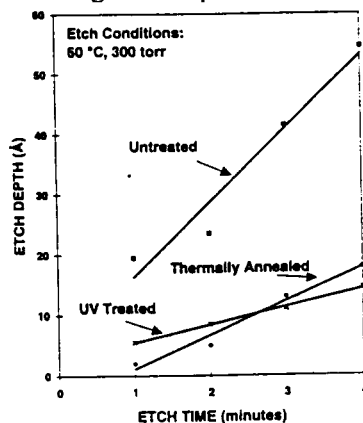


Figure 4 Etch rate for untreated, thermally annealed, and UV irradiated wafers

The Surface Charge Profiler (SCP)<sup>4</sup> was explored as a means of monitoring the hydration of oxides prior to oxide etch because of its sensitivity to single monolayer changes at the surface, and because of its non-contact nature which does not alter the surface during measurement. In the case of wafers stored in the desiccator (DS), the surface charge remained near the level that it started with immediately following the oxidation while the wafer exposed to the cleanroom (CR) ambient showed a decay of charge, possibly related to the addition of hydroxyl groups to the surface tending to neutralize the charge.

The results of the SIMS analyses are summarized in Table 1 with the corresponding etch rates. The aging of the oxide results in higher concentrations of both chemisorbed hydroxyl groups and physisorbed water on the surface. Storage in a desiccator reduced the amount of physisorbed water present on the surface after a week, but did not significantly affect chemisorption. The UV treatment significantly reduced the amount of physisorbed moisture present but did not appear to affect chemisorbed moisture. The concentration of physisorbed moisture has the strongest effect on the etch rate of the AHF:methanol process.

**Table 1**

| Wafer History       | Physisorbed Ratio | Chemisorbed Ratio | Etch Rate |
|---------------------|-------------------|-------------------|-----------|
| No aging            | .01               | .05               | 25 Å/min  |
| Aged one week in CR | .04               | .08               | 40 Å/min  |
| Aged one week in DS | .01               | .08               | 28 Å/min  |
| Aged in CR and UV   | .01               | .08               | 26 Å/min  |

#### 4. CONCLUSIONS

The surface hydration of an oxide, which may be affected by aging or process history, may cause variations in the gas phase etch process which are negligible in the liquid phase. These variations can be controlled by thermal treatments, or by UV irradiation of the surface in vacuum. The latter method can be integrated with subsequent gas-phase oxide etch and as such is a method of choice.

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## CHARACTERIZING VARIOUS PROCESS EFFECTS OF AN ANHYDROUS HF SYSTEM ON SURFACE AND SUBSURFACE FLUORINE CONCENTRATION

J. Barnett, D. Frystak<sup>1</sup>, R. Wise<sup>1</sup>, T. Fayfield<sup>2</sup>, J.S. Martin<sup>2</sup>, P. Grothe<sup>2</sup>

FSI International, 4020 S. Industrial Blvd., Suite B130, Austin, TX 78744

<sup>1</sup>Texas Instruments, SPDC, P.O. Box 655012, MS 944, Dallas, TX 75265

<sup>2</sup>FSI International, 322 Lake Hazeltine Dr., Chaska, MN 55318-1096

### 1. INTRODUCTION

The purpose of this study was to investigate the effects of various HF silicon cleaning processes on surface and subsurface fluorine concentration. Although some vapor HF processes left more fluorine and oxygen than standard wet HF processes, vapor processes were developed which were comparable or better in this respect. It was determined that the fluorine profile varied with the HF cleaning process, and the total measured fluorine concentration at the surface was directly correlated to the measured oxygen concentration. In addition, the fluorine profile was modified by the subsequent processing steps. For example, the ability to achieve relatively oxygen free surfaces led to nearly fluorine free films when using non-oxidizing CVD processes. Whereas, during oxidation processes, fluorine diffuses from the subsurface to the interface. The resulting interfacial fluorine concentration is high and appears to be independent of the HF cleaning process.

### 2. EXPERIMENTAL

The vapor phase processor used in this study was an FSI International EXCALIBUR® MVP clustered to a reduced pressure Applied Materials Centura platform with single-wafer epitaxial and polysilicon process modules attached. The MVP is a single wafer atmospheric system that utilizes anhydrous hydrogen fluoride (HF), anhydrous hydrogen chloride (HCl) and ozone (O<sub>3</sub>) gases as cleaning reagents. The machine has the capability to produce a reactive rinse process by dispensing HF during the DI rinse. Additionally, *insitu* spin drying was used which enabled the reactive rinse to be used without the need for subsequent water rinses.

All processes were performed on bare silicon wafers with a chemical oxide (table 1). Oxygen, carbon and fluorine measurements were done by secondary ion mass spectrometry (SIMS) and by X-ray photoelectron spectroscopy (XPS) at 30° and 45° take-off angles. Wafers which were measured by XPS were transported to the analytical lab within one hour of processing; wafers measured by SIMS were transferred directly to the process modules through the cluster platform where they were encapsulated with 1500Å of amorphous polysilicon at 690°C. The SIMS analysis involved profiling through the encapsulating polysilicon film and into the bulk silicon.

### 3. RESULTS

#### 3.1 HF VAPOR ETCH PROCESS

The XPS results [figures 1,2] show that the samples treated with the HF vapor etch process [YNN] exhibit higher fluorine and oxygen than those etched in the HF solution. The addition of a subsequent seven second DI rinse slightly reduces the fluorine, however, the oxygen is not effected. These data indicate that an oxygen free surface was not achieved by this vapor etch only process, and that some fluorine remains despite the use of a water rinse.

It is unclear as to the chemical state of the oxygen and fluorine measured after a vapor HF etch process. It is documented that anhydrous HF vapor etch of a chemical oxide generates non-volatile residue -- usually attributed to fluosilicic acid formation.<sup>1</sup> This residue, though non-volatile at room temperature and atmospheric pressure, is largely soluble and generally removed by water rinsing.

#### 3.2 HF REACTIVE RINSE PROCESS

An HF reactive rinse was substituted for the water rinse step after the HF vapor etch. The process equipment configuration allows this chemical rinse to be instantaneously spun-off and the

### 3.2 HF REACTIVE RINSE PROCESS

wafer dried in a nitrogen environment. The resulting wafer surface, as measured by XPS, shows significantly lower levels of oxygen [YYN] but slightly higher levels of fluorine. The XPS results also show that subsequent water rinse treatments as short as one second can reduce fluorine substantially [YY1, YY4, YY7]. The resultant levels are comparable to conventional wet HF etch/rinse treatments [WHFN45, WHFN30].

During the reactive rinse process, the non-volatile/water-soluble residues are continuously removed, in contrast to the HF vapor etch only process. The result is a much lower oxygen concentration. In addition, the remaining fluorine and oxygen are probably bound directly to the silicon surface.

### 3.3 BURIED FLUORINE

To confirm the presence of buried fluorine, oxidation was used to promote fluorine diffusion from the subsurface to the surface<sup>2</sup> where it could be measured by surface sensitive XPS. One HF etch process was selected and oxides of various thicknesses were grown by changing the ozone process parameters. In this way, the total quantity of buried fluorine was held constant and only its profile was changed by the oxidation.

Surface sensitive XPS was used to measure fluorine concentration and the chemical oxide thickness was calculated from the Si 2p peak.<sup>3</sup> As seen in figure 3, the fluorine concentration increases monotonically with oxide thickness, saturating at an oxide thickness of 6Å. Because of this, 6Å oxides were grown to determine the amount of fluorine buried by various vapor etch/reactive rinse/DI rinse processes. Figure 4 shows that this oxide produces an average of 4.5% fluorine, and is largely independent of the HF etch process. This result contrasts with the variance and reduced magnitude of surface fluorine measured by XPS for the HF processes run without ozone (figure 1). Evidently, the amount of buried fluorine overwhelms the amount of surface fluorine remaining after the HF etch processes.

### 3.4 POLYSILICON ENCAPSULATED SIMS RESULTS

The fluorine measured by SIMS at the polysilicon-Si interface confirms the trends observed by XPS. The samples with a saturated ozone oxide (approximately  $2 \times 10^{15}$  atoms/cm<sup>2</sup>) had about the same fluorine concentration (approximately  $1 \times 10^{14}$  atoms/cm<sup>2</sup>) independent of HF etch process. In contrast, the non-oxidized samples exhibited a range in fluorine concentration of nearly two orders of magnitude. The lowest fluorine was measured on samples that received the reactive rinse processes and the highest fluorine was observed on those samples that were etched with the vapor etch only processes.

The data suggest modification of the subsurface fluorine is occurring during temperature stabilization in the poly reactor prior to encapsulation. It was also observed that the oxygen concentration varied with the different etch and rinse processes, although the range was much smaller. The ability to perform a clustered clean and encapsulation ensured that any oxygen detected was a result of the cleaning process and not from the fab environment. The graph of fluorine vs. oxygen SIMS data (figure 5) shows that the fluorine concentration increases monotonically with oxygen concentration over a large range.

## 4. DISCUSSION

The XPS and SIMS results both show that surface oxygen can be controlled by various process techniques. This oxygen enhances diffusion of fluorine from the subsurface to the surface where it is trapped by, and perhaps bonded to, the oxygen.<sup>2</sup> Consequently, the quantity of the oxygen directly correlates to the amount of observed fluorine. Thus, if the amount of oxygen on the silicon surface can be eliminated or minimized, the fluorine will also be eliminated or minimized when exposed to elevated temperatures under a reduced pressure, hydrogen/silane ambient. The SIMS and XPS data also show that, regardless of process, the fluorine appears to saturate at a high level when oxidized.

#### 4. DISCUSSION

These results indicate that there is always some subsurface fluorine independent of the HF step. In addition, the magnitude of the subsurface fluorine is greater than the surface fluorine. The influence of the subsurface fluorine is dependent upon the subsequent process.

For example, following an epitaxial pre-clean, the subsurface fluorine will desorb and volatilize when exposed to elevated temperatures and reduced pressure provided that it is not trapped by oxygen prior to deposition. This condition can be achieved with the reactive rinse process in a clustered environment. The result is an epitaxial film with an oxygen and fluorine free interface.<sup>4</sup>

When the HF clean process is followed by thermal oxidation, the subsurface fluorine might form SiOF complexes and be trapped in the oxide. The magnitude of the incorporated fluorine appears to be independent of the HF cleaning process, as shown throughout this paper. Additional work has shown that there are no significant differences in device performance between wet HF and vapor HF.<sup>5</sup> This is supported by the work of Kasi *et al.* which has shown that this fluorine can improve oxide quality.<sup>6</sup>

#### 5. CONCLUSIONS

After HF cleans, fluorine is observed not only on the wafer surface but in the subsurface. The amount of fluorine was not only affected by the clean which was employed, but also by the process conditions encountered after the cleaning process and was directly correlated to the amount of oxygen available. This had an effect on the diffusion of fluorine from the subsurface silicon to the surface. For non-oxidizing CVD processes, the ability to achieve relatively oxygen free surfaces led to relatively fluorine free films. For oxidation processes, the abundance of oxygen, regardless of the post clean levels of fluorine, resulted in equivalent fluorine levels.

Table 1. Process sequences

| Vapor Etch | Reactive Rinse | Water Rinse    | Dry | Nomenclature |
|------------|----------------|----------------|-----|--------------|
| YES        | NO             | NO             | NO  | YNN          |
| YES        | NO             | 7 SECONDS      | SD  | YN7          |
| YES        | YES            | NO             | SD  | YYN          |
| YES        | YES            | 7 SECONDS      | SD  | YY7          |
| YES        | YES            | 4 SECONDS      | SD  | YY4          |
| YES        | YES            | 1 SECOND       | SD  | YY1          |
| NO         | YES            | NO             | SD  | NYN          |
| 4.9% HF    | NO             | 45 SEC CASCADE | SD  | WHFN45       |
| 4.9% HF    | NO             | 30 SEC CASCADE | SD  | WHFN30       |

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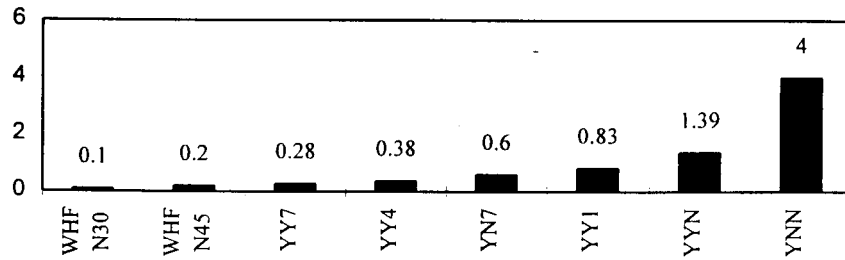


Figure 1. % Fluorine by XPS

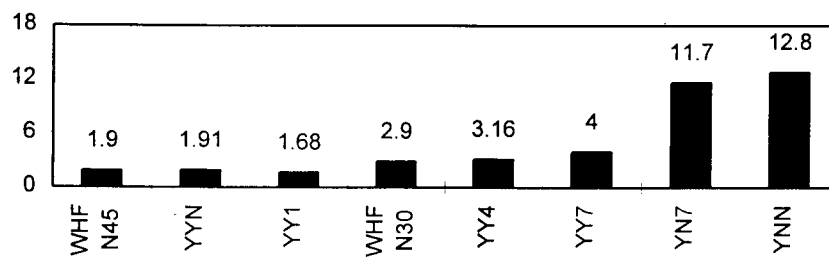


Figure 2. % Oxygen by XPS

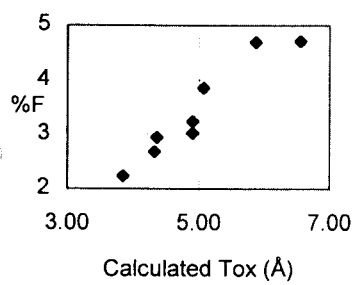


Figure 3. XPS - % Fluorine by Oxide Thickness

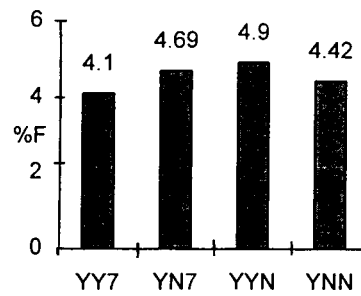


Figure 4. XPS of Fluorine after 6Å ozone oxidation

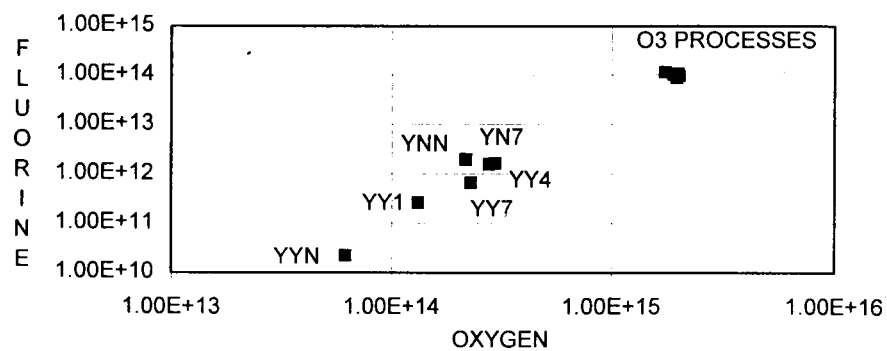


Figure 5. SIMS - Log Plot of Fluorine vs. Oxygen Concentrations (Atoms/cm³)

## THE IMPORTANCE OF H-PASSIVATION FOR LOW TEMPERATURE APCVD SILICON EPITAXY

Marie-José MOUCHE, Matty CAYMAX, Hugo BENDER, Wolfgang STORM and Wilfried VANDERVORST.

Imec, Kapeldreef 75, B-3001 Leuven, Belgium.

The evolution of the H-coverage of Si wafers during a pre-epitaxial thermal treatment step in H<sub>2</sub> at 1 bar has been studied over a wide temperature range by means of MIR-IR. Simultaneously, C and O contamination have been measured by ESCA. In addition, epi layers have been grown at low temperatures and analysed by Nomarski microscopy, SIMS and x-TEM.

### 1. INTRODUCTION

In order to reduce the thermal budget for Si epitaxial growth, the preparation of the surface before deposition is a major point which needs better understanding. An *in-situ* prebake step under H<sub>2</sub> at high temperature is mainly used to desorb native oxide and to prepare a perfect surface, leading to zero density of lattice defects in subsequent epitaxial layers. However, for advanced device structures, temperatures below 700°C are required. We focused our work on the evolution of H-coverage during the prebake step using MIR-IR and ESCA analysis. As a final test, Si epi layers were deposited with as low as possible prebake temperatures.

### 2. EXPERIMENTAL

Epitaxial silicon growth with dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>) and hydrogen was carried out in a commercially available single wafer, radiantly heated, load-locked CVD reactor (ASM Epsilon-One) working at atmospheric pressure. It is interesting to note that this is not an UHV system, as all sealings are made with Viton O-rings. All samples got a modified RCA clean in an automated spray tool (standard 6" wafers) or a manual RCA clean in beakers (MIR-IR samples), followed by an HF dip (2% during 30 s) in order to remove the native oxide. No DI water rinse was performed after, but the wafer was blown dry with N<sub>2</sub>. Wafers were then immediately introduced into the load-lock of the epitaxial reactor. After purging with N<sub>2</sub> for some time ("purging time"), the wafer was transferred to the reaction chamber for the prebake step. Normally, the reactor is maintained at a temperature of 900 °C under H<sub>2</sub> during loading ; for these experiments however, this temperature was lowered to the appropriate pre-bake value. After prebake, the reactor was cooled down under H<sub>2</sub> to room temperature before unloading the wafer. Multiple Internal Reflection InfraRed (MIR-IR) and ESCA measurements were then performed. In other experiments, epi-layers were grown after the prebake at the same temperature to a thickness of about 100 nm for microscope, SIMS and TEM analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1. Si surfaces and H<sub>2</sub> bakes

By heat treatments at different temperatures at 1 bar of H<sub>2</sub> followed by ex-situ IR-spectroscopy it is possible to study how the Si surface is changed during this process. Still, in order to detect any H<sub>2</sub> on this surface, it is required to cool down the wafer under H<sub>2</sub>: at high T, the surface will be almost free of H, but upon cooling down H<sub>2</sub> re adsorbs again. The surface structure on the atomic level as it was at the highest temperature will determine completely the resulting Si-H<sub>x</sub> binding geometry's.

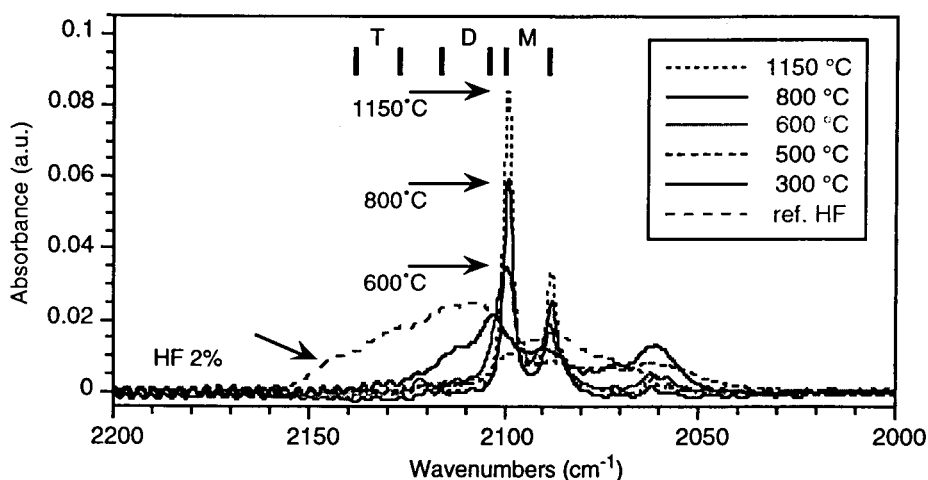


Figure 1 FTIR spectra (p-polarisation) of H-evolution during thermal treatments (M = monohydride, D = dihydride, T = trihydride)

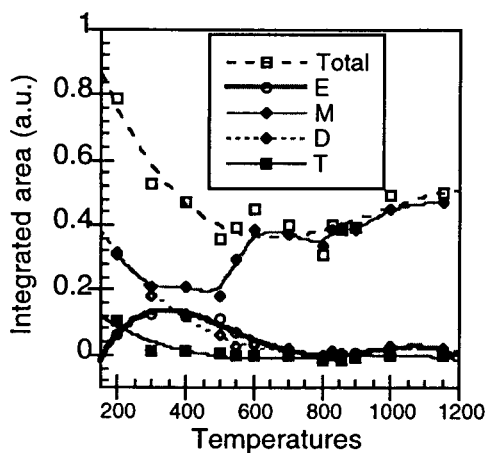


Figure 2 Evolution of absorption peak integrals with temperature

We have been doing heat treatments for 10 minutes at 100 °C intervals between 200 and 1150 °C. A complete overview of MIR-IR results is shown in Fig. 1. Baking at 200 °C does not yet change the surface, still showing a broad absorption peak of tri and dihydrides. By increasing the temperature, the higher hydrides gradually disappear; from 600 °C on, the monohydride shows up and becomes more and more important. Finally, at the highest temperatures, the polyhydride coverage as obtained after a wet HF dip is completely changed into monohydride. However, not only the peak heights change, also their width becomes smaller

at higher temperatures. Now, as the total H-coverage is given by the area under the peak, we have integrated the different peaks (taking the double peaks together) and normalised to Si sites : one trihydride covers one Si site but adsorbs 3 times more IR light. The result is shown in Fig. 2. It is rather surprising to see that the total H coverage does not change very much with temperature, with a minimum at 600-700 °C of 50 % of the room temperature value.

The peak width is related to the amount of disorder on the Si surface, with highly organised and well structured surfaces resulting in the narrowest peaks. By comparing the change in peak heights and widths, as well as the change from polyhydrides to monohydrides, one can conclude that the thermal treatment has a pronounced smoothing effect on the surface leading to well reconstructed (2x1) surfaces at the highest temperatures.

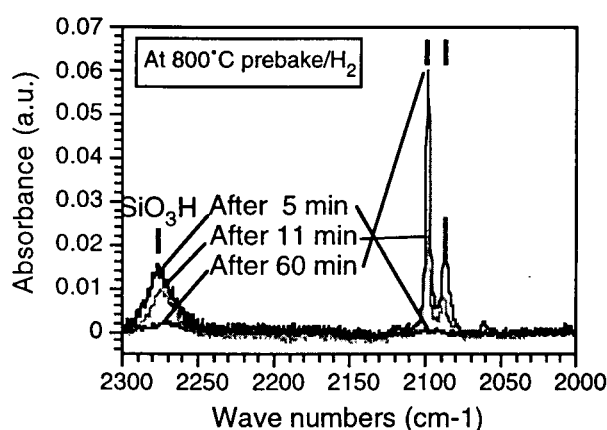


Figure 3 IR spectra of the SiO<sub>3</sub>-H and Si-H evolution at 800 °C with load lock purging time

From MIR-IR and ESCA measurements, it was found that a sufficiently long purging time (> 30 minutes) in the load-lock is needed to obtain a very clean surface without oxygen contamination (Fig. 3 and Table 1). This is probably because during the load lock purge, adsorbed water has to be desorbed which is of lesser concern at higher bake temperatures where the O is desorbed as SiO. At these lower T's, the adsorbed water reacts with the Si to form oxidised compounds.

Table 1 : ESCA measurement of the evolution of the concentration of SiO<sub>x</sub> on the surface after a prebake at 800 °C for different load lock purging times

| Purging time                            | 5 min                | 28 min               | 51 min             |
|-----------------------------------------|----------------------|----------------------|--------------------|
| SiO <sub>x</sub> (at.cm <sup>-2</sup> ) | 1.3 10 <sup>15</sup> | 2.3 10 <sup>14</sup> | 9 10 <sup>13</sup> |
| SiO <sub>x</sub> /Si(100)<br>monolayers | 1.9                  | 0.34                 | 0.14               |

### 3.2 Low temperature prebake and epitaxy

Based on these results, epi-layers were grown at 600, 700 and 800 °C after a prebake step at the same temperature for 10 min. For each experiment, the load lock was purged for at least one hour. The layer thickness was about 100 nm.

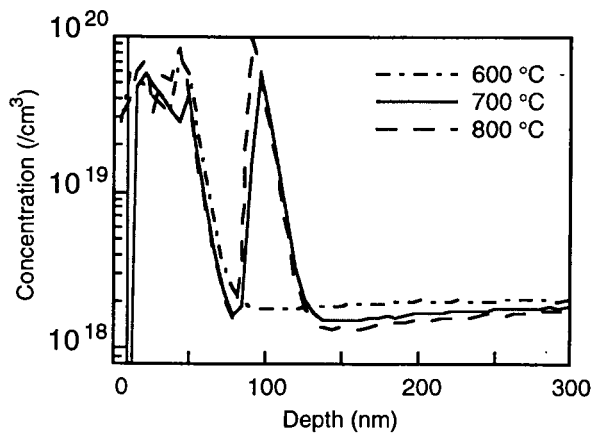


**Figure 4** Oxygen profile in epi layers with prebake/dep temperature at indicated values ; the double surface peak is an SIMS artefact ; interface is at ~ 100 nm depth for all three layers.

At 700 and 800 °C, SIMS detects about 20 % of a monolayer of oxygen at the interface (Fig. 4). No trace of C, Cl, F or B could be found. Surprisingly, at 600 °C, no contaminants at all were found at the interface by SIMS, even no O. In x-TEM, the layers show a superb crystalline quality (Fig. 5). The O at the interface becomes visible as a thin, vague line in the 700 °C sample. The 600 °C interface is completely invisible. Initial Nomarski microscope observations showed a very smooth surface, decorated by very

small defects in rather low densities, in the order of  $10^4 - 10^6/\text{cm}^2$ . By growing the layers to larger thicknesses, we could identify these defects. There are two kinds of defects, one of which are stacking faults and the other is kind of depression or dimple in the surface. Better characterisation by TEM or AFM proved to be very difficult due to the low density. Further characterisation is underway.

#### 4. CONCLUSION

In conclusion, we have characterised the H-coverage and possible contamination of the surface of Si wafers after the pre-epi bake step for the temperature range between 200 and 1150 °C with MIR-IR and ESCA. Based on this we found it should be possible to use a low prebake temperature for high quality epi growth. This was shown to be the case indeed for temperatures as low as 600°C, although a thorough purging of the load-lock before transferring the wafer appears to be crucial. A remaining problem is the presence of stacking fault densities in the order of  $10^5/\text{cm}^2$ . Ways to eliminate these defects are being explored.

#### ACKNOWLEDGEMENTS

The authors are indebted to the CEC for granting a post-doctoral fellowship to one of us (MJ M) in the frame of the HCM Network on Low Thermal Budget Si-alloys Epitaxy with Contract Nr. ERBCHRXCT930213.

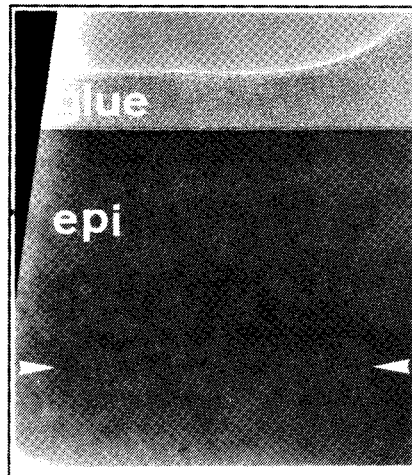


**Figure 5** x-TEM of sample @ 700 °C showing interfacial line (marked by arrows) ; epi-thickness is 79 nm



## EARLY STAGE OF NATIVE OXIDE GROWTH ON AN ATOMICALLY FLAT HYDROGEN TERMINATED Si(111) SURFACE

Shuzo Fujimura, K. Ishikawa and H. Ogawa  
Process Development Division, FUJITSU LIMITED

The early stage of oxidation of an atomically flat Si (111) surface was analyzed by XPS, FT-IR-ATR and FT-IR-RAS. Results of FT-IR-ATR and XPS showed that oxidation started from a site where oxidize species adsorbed. FT-IR-RAS spectra were interpreted through theoretical calculation and supported that oxide grew insularly.

### 1. INTRODUCTION

Analysis of the early stage of the oxide film growth is useful to control thin oxide film properties and provides guidelines for solving the mechanism of oxidation reaction. In the research of the early stage of native oxide growth on silicon surfaces terminated by hydrogen using X-ray photoelectron spectroscopy (XPS), Taft and Morita found an very attractive phenomenon independently, which was that the amount of oxygen calculated from area of a shifted Si2p peak increased step-by-step with oxidation time [1, 2]. This phenomenon seemed to indicate that the oxidation of the silicon substrate progressed layer-by-layer. Hirose et al. investigated the mechanism of the early stage of oxidation on the basis of this phenomenon and proposed a model that oxidation of the hydrogen terminated silicon surface started from a step or a kink and progressed layer-by-layer [3].

On the other hand some other investigators insist that oxidation does not start from steps or kinks but terrace or any other place randomly and progressed insularly. No experiments leading such model, however, followed Hirose's oxidation condition; Ono *et al.* observed the oxidation of Si (111) 7×7 by O<sub>2</sub> molecule in high vacuum, Hattori *et al.* analyzed the oxide layer grown on Si (111) surface but by dry O<sub>2</sub> in vacuum. Neuwald *et al.* did not observe oxide directly [4-6]. In this study, we analyzed the early stage of oxidation of the atomically flattened Si (111) surface in pure water by XPS, FT-IR-ATR using silicon prism and Fourier transformed infrared reflection absorption spectroscopy (FT-IR-RAS) [7-9].

### 2. EXPERIMENT

Details of experimental set up have described in the previous paper [7, 8]. The FT-IR spectrometer used in this study was JIR-6500 (JEOL). A commercial RAS kit (JEOL IR-RSC120) and an ATR kit (JEOL) were used for IR-RAS and IR-ATR spectra respectively. In RAS measurement, incident angle of p-polarized light was 80°, resolution was 8cm<sup>-1</sup> and the number of accumulation times was 250.

A silicon prism for ATR measurement was also used for RAS measurement. The prism was made of a both sides polished p-type FZ(111) wafer with resistivity of 80-120 Ωcm. After formation of the hydrogen terminated atomically flat surface by 40 wt% NH<sub>4</sub>F solution following surface cleaning, the prism was oxidized in pure water containing dissolved oxygen of 8ppm. RAS measurement was performed after ATR measurement immediately.

XPS analysis was performed using an in-situ observation system which was furnished with FT-IR-ATR and XPS. In XPS measurements,  $\text{MgK}\alpha$  line ( $h\nu = 1253.6 \text{ eV}$ ) was used as the X-ray source, and we measured using a 15 degrees take off angle to improve the surface sensitivity. In XPS analysis, we oxidized H-terminated surfaces at 1 Torr in dry  $\text{O}_2$  at comparatively low temperatures in order to avoid desorbing terminating H atom. All measurements were performed after the sample reached room temperature.

### 3. RESULTS AND DISCUSSION

#### 3.1. ATR [7]

Figure 1 shows the time dependence for immersion in pure water of the IR absorption spectra arising from Si-H bonds using FT-IR-ATR. Since the amount of Si-H bonds of native oxide formed in an  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solution is negligible, IR absorption spectra of this native oxide were used as reference spectra [10, 11]. p- and s-polarized spectra at 5 min indicate that an almost atomically flat H-terminated Si (111) surface was obtained. The slight absorption in the s-polarized spectra indicates the existence of a small number of steps due to miss orientation of the silicon surface [12]. The absorption at  $2250 \text{ cm}^{-1}$  arising from three oxygen atoms back-bonded Si-H bonds increases with immersion time (5 - 625 min) for both p- and s-polarized spectra, which reflects native oxide growth [10, 11, 13]. In the same time range, the height of the sharp absorption peaks at  $2083 \text{ cm}^{-1}$  for p-polarized spectra decreases noticeably.

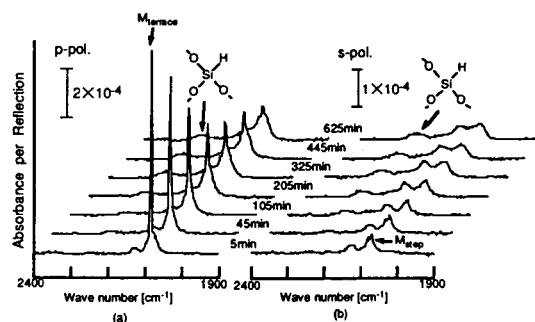


Fig. 1. Dependence of the IR absorption spectra arising from Si-H bonds on the immersion time in pure water obtained for an atomically flat H-terminated Si (111) surface using FT-IR-RAS. Resolution is  $4 \text{ cm}^{-1}$ ; (a) p polarized, (b) s polarized.

If native oxide growth arises at the surface steps, then the absorption peak at  $2071 \text{ cm}^{-1}$  due to silicon monohydrides at the surface steps must immediately decrease. Moreover, the absorption at  $2250 \text{ cm}^{-1}$  must increase with immersion time in the case of s-polarization. In order to clarify the effects of surface steps, we performed a similar experiment on a vicinal ( $4^\circ$  off) Si (111) surface. This result is shown in Fig. 2. The absorption peak at  $2250 \text{ cm}^{-1}$  increases with immersion time in spectra measured  $4 \text{ cm}^{-1}$  resolution (Fig. 2 (a)), also indicating the progress of native oxide growth. High-resolution ( $1 \text{ cm}^{-1}$ ) spectra (Fig. 2(b)) show three major sharp absorption peaks at  $2071$ ,  $2083$ , and  $2087 \text{ cm}^{-1}$ . The absorption peak at  $2083 \text{ cm}^{-1}$  is attributed to silicon monohydrides at the terrace. The

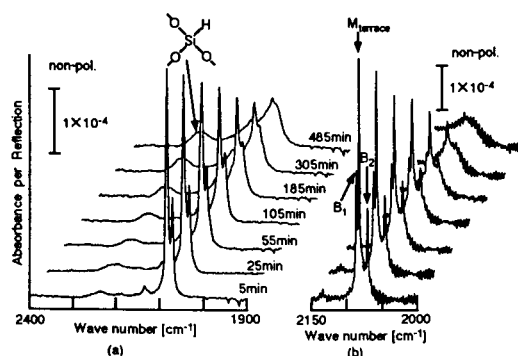


Fig. 2. Dependence of the IR absorption spectra arising from Si-H bonds on the immersion time in pure water obtained for an H-terminated 4° off Si(111) surface using FT-IR-ATR. (a) with 4 cm<sup>-1</sup> resolution, and (b) with 1 cm<sup>-1</sup> resolution.

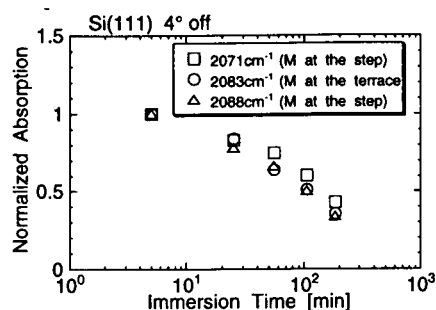


Fig. 3. Dependence of normalized spectral height of silicon monohydrides (M) on the immersion time in pure water shown in Fig. 2.

absorption peaks at 2071 and 2087 cm<sup>-1</sup> are attributed to silicon monohydrides at the step edges. The height of such absorption peaks decrease as they broaden with increasing immersion time. This dependence on immersion time, shown in Fig. 3, shows that the three absorption peaks decrease at approximately the same rate. Since such a decrease and broadening in the spectra reflect the progress of native oxidation, native oxide growth on H-terminated Si (111) surfaces in pure water arises simultaneously from both the surface terrace and the steps, and not preferentially at the steps.

### 3. 2. XPS [8]

Figure 4 shows the results in-situ observation of oxide growth with FT-IR-ATR. Fig. 4 (a) is IR-ATR spectra of an initial atomically flat H-terminated surface, and Fig. 4 (b)-(f) shows difference spectra between the initial surface (a) and after exposure to N<sub>2</sub> or O<sub>2</sub> at various temperatures. From these difference spectra, we found that there is little spectra change after exposure in N<sub>2</sub> at 180 °C (Fig. 4 (b)) and the M<sub>terraces</sub> peak decreases as the O<sub>2</sub> exposure temperature or time increases (Fig. 4 (c)-(f)). In addition, the absorption arising from Si-H bonds back-bonded with oxygen atoms at 2150 - 2250 cm<sup>-1</sup> was not observed. XPS measurement were also performed on these surfaces, and Si2p and O1s photoelectron spectra are shown in Fig. 5 (a) and (b), respectively. We hardly observe the clear signal due to the intermediate silicon oxide or SiO<sub>2</sub> at the binding energy of 100 - 103 eV, the spectra obtained after exposure are almost identical with the spectra obtained on the initial surface in Si2p<sub>3/2</sub> photoelectron spectra Fig. 5 (a). On the other hand, we found that the O1s spectra intensity increases as the O<sub>2</sub> exposure temperature or time increases in O1s photoelectron spectra Fig. 5 (b). It should be noted that the amount of oxygen atoms is approximately 0.25 monolayer after treatment in O<sub>2</sub> at 190 °C for 30 min, if all these oxygen atoms contribute to form Si-O bonds, the spectral intensity of Si2p<sub>3/2</sub> photoelectron spectrum due to the Si bonded with oxygen atom have to be the level showed in Fig.

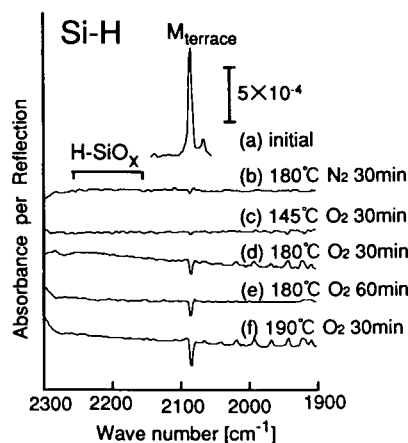


Fig. 4. Change in IR absorption spectra arising from Si-H bonds as a function of exposure time in 1 Torr dry O<sub>2</sub> or N<sub>2</sub>. Spectra (b)-(f) are difference from spectrum obtained for initial surface (a).

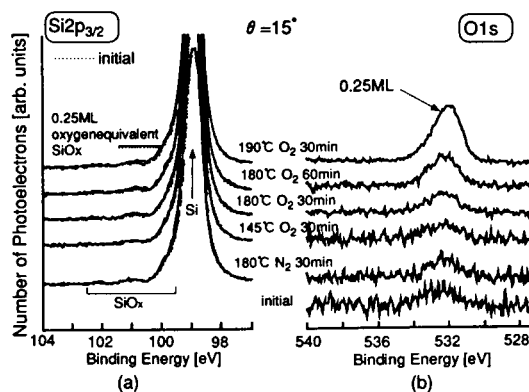


Fig. 5. Change in Si2p<sub>3/2</sub> (a) and O1s (b) photoelectron spectra as a function of exposure time in 1 Torr dry O<sub>2</sub> or N<sub>2</sub>. Dashed line in (a) means the spectrum obtained for the initial surface.

5 (a). These results are summarized as follows: there are little Si-O bonds on the silicon surface, however, the  $M_{\text{terrace}}$  peak in IR spectra decreases as the exposure temperature or time increases, and these changes are linked with the increase in the amounts of oxygen on the silicon surface.

### 3. 3. RAS [9]

Figure 6 shows the FT-IR-RAS spectra change in Si-O stretch bond signals of the native oxide grown in pure water as a function of oxidation time. Over 445 min oxidation, two peaks were observed on every charts; one was a peak at about 1080 cm<sup>-1</sup> and another was a peak broadening from about 1250 to 1100 cm<sup>-1</sup>. The broad peak at higher wavenumbers shifted a little to higher wavenumbers with increase in oxidation time from 325 min to 865 min and then the narrow peak at about 1080 cm<sup>-1</sup> also shifted a little to lower wavenumbers. However, these peak shifts did not detect clearly in longer oxidation time than 1245 min. Spectra shape of the oxide grown in the pure water did not change so much after longer oxidation than 43645 min even in the 170545 min oxidation in which the amount oxide was probably larger than that in the oxide formed by the SPM solution. The FT-IR-RAS spectra of the native oxide layer formed by SPM solution have the clear TO and LO phonon peaks and are similar to a thermally grown oxide. They are different from the RAS spectra shown in Fig. 6.

A model to explain the early stage of oxidation process have to reveal the origin of two phenomena; shifts of the TO and the LO phone peaks and the spectra shape difference between the oxide layer grown in the pure water and that formed by the SPM solution or thermally grown oxide layer.

We tried to analyze the IR-RAS spectra assuming that oxide grows insularly. In the analysis, we calculated the spectra theoretically using the effective media approximation

and the ellipsoidal approximation [14, 15]. Since the space for this article is limited, details of calculation method are not shown here.

Figure 7 shows the results of the calculated spectra. ( $L$  is the depolarization factor along one of the axes of the ellipsoid, which is perpendicular to the surface, and is relate to flatness of ellipsoid.  $f$  is the volume fraction of the particles in the matrix.  $d$  denotes the length of the ellipsoid along the axis which is perpendicular to the silicon surface.) Absorption peaks on the calculated spectra are located higher frequency by about  $50\text{ cm}^{-1}$  from those on the measured spectra but both spectra shape are very similar. It has reported that an IR-RAS spectra of a CVD oxide film showed similar shape to that of a thermally

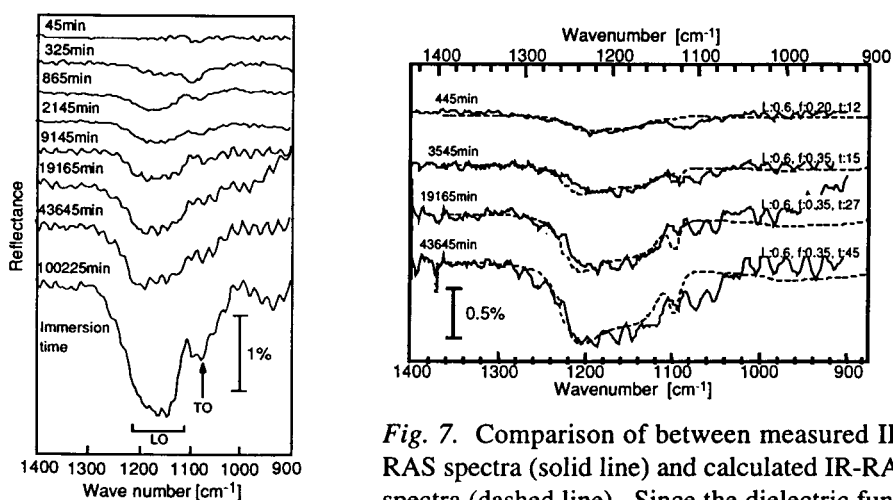


Fig. 6. Change in the FT-IR-RAS spectra arising from Si-O bonds with increase in immersion time in pure water. Resolution is  $8\text{ cm}^{-1}$ .

Fig. 7. Comparison of between measured IR-RAS spectra (solid line) and calculated IR-RAS spectra (dashed line). Since the dielectric function of thermally grown oxide is used for the spectra calculation as the dielectric function of the ellipsoidal oxide particle, the calculated spectra shift toward higher wavenumbers by about  $50\text{ cm}^{-1}$ .

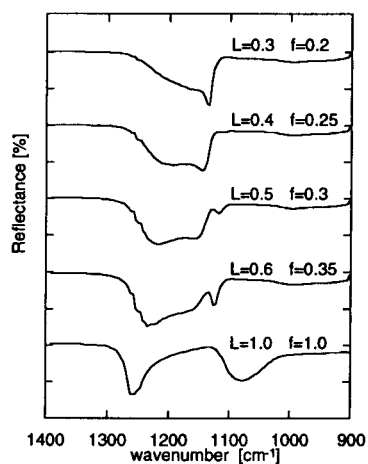


Fig. 8. Dependence of IR-RAS spectra shape on the depolarization factor and the volume function of the oxide particles.

grown oxide but shifted to lower frequency by about  $50\text{ cm}^{-1}$  from that [16]. Thus this frequency difference of  $50\text{ cm}^{-1}$  between the simulation and the measurement is acceptable as it is due to the difference of dielectric function between the thermally grown oxide and the real oxide particles.

Figure 8 shows the calculated spectra with various  $L$  and  $f$  values. Except in the case of  $L = 1.0$  and  $f = 1.0$ , each calculated spectra has similar shape to IR spectra of one of the native oxides formed in pure water after different immersion time.  $L = 1.0$  and  $f = 1.0$  mean that oxide is a layer. Then the calculated RAS spectra have clear LO and TO phonon peaks and are similar to the spectra of the thermally grown oxide layer and the native oxide layer formed in SPM solution. The RAS spectra of the native oxide grown in pure water did not fit to the calculated spectra with  $L = 1.0$  and  $f = 1.0$  even after 100220 min immersion. Therefore, the native oxide formed in pure water is not a layer but grows insularly.

#### 4. CONCLUSION

Native oxide growth on a hydrogen terminated atomically flat Si (111) surface starts from a point of the surface where oxidation species adsorb and progresses insularly.

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# INITIAL OXIDATION ON CLEAN AND HYDROGEN-TERMINATED SILICON SURFACES BY HIGH-PURITY OZONE IN AN ULTRAHIGH VACUUM ENVIRONMENT

**Ken Nakamura, Akira Kurokawa and Shingo Ichimura**

*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan*

High purity ozone beam was exposed to Si(111) and Si(100) surfaces at room temperature. Rates of initial ozone adsorption per dangling bond on Si(111)7x7 and Si(100)2x1 were found to be identical, which is different from the case of molecular oxygen adsorption. This difference between ozone and molecular oxygen suggests that there is no precursor state of molecularly adsorbed ozone since it does not require any optimized configuration of surface atomic arrangement which molecular oxygen does.

## 1. INTRODUCTION

Some complimentary oxidants or oxidation processes are strongly required for low temperature oxidation of silicon surfaces to avoid thermal damage in the microstructure of electronic device. Ozone ( $O_3$ ) is one of such candidates because it is highly active oxidant to release atomic oxygen. So far, however, only the mixture of ozone less than 10% concentration and oxygen gas has been used for oxidation. To get concentrated ozone, we have invented high-purity ozone jet generator system[1,2] with which we can obtain ozone jet with the purity more than 80% at the sample position. With the use of this generator, the enhancement of oxidation in the initial stage was clearly observed for Si(111)7x7 surface by X-ray photoelectron spectroscopy (XPS)[3].

By use of this ozone beam, we found by second harmonic generation (SHG)[4] that initial oxidation process was also enhanced on Si(100)2x1 and that its rate of adsorption per dangling bond is almost identical as that on Si(111)7x7. Si(100)2x1 is known to have much lower sticking probability than that on Si(111)7x7 for molecular oxygen. This characteristics of kinetics of ozone adsorption ensures itself to be much more effective oxidant also for Si(100)2x1.

## 2. EXPERIMENTAL

The experimental system in Fig.1 is consisted of an ultrahigh vacuum chamber with its base pressure of about  $3 \times 10^{-8}$  Pa., a high purity ozone beam generator, a low energy electron diffraction(LEED) apparatus, an X-ray source with

a double-pass cylindrical mirror analyzer (CMA) for XPS and a Nd:YAG laser with a monochromator and a photomultiplier for surface SHG measurement.

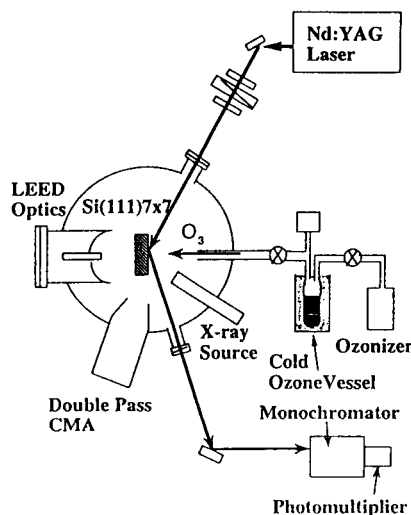


Figure 1. Schematic diagram of experimental setup.

After cleaned chemically to remove organic contaminants, the sample was introduced into the vacuum chamber and was heated up to 1200°C to remove an oxide thin film and cooled down to room temperature. Clean and reconstructed surfaces of Si(111)7x7 and Si(100)2x1 were detected by XPS and LEED.

Ozone jet generator system[1,2] is consisted of an ozonizer, an ozone vessel and a evacuation system. The mixture gas of O<sub>2</sub> and O<sub>3</sub> with an O<sub>3</sub> concentration of about 5% generated from pure O<sub>2</sub> by electric discharge was introduced into the ozone vessel cooled down below 100K. Its temperature was controlled within an accuracy of 0.1K. In the vessel only O<sub>3</sub> was liquefied and accumulated because O<sub>2</sub> was evacuated due to a large saturation vapor pressures by several orders of magnitude at such temperature. After liquid O<sub>3</sub> was accumulated, the vessel was isolated from the evacuation system. The flux of the O<sub>3</sub> beam on to the sample was controlled by adjusting the vessel temperature (i.e., saturated vapor pressure) and the conductance of an introduction tube between the O<sub>3</sub> vessel and the chamber. The purity of O<sub>3</sub> is estimated to be more than 80% at the sample position[2].

P-polarized Nd:YAG laser beam ( its wavelength:1.064  $\mu$  m, pulse repetition rate:10Hz and pulse width:10ns ) was incident onto the surface after focusing it into a spot of 2.5mm  $\phi$  on the sample surface with the incidence angle of 55°. The intensity of the incident beam was 70mJ/pulse, i.e.  $1.4 \times 10^8$  W/cm<sup>2</sup>, which is under



the threshold for optical breakdown. *P*-polarized second harmonics (SH) light of 532 nm was detected in the direction of the mirror reflectance. In each measurement, SH intensity averaged by a boxcar for 100 laser shots was recorded. The adsorbed oxygen species were monitored also by XPS.

### 3.RESULTS AND DISCUSSION

The characteristics of ozone oxidation kinetics in the initial stage was indicated in Fig.2 by the comparison of O<sub>3</sub> adsorption on Si(111)7x7 and Si(100)2x1 observed by SHG. Here decrease of SH intensity indicates that vacant dangling bond is decreasing in number by the adsorption. The flux to the surfaces is converted to the number of incident O<sub>3</sub> molecules per one dangling bond (DB) per a second based upon the structure model of surfaces[5,6] and upon the assumption that all oxygen atoms can rest on the surface. It is clearly indicated that rates of adsorption per one dangling bond on the Si(111) and Si(100)2x1 are to be almost identical. This means that sticking probability of O<sub>3</sub> is not effected by the difference of surface structure.

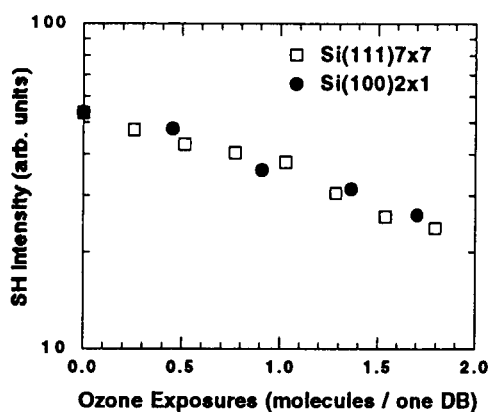


Figure 2. SHG intensity during O<sub>3</sub> exposure to Si(111)7x7 and Si(100)2x1.

As was investigated in detail so far[7], sticking probability of O<sub>2</sub> on Si(111)7x7 is one order of magnitude larger than that on Si(100)2x1: At 300K, Si(111)7x7 has the probability of 0.13 while Si(100)2x1 has the value of 0.02[8,9]. Also it has been known that O<sub>2</sub> adsorption requires molecularly adsorbed precursor state on the surface dangling bond so that sticking probability is decreasing while increasing the surface temperature[8,9], which was also clearly observed by SHG[10].

However, initial adsorption rate of  $O_3$  is independent of surface structure. We also observed reverse temperature dependence between ozone and molecular adsorption rate. These imply that, in the case of  $O_3$  adsorption, no precursor state with any specific configuration of surface active site is required. On Si(111) with hydrogen termination in vacuum, it has been already observed[3] clearly that oxygen species increase during ozone exposure, although the initial rate decreased. This supports the above idea that dangling bond as the active site for a precursor for dissociation is not always necessary. This mechanism can be effectively utilized for oxide formation on the clean and hydrogen-passivated surfaces.

Further studies are required to interpret the difference in temperature dependence of ozone adsorption rate between SHG and XPS measurement. This is expected to be due to different information depth between the two since SHG is sensitive mainly to vacant dangling bond while XPS is due to photoelectron emitted within the depth of about 20Å.

#### 4.CONCLUSION

High purity ozone beam was exposed to Si(111) and Si(100) surfaces at room temperature. We found by SHG that initial adsorption rates of ozone per dangling bond on Si(111)7x7 and Si(100)2x1 were identical. This is different kinetics from the case of molecular oxygen adsorption. This characteristics suggests that precursor state of molecularly adsorbed ozone which requires optimized configuration of surface atomic arrangement is not necessary for ozone dissociation.

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# CHEMICAL PREPARATION OF THIN OXIDE LAYERS ON H-TERMINATED SI-SURFACES STUDIED BY SURFACE STATE DENSITY MONITORING AND SPECTROSCOPIC ELLIPSOMETRY

**H. Angermann, W. Henrion, M. Rebien, K. Kliefoth, W. Füssel,**

Hahn-Meitner-Institut, Abt. Photovoltaik; Rudower Chaussee 5, D-12489 Berlin, Germany

**D. Fischer, and J.-T. Zettler**

Institut für Festkörper-Physik, Technische Universität Berlin, Hardenbergstr. 35 D-10623 Berlin, Germany

## 1. INTRODUCTION

Monitoring and control of Si surface reoxidation has recently received increasing attention because this process is essential for the preparation of passivating interlayers for ultralarge-scale integrated circuits as well as for solar cells. The properties of the thin oxide layers and the silicon-oxide interface are strongly influenced by the chemical integrity and morphological structure of the semiconductor surface prior to preparation [1]. In this paper we report on investigations of surface Fermi level position and of the energetic distribution of interface states  $D_{it}(E)$  which have been performed to study the influence of the chemical treatment on the electronic properties of the interface of thin oxide layers. Because of their cleanliness and smoothness and their excellent electronic properties [2] we used H-terminated silicon surfaces as a starting point for the chemical preparation of oxide passivating layers of 2 to 20 Å. Additionally, both ex-situ and in-situ spectroscopic ellipsometry (SE) was utilised to investigate the oxidation process.

## 2. EXPERIMENTAL

Polished Si(111) and Si(100) p-type samples (5 - 10  $\Omega\text{cm}$ ) were cleaned by the conventional RCA-process [3]. After removing the native oxide the samples were chemically reoxidised using a boiling solution of  $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$  (1:1) for 10 minutes, rinsed and afterwards placed into pure  $\text{NH}_4\text{F}$ -solution (40%) pH = 7.8 for 6.5 minutes. Using these H-terminated surfaces the preparation of oxide layers was carried out in deionised water of 18 M $\Omega$  resistivity. The ultra pure water we used was assumed to be equilibrated with dissolved air-oxygen resulting in a dissolved oxygen concentration (DOC) ranging from 9 ppm at 20°C to 3 ppm at 80°C. To investigate the influence of the RCA cleaning process itself, already H-terminated samples were again treated by conventional RCA I and RCA II processes following the H-termination treatment.

For control and optimisation of the oxidation procedure we used the large-signal field-modulated surface photovoltage technique (SPV) for contactless measurement of the surface band-bending and the energetic distribution of interface states  $D_{it}(E)$ . The SPV measurements were performed under flowing dry  $\text{N}_2$  in the same

experimental configuration as described in [4]. From a large-signal photovoltage pulse the surface potential was obtained.  $D_{it}$  is determined from a series of photovoltage pulses measured with different field voltages between the transparent electrode and the wafer [5].

The SE data of H-terminated and differently oxidised surfaces were collected immediately after preparation, ex-situ, using a Woollam Variable Angle Spectroscopic Ellipsometer (VASE) working in a spectral range of 250 to 1700 nm. In order to obtain data rapidly (10 min) only a limited photon energy range, 3.2 - 4.5 eV was studied. The angle of incidence during the measurement was  $77 \pm 0.02^\circ$ .

A home-made spectroscopic in-situ Ellipsometer described elsewhere [6] was used for studying the pure water treatment. For that purpose the sample was placed into a Teflon cell with quartz-windows allowing for ellipsometric measurements through the water ambient at  $65^\circ$  angle of incidence. The quartz-windows have been carefully selected for minimising strain induced anisotropy that would modify the spectra. Additionally, the residual window-strain contribution has been reduced by a calibration procedure described in [7].

### 3. RESULTS AND DISCUSSION

The results from ex-situ SE-measurements on H-terminated and differently oxidised surfaces are shown in Fig 1. Also the reference data according to Aspnes [8] were plotted which were obtained in a dry  $N_2$  ambient after multistep chemical preparation to remove surface overlayers and reduce roughness. An excellent agreement for  $E > 3.5$  eV verifies that H-termination provides an ideal smooth

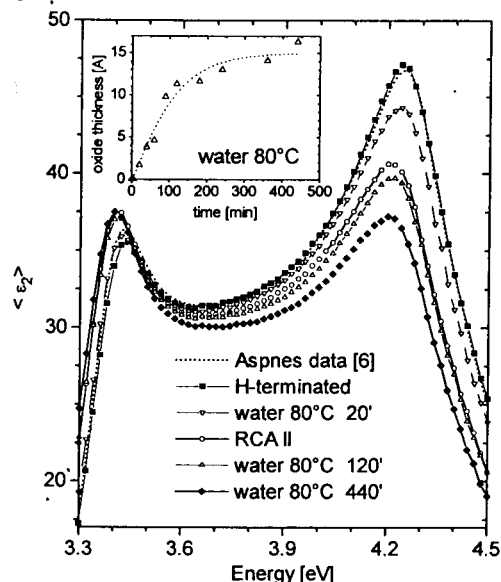


Fig. 1:  $\epsilon_2$  for H-terminated and oxidised Si surfaces  
Insert: oxide thickness vs. immersion time in  $H_2O$

The thicknesses of the oxide films on formerly H-terminated surfaces ranging from 0 to 17 Å were derived from the experimental data in Fig. 1 and given as function of immersion time in deionised water at  $80^\circ C$  (Fig 1, insert).

surface without any native oxide coverage. Because of the anisotropy of the Si-H-bonds and because of their electronic resonance energy laying in the IR outside of our spectroscopic range (at about 0.26 eV) [9] the hydrogen-terminated layer is apparently invisible for our uv-vis ellipsometric systems. This result is different to a recent publication [10] where probably a remaining surface roughness caused a decrease in  $\langle \epsilon_2 \rangle$  in the 4.2 to 4.4 eV region.

For the oxidised samples the actual values of the oxide thickness are determined using an iterative regression fitting algorithm. The

In order to compare with conventional preparation, Si(111) surfaces were examined immediately after applying RCA I, RCA II and RCA I + RCA II processes. The resulting layer thicknesses were determined to 13, 11 and 12 Å, respectively. The respective spectrum for the RCA II process is added in Fig. 1 for reference.

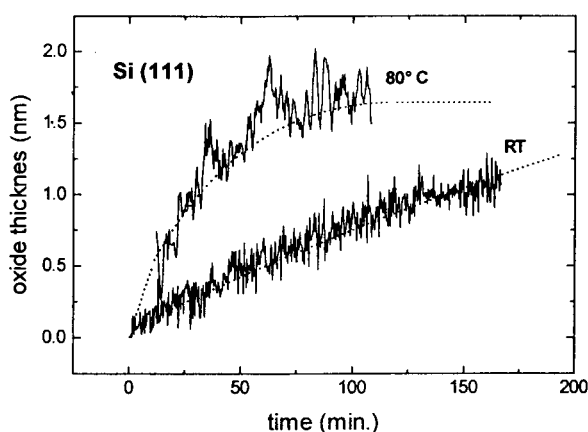


Fig. 2 Evolution of oxide thickness during water rinse at different temperatures measured in-situ with SE

A second set of experiments aimed at insight into the kinetics of oxide formation. We performed in-situ ellipsometric measurements monitoring the formation of the oxide layers during water rinsing at 30 and 80°C. At both temperatures, the oxide thickness saturated at 17 Å as measurements immediately after oxidation confirmed (Fig. 2). The oxide growth follows an exponential law with a temperature-dependent time constant.

It is well accepted that the interface state distribution depends significantly on the chemical treatment. Therefore having monitored in detail the oxidation of an H-terminated surface by ellipsometry we now concentrated on correlated changes in the interface state distribution. Results obtained by SPV on H-terminated and oxidised surfaces are presented in Fig. 3. Following the dangling bond model for the Si/SiO<sub>2</sub> interface [11] the continuous energetic distribution of interface states can be separated into several groups of states. Two groups of intrinsic states  $U_T$  resulting from strained ( $\text{Si}_3\text{Si-Si-Si}_3$ ) bonds and  $U_M$  resulting from dangling bond (DB) defects back-bonded only to silicon ( $\text{Si}_3\text{Si-}$ ) give rise to U-shaped distributions. DB defects correlated to Si atoms of lower state of oxidation,  $\text{Si}^{+1}$  ( $\text{Si}_2\text{O-Si-}$ ) and  $\text{Si}^{+2}$  ( $\text{SiO}_2\text{Si-}$ ) additionally form Gaussian distributions of extrinsic states  $P_L$  and  $P_H$  in the lower and upper half of the gap, respectively. Successfully prepared H-terminated surfaces are characterised by an U-shaped intrinsic surface state distribution and very low surface state density  $D_{it,min} < 5 \cdot 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$  on Si (100) and  $D_{it,min} < 3 \cdot 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$  on Si (111) surfaces. This is different to all standard RCA treatments which result in a high interface state density  $D_{it,min}$  of about  $10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$  [12]. The RCA II treatment subsequent to originally H-terminated surface yields slightly lower values  $D_{it,min}$  of about  $2 \cdot 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ .

In this study during pure water treatment we observed three phases of interface state evolution, each characterised by a specific defect structure. The initial phase of oxidation is characterised by an increasing density of extrinsic states below midgap ( $P_L$ ) correlated to ( $\text{Si}_2\text{O-Si-}$ ) DB defects. These states decrease when the second monolayer is formed while the  $P_H$  group correlated to ( $\text{SiO}_2\text{Si-}$ ) DB-defects additionally appears in the upper half of the gap. During the further forma-

tion of the oxide layer a slow decrease of density of these extrinsic defects can be observed. The final surface state distribution and value of  $D_{it,min}$  was found to be dependent on details of the preparation.

Best results were obtained using a hot water treatment ( $T: 80\text{ }^{\circ}\text{C}$ ) of H-terminated surfaces yielding oxide layers up to  $15\text{ \AA}$  thickness characterised by a nearly intrinsic surface state distribution.

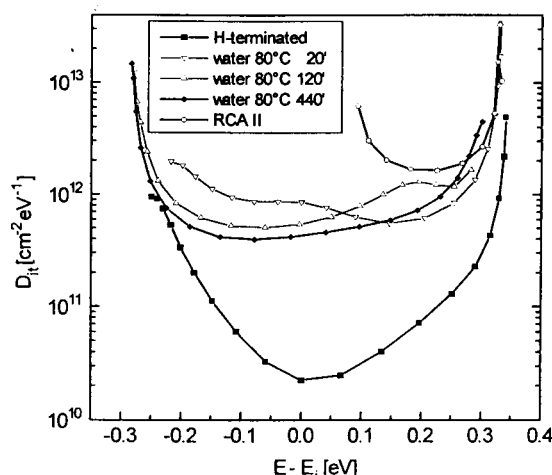


Fig. 3 Interface state distribution of H-terminated surfaces after different oxidation methods

The interface state density of thin oxides  $D_{it,min} < 4 \cdot 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  prepared in such a way was found to be significantly lower than that of conventionally (RCA) prepared oxides on Si surfaces.

The application of these thin oxides as passivating interlayers in  $n^+$ -SIPOS/p-silicon heterojunction solar cells has shown that the interface related recombination loss can be markedly reduced [13].

#### 4. SUMMARY

We demonstrated that combined monitoring of interface state distribution by SPV and surface morphology and oxide coverage by SE can serve as a sensitive tool for optimisation and control of Si(111) preparation methods aimed at very thin passivation layers with outstanding electronic interface properties. By the comparison of SE data and interface state distributions during the initial oxidation of H-terminated surfaces the development of electronic defects was correlated with the layer by layer oxide growth on Si(111) surfaces.

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## THE MECHANISM OF GROWTH OF THIN OXIDE FILMS ON SILICON USING OZONATED WATER

S. L. Nelson\*, R. T. Fayfield\*, K. K. Christenson\*, B. E. Deal\*\*

### 1. ABSTRACT

The growth of room temperature oxide on silicon with ozonated water can be explained by the Cabrera-Mott model, which is also a model for the growth of low temperature oxide on metal.<sup>1</sup> Ellipsometry is used to measure the thickness of the oxide layer for different treatments. These treatments include variations in ozone dispense time, ozone concentration, silicon doping level, temperature. The oxidation kinetics are found to be consistent with the Cabrera-Mott model for low temperature oxidation and the rate limiting step is determined.

### 2. INTRODUCTION

For low temperature oxidation beyond one monolayer to occur, the energy required for oxygen to overcome the activation energy of SiO<sub>2</sub> and diffuse must be supported by some mechanism other than thermal energy. The Cabrera-Mott model offers a mechanism by postulating that an electric field is created in the oxide.<sup>1</sup> This electric field is given by  $E = V/x$ , where  $V$  is the difference in the electronic levels of silicon and oxygen, and  $x$  is oxide thickness. Upon adsorption, the acceptor level of oxygen is below the silicon conduction band by the quantity:

$$eV = Y + W_b - \phi_v \quad (1)$$

where  $Y$  is the electron affinity of oxygen,  $W_b$  is the binding energy of oxygen on the surface, and  $\phi_v$  is the work function of silicon. An estimate of  $W_b$  allow an estimate of  $V \approx 1$  Volt.<sup>1</sup> An electron fills the oxygen level by one of the following reactions and an electric field is created between the oxygen anion and the silicon.



The electron in equation 2 tunnels by Fowler-Nordheim tunneling from the Si-oxide interface to the surface, while the hole in equation 3 tunnels by Fowler-Nordheim tunneling from the surface to the Si-oxide interface. The oxygen anion is pulled by the electric field over the activation energy barrier to diffuse and react at the silicon-oxide interface. As the oxide grows the electric field strength is reduced until it is no longer strong enough to support diffusion.

### 3. EXPERIMENTAL

These experiments were performed in an FSI MERCURY® MP acid spray processor. The chemical sequence used was SPM, DI water rinse, 100:1 HF, DI water rinse, ozonated water, followed by a DI water rinse and spin dry.

\* FSI International, Surface Conditioning Division

\*\* Stanford University, Electrical Engineering Department

### 3.1 Ellipsometry

Oxide thickness was measured using a Gaertner ellipsometer. Test wafers, unless otherwise noted, were 150 mm, <100> silicon, boron doped, and 10-14 ohm-cm. Wafers were placed in slots 1, 13, 24 and 25 of a cassette with filler wafers in the remaining slots. The oxide thickness was measured at five points on each test wafer and the average oxide thickness and standard deviation were calculated.

The technique of ellipsometry in measuring thin oxides can be sensitive to error or variation from organics on the surface, surface roughness, or material optical properties. These sources of variation or error were either controlled during the measurement or eliminated by duplicating with another analytical technique. To minimize the potential problem of organics on the surface, an SPM step was used in the cleaning process. Measurements were taken within five minutes to minimize the amount of organics absorbed from the environment. To minimize the potential problem of surface roughness, new prime wafers were used for each experiment. For <100> silicon, the index of refraction is 3.88 and the extinction coefficient is 0.02, and for oxide the index of refraction is 1.46.<sup>2</sup> Because these optical parameters are held fixed when measuring thin oxides, the measurement will be repeatable but may not be accurate. To verify the accuracy of the ellipsometer data, an Auger spectroscopy sputter depth profile was performed. It was found that the Auger measurement was 14% higher than the ellipsometer.

## 4. DATA AND RESULTS

### 4.1 Oxide Thickness versus Ozone Dispense Time

Figure 1 shows that the thickness of the oxide layer does not follow the kinetics of a purely diffusion controlled process. Instead, a maximum oxide thickness is observed independent of additional exposure to ozone. When the oxide is thin, the electric field is strong and the oxide grows rapidly. As the oxide thickness increases, the electric field strength is reduced and oxide growth slows. The required electric field strength can be calculated from the formula  $E = V/x$ . In section 2,  $V$  was estimated to be about 1 Volt. With a 10.0 oxide this corresponds to an electric field of  $1 \times 10^7$  V/cm. It has been shown by other researchers that by applying a negative voltage on a scanning probe microscope

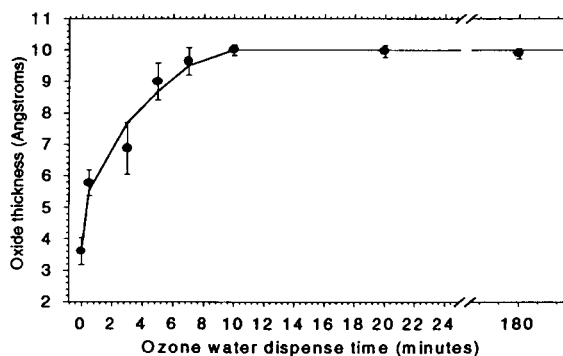


Figure 1. Oxide thickness measured with ellipsometry for different ozone times



tip with respect to the substrate while holding the tip in close proximity to a silicon surface, a thick oxide layer can be grown from oxygen.<sup>3</sup> An induced electric field of  $1 \times 10^7$  V/cm resulted in an 80 Å oxide layer. In both experiments when the electric field strength reduced to below  $1 \times 10^7$  V/cm oxidation stopped.

#### 4.2 Oxide Thickness versus Ozone Concentration

The low temperature oxidation rate of silicon with ozonated water could be limited by one of several variables including ozone concentration, diffusion of ozone to the surface, adsorption of ozone at active sites on the surface, number of electrons or holes, oxygen diffusion through the existing oxide, or reaction of oxygen and silicon at the interface. Figure 2 shows that the ozone concentration in DI water has a large effect on the oxidation kinetics. In the range of ozone concentrations between 1.0 and 10.0 ppm, the amount of ozone in the liquid is limiting the rate of oxide growth. If the ozone concentration could be increased above 10.0 ppm, at some point a different variable could become rate limiting.

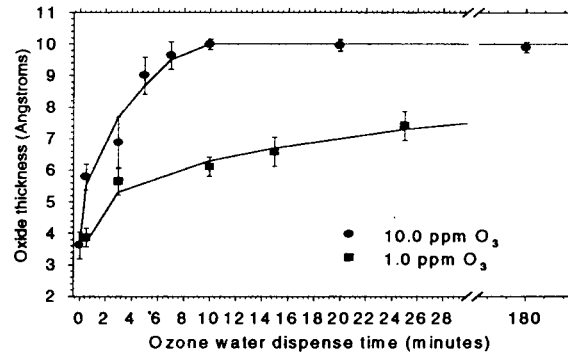


Figure 2. Oxide thickness for two different ozone concentrations

#### 4.3 Oxide Thickness versus Silicon Doping Type and Level

The oxidation of silicon involves either an electron or a hole as given by formulas 2 and 3 of section 2. The availability of electrons may limit the rate of oxide growth if an ozone molecule chemically adsorbs on the surface and must wait to react. The N+ doped substrate will have the most electrons, while the P+ doped

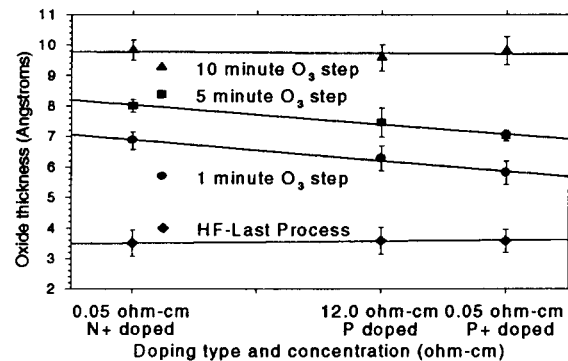


Figure 3. Oxide thickness as measured by ellipsometry versus substrate doping

substrate will have the fewest. For these experiments, four wafers for each doping level were processed in the same run to ensure that the dispense time, ozone concentration, and temperature were the same. Because the ellipsometer reads the same at each doping level for the HF-last process, the doping level does not have an effect on the optical properties of the substrate. Figure 3 shows that the oxidation rate is increased as the number of electrons increases.

#### 4.4 Oxide Thickness verses Temperature

At 60°C ozone is less soluble in DI water and is also less stable than at room temperature resulting in slower oxidation. Temperature does effect the final oxide thickness by adding thermal energy to the electric field energy, allowing anions to diffuse farther. Figure 4 shows that at 60°C the final oxide thickness was 12.0 .

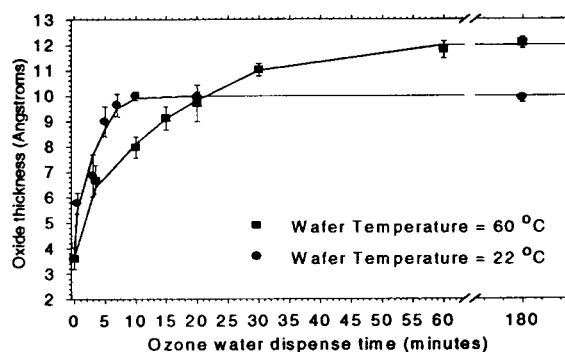


Figure 4. Oxide thickness for two different temperatures

## 5. CONCLUSIONS

The growth of low temperature oxide on silicon is found to follow Cabrera-Mott oxidation kinetics. In our experiments the rate limiting step was determined to be the amount of ozone in the liquid. We found that substrate doping had an effect on the oxidation kinetics. When more electrons were available in the substrate conduction band the oxide grew faster. Higher temperatures will increase the final oxide thickness by contributing thermal energy to the electric field energy, increasing anion diffusion lengths. We found that the minimum electric field strength to support diffusion of oxygen through the existing oxide layer was about  $1 \times 10^7$  Volts/cm.

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## ULTRA-THIN GATE OXIDES BELOW 3 nm GROWN IN A CLUSTER TOOL FURNACE

M. Depas\* , T. Nigam, K. Kenis and M.M. Heyns  
IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

H. Sprey and R. Wilhelm  
ASM Europe, Rembrandtlaan 7, 3723 BG Bilthoven, The Netherlands

**ABSTRACT:** In this work the growth of ultra-thin (1.5 to 3 nm) SiO<sub>2</sub> layers on Si in a cluster tool furnace is examined. The tunnelling and breakdown characteristics of these ultra-thin gate oxides are discussed for different Si surface conditioning.

### 1. INTRODUCTION

The electrical properties of thermally grown ultra-thin SiO<sub>2</sub> layers on Si are a critical issue for the characteristics of deep sub micron CMOS (Complementary Metal Oxide Silicon) transistors. It has recently been demonstrated that thermally grown SiO<sub>2</sub> layers thinner than 3 nm can still be used as a gate dielectric in 0.1  $\mu$ m or smaller MOS transistors [1]. Very severe requirements exist for the ultra-thin gate oxide thickness uniformity, yield and reliability.

### 2. EXPERIMENTAL

The Si wafers are 150 mm p/p<sup>+</sup> epi material from Wacker. The wafers received a Piranha treatment followed by an RCA clean in a spray tool. Some wafers were 2 min. dipped in a 2% HF solution to remove the chemical oxide layer after the SC2 step, rinsed in DI water and dried using a Marangoni tool. Metal contamination was of the order of 10<sup>10</sup> atoms/cm<sup>2</sup> as determined by DSE-VPD-TXRF. The thermal growth of the oxide layers was done in the vertical furnace of an ASM Advance 600 cluster tool [2]. The loading of the wafers was done at 650°C in a 25% O<sub>2</sub>/N<sub>2</sub> ambient at a reduced pressure of 1 Torr to limit the growth during this critical step. The temperature ramp-up and a 10 min. stabilisation period was done in 1% O<sub>2</sub>/N<sub>2</sub> at atmospheric pressure. This was followed by an oxidation period  $t_{ox}$  in 10%O<sub>2</sub>/N<sub>2</sub> and cooling in N<sub>2</sub>. The electrical evaluation of the gate oxide was done with n<sup>+</sup>poly-Si gate MOS capacitor structures. Poly-Si deposition was done in the LPCVD reactor of the cluster tool and P solid source diffusion was used to make degenerately doped n<sup>+</sup> gate material. Capacitor structures were defined using poly wet etch and an aluminium capping on the poly-Si gate. The wafers received a final anneal in forming gas after backside metalisation.

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\* E-mail: depas@imec.be

### 3. RESULTS AND DISCUSSION

#### 3.1 Oxide growth

The ultra-thin SiO<sub>2</sub> growth characteristics are presented in Fig.1. A linear growth law is observed with an offset at  $t_{ox}=0$  due to the growth during the loading, ramp-up and stabilisation step. It is seen from Fig.1 that by reducing the oxidation temperature, the growth of oxide layers as thin as 1.5 nm can still be controlled in a cluster tool. The advantage of the cluster tool over a conventional open furnace is the better control of the ambient during the loading of the wafers. Only a very small influence of the removal of the chemical oxide by an HF dip on the thermal oxide layer was observed. In Table 1 the oxide thicknesses are compared in the case of an SC2 and HF last cleaning process. As determined by ellipsometry, in the case of the removal of the SC2 chemical oxide by the HF dip the grown oxide layer is 0.04-0.07 nm thinner. The chemical oxide layer is already incorporated in the thermal oxide during the very initial oxidation of the Si surface. In both cases extremely uniform oxide layers were obtained as demonstrated by the very low 3 sigma values in Table 1.

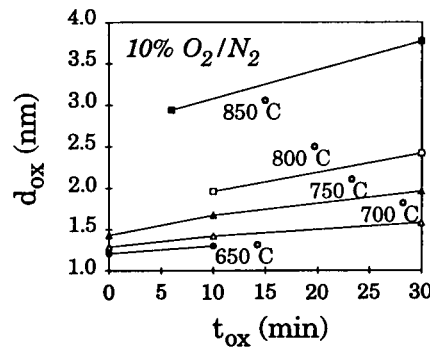


Figure 1. Growth kinetics for Si oxidation in 10% O<sub>2</sub>/N<sub>2</sub> at 650 to 850°C in the ASM A600 cluster tool furnace (SC2 last Si surface preconditioning).

Table 1. Influence of the Si cleaning process (SC2 and HF last) on the oxide thickness  $d_{ox}$  ( $T_{ox}$ ,  $t_{ox}$ : oxidation temperature, period).

| $T_{ox}$<br>(°C) | $t_{ox}$<br>(min) | clean | $d_{ox}$<br>(nm) | 3sigma<br>(nm) |
|------------------|-------------------|-------|------------------|----------------|
| 650              | 0                 | HF    | 1.17             | 0.13           |
| 650              | 0                 | SC2   | 1.21             | 0.07           |
| 650              | 10                | HF    | 1.25             | 0.04           |
| 650              | 10                | SC2   | 1.30             | 0.03           |
| 800              | 30                | HF    | 2.34             | 0.04           |
| 800              | 30                | SC2   | 2.42             | 0.03           |

### 3.2 Electrical characteristics

The extremely good oxide thickness uniformity was also demonstrated from the tunnel current measurements on MOS structures [3-5]. In Fig.2 the exponential increase of the direct tunnel current (DT) in ultra-thin oxide layers below 3 nm is observed with the decrease of the oxide thickness. The distribution of the gate voltage  $V$  corresponding with a  $0.01 \text{ A/cm}^2$  direct tunnel current density is compared in Fig.3 for the two different Si wafer cleanings (a: HF last, b: SC2 last). The tail in the distribution is caused by pinholes in the oxide [4]. For both cases a low defect density of  $0.3\text{-}0.4 \text{ defects/cm}^2$  was measured for these ultra-thin oxides. The difference between the distributions a and b in Fig.3 can be explained by a  $0.05 \text{ nm}$  smaller oxide thickness in the case of the removal of the chemical oxide prior to oxidation, in good correspondence with the ellipsometric results of Table 1.

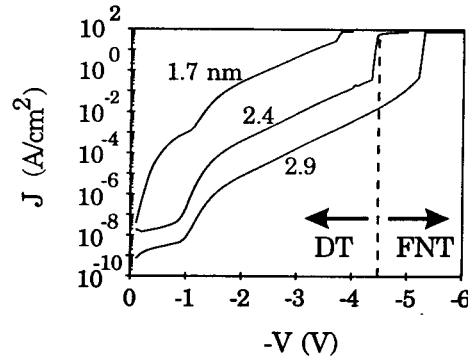


Figure 2. Tunnel current density  $J$  in gate oxides below  $3 \text{ nm}$  (DT: direct tunnelling, FNT: Fowler-Nordheim tunnelling)

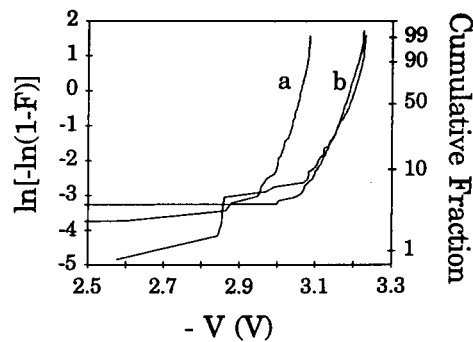


Figure 3. Cumulative distribution of the measured gate voltage  $V$  at  $0.01 \text{ A/cm}^2$  DT current through a)  $2.34 \text{ nm}$  (HF last) and b)  $2.42 \text{ nm}$  (SC2 last) gate oxide ( $16 \text{ mm}^2$  capacitor structures).

The intrinsic reliability of these ultra-thin gate oxide layers was investigated with Time Dependent Dielectric Breakdown (TDDB) measurements. It is known that the charge to breakdown (QBD) value strongly increases with the transition from FNT to DT constant current stressing [5,6]. A strong asymmetry between substrate and gate injection has been observed for these ultra-thin gate oxide layers [6]. Dielectric breakdown of sub 3 nm oxide can still occur in the DT regime for the worst case condition of gate injection but for substrate injection breakdown could only be observed under FNT conditions. In Fig.4 the QBD distribution of 2.4 nm oxide is compared for the different cleaning conditions. A small decrease of the QBD value is observed if the HF last preconditioning is used. This decrease cannot be explained by the slight difference in gate oxide thickness because for both polarities a QBD increase is expected in this regime for thinner oxides [5-6].

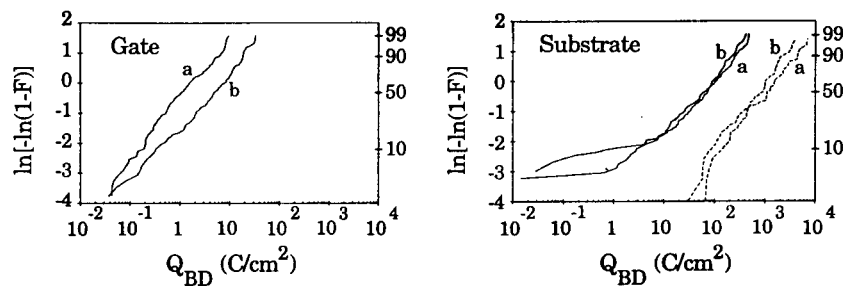


Figure 4. QBD distribution of a) 2.34 nm (HF last) and b) 2.42 nm (SC2 last) oxide for 0.1 A/cm<sup>2</sup> gate injection (DT) and 1 A/cm<sup>2</sup> substrate injection (FNT). The full and broken lines are for 10<sup>-3</sup> cm<sup>2</sup> and 10<sup>-4</sup> cm<sup>2</sup> area respectively.

#### 4. CONCLUSIONS

It was demonstrated that the growth of extremely uniform ultra-thin 1.5 nm to 3 nm gate oxides can be controlled by thermal oxidation in a low pressure cluster tool furnace. It was shown that the removal of the SC2 chemical oxide by an HF dip has only a minor influence on the growth and electrical characteristics of these extremely thin oxide layers. For both cases good quality ultra-thin gate oxides were demonstrated.

*Acknowledgements:* This work is done within the ESPRIT project 20182 (ASPYP)

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## ULTRA-THIN SiO<sub>2</sub> FORMATION AT LOW TEMPERATURES USING ACTIVATED OXYGEN

T. FUYUKI, S. MURANAKA, and H. MATSUNAMI

Dept. Electronic Sci. & Eng., Kyoto University  
Sakyo, Kyoto 606-01 JAPAN

Ultra-thin SiO<sub>2</sub> was formed at low temperatures (300 ~ 500 °C) by oxidation of Si using activated oxygen species. Initial growth of SiO<sub>2</sub> films was found to grow following the parabolic law, and the estimated activation energy of the oxidation rate was about one order of magnitude smaller than that in the thermal oxidation case, which shows the activated oxygen enhanced oxidation. The obtained oxidation rate of a 10<sup>-2</sup> ~ 10<sup>-1</sup> nm/min range is appropriate to get the atomically controlled interface formation.

### 1. INTRODUCTION

For future ultra-large scale integrated circuits (ULSIs), low-temperature processes of high-quality ultra-thin oxide are strongly required. Device-quality SiO<sub>2</sub> films for MOSFET gate insulators could be achieved by remote plasma-assisted CVD [1-4] in which activated oxygen react with SiH<sub>4</sub> forming SiO<sub>2</sub>. Ultra-thin SiO<sub>2</sub> formation by oxidation of Si surfaces before the CVD process yielded very low interface state density in the mid 10<sup>10</sup> cm<sup>-2</sup>eV<sup>-1</sup> range, and performances of fabricated FETs were improved [1]. Oxidation kinetics at relatively high temperatures (above 700 °C) in an oxygen atmosphere are extensively studied [5], but very few has been reported on the oxidation mechanism in a concerned temperature range of 300 ~ 500 °C. Hattori et al. studied [6,7] thin SiO<sub>2</sub> formation by thermal oxidation of Si surfaces, and revealed the interface atomic configurations, but electrical properties of thin SiO<sub>2</sub> films were not reported. In this study, ultra-thin SiO<sub>2</sub> formation at low temperatures using activated oxygen species is investigated in detail. The specific features induced by activated oxygen are shown, and the atomic level control of interface formation is discussed. Electrical properties of the formed SiO<sub>2</sub> films are also characterized.

### 2. EXPERIMENTAL

A schematic diagram of an experimental apparatus is shown in Fig.1. Activated oxygen species were produced by ECR plasma generated by microwave (2.45 GHz) of 100 W. The back-pressure of the main chamber was

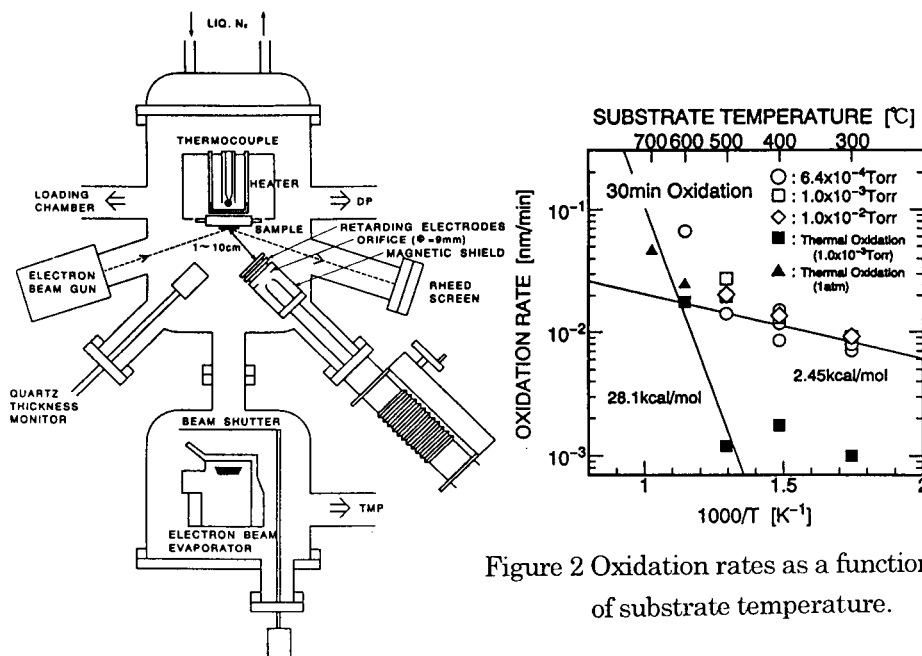


Figure 2 Oxidation rates as a function of substrate temperature.

Figure 1 Schematic diagram of experimental apparatus.

$10^{-9}$  Torr, and the working pressure during oxidation was maintained in a range of  $10^{-4} \sim 10^{-2}$  Torr by regulating the flow rate of oxygen in a range of 3  $\sim$  50 sccm. The number of atomic oxygen flux was estimated from the oxidation rates of silver foils, and was in the order of  $10^{15} \text{ cm}^{-2}\text{s}^{-1}$  regardless of working pressure. High-purity metallic Si can be evaporated using an electron-beam heating system in the sub-chamber attached below the main one. Sample surfaces of Si (100) wafers were cleaned by the conventional RCA procedure with the final treatment of SC1. The thickness of formed  $\text{SiO}_2$  was estimated from  $\text{Si}_{2p}$  peaks measured by angle-resolved XPS.

### 3. RESULTS AND DISCUSSIONS

In a concerned temperature range of  $300 \sim 500^\circ\text{C}$ ,  $\text{SiO}_2$  was found to grow following the parabolic law with a rate constant of  $3.3 \times 10^{-9} \mu\text{m}^2\text{s}^{-1}$ , which is two orders of magnitude higher than that in the dry  $\text{O}_2$ . Typical oxidation rates were shown by open notations in Fig.2 as a function of the substrate temperature. The results of thermal oxidation in the pure oxygen without the activated one were shown by solid ones as a reference. It should be noted that in the range of  $300 \sim 500^\circ\text{C}$ , the oxidation rates by the activated oxygen were higher than that of thermal oxidation (the observed constant oxidation



rate in the case of thermal oxidation might be due to native oxide formations by the RCA cleaning), which shows the activated oxygen enhanced the oxidation process. Moreover, the estimated activation energy was 2.45 Kcal/mol, which was about one order of magnitude smaller than that in the thermal oxidation case. The obtained oxidation rate of a  $10^{-2} \sim 10^{-1}$  nm/min range is appropriate to get the atomically controlled interface formation.

Typical atomic configurations at the interfaces of SiO<sub>2</sub>/Si were revealed by angle resolved XPS. Based on the analyses of chemical shifts of Si<sub>2p</sub> peaks, the atomic configurations at an interface was found [8] to be the same as the case of the thermally oxidized interface [6,7], even though the dominant process in the oxidation by the activated oxygen might differ from that in the pure thermal oxidation as discussed above. Further experimental studies are required to reveal the oxidation mechanisms in detail.

Owing to the limited thickness of oxidized layer by direct oxidation of Si surfaces at low substrate temperatures, the novel technique of alternating processes of Si-deposition and oxidation was proposed. High-purity Si was deposited on the substrate at a precisely controlled rate, and then, the deposited Si layer was fully oxidized by the activated oxygen species. As shown in Fig.3, the deposited Si layer (0.9 nm thick) could be fully oxidized within 10 minutes, and the expected SiO<sub>2</sub> layer thickness was 1.7 nm

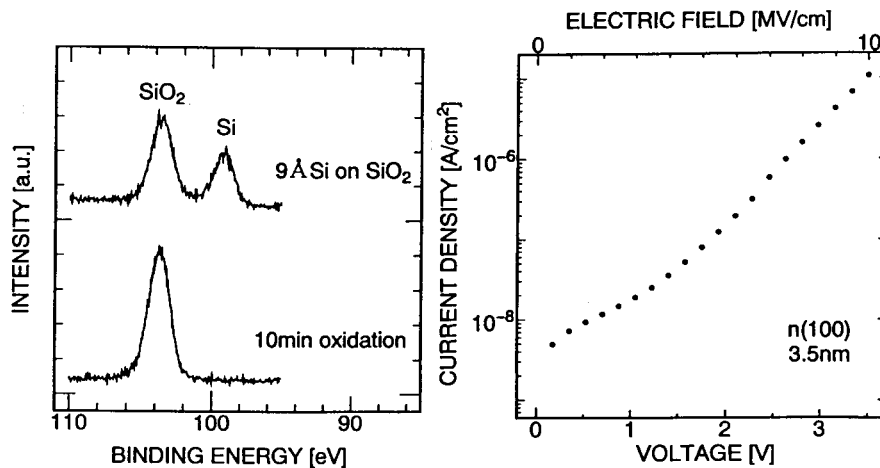


Figure 3 Typical XPS spectra of Si<sub>2p</sub> peaks of deposited Si layer and its oxidized layer.

Figure 4 Current-voltage characteristic in Al/SiO<sub>2</sub>(3.5 nm thick)/Si structure.

following the published data of the densities of Si and SiO<sub>2</sub>. Fixed thickness of SiO<sub>2</sub> was reproducibly obtained by controlling the deposited Si thickness and the number of repeating cycle. Figure 4 shows a typical current-voltage characteristic for the sample of Al / SiO<sub>2</sub> (3.5 nm) / Si MOS structure. A direct tunneling current was clearly observed. Preliminary capacitance-voltage analyses showed the interface state density in the  $10^{11}\text{cm}^{-2}\text{eV}^{-1}$  order, which is one order higher than that at the thermally grown SiO<sub>2</sub>/Si interface. Precise surface treatments and improved process sequences (e.g. direct oxidation before Si deposition) are now under investigations.

#### 4. CONCLUSIONS

Ultra-thin SiO<sub>2</sub> films was obtained at low temperatures (300 ~ 500 °C) by direct oxidation using activated oxygen species. SiO<sub>2</sub> was found to grow following the parabolic law, and the estimated activation energy of the oxidation rate was about one order of magnitude smaller than that in the thermal oxidation case, which shows the activated oxygen enhanced the oxidation process. The atomic configurations at interfaces were revealed by the chemical shift of Si2p peaks of XPS signals, and were found to form the similar configuration as that in the case of thermal oxidation. The obtained oxidation rate of a  $10^{-2} \sim 10^{-1}$  nm/min range is appropriate to get the atomically controlled interface formation. The tunneling current was observed using MOS structures with a gate SiO<sub>2</sub> thickness of 3.5 nm, and the feasibility of activated oxygen oxidation to form a high-quality SiO<sub>2</sub>/Si interface was discussed.

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## **Identification and Removal of Trace Organic Contamination on Silicon Wafers Stored in Plastic Boxes**

**K. Saga and T. Hattori**

ULSI R&D Labs., Sony Corp., Atsugi, 243 Japan

### **1. INTRODUCTION**

As semiconductor device geometries continue to shrink, trace volatile organic contamination adsorbing on silicon surfaces has an increasingly detrimental impact on product performance and yield[1,2]. Therefore, it becomes important to identify the origin of the organic contaminants and to eliminate them from the wafer. When wafers are stored in a plastic box in order to protect them from airborne contaminants, volatile organics from the polymeric construction material adsorb onto the wafer surfaces[3,4]. Thus, in order to eliminate these contamination sources, it is required to determine the origin of the contaminants by identifying organic compounds adsorbing on the surface of silicon wafers.

In this paper[5], we have analyzed organic contaminants on the surface of silicon wafers stored in various types of plastic boxes supplied by major silicon-wafer vendors as well as volatiles outgassing from the materials which compose these plastic boxes to identify the source of the organic contaminants on the wafers. We then evaluated various wet cleaning solutions in terms of their ability to remove these trace organic contaminants. The re-adsorption behavior of organics on the resultant wet-cleaned silicon surfaces was also examined. Possible mechanisms for the organic re-adsorption on silicon surfaces are discussed.

### **2. EXPERIMENTAL**

#### **2.1. Analysis of organics on as-received wafers from silicon vendors**

Organic contaminants adsorbing on the surface of silicon wafers, which had been stored in different types of plastic boxes from several silicon suppliers for more than one month, were analyzed using a gas chromatography-mass spectrometer following thermodesorption (TD-GC/MS) without wafer cleaning as a pre-treatment. The organic compounds were desorbed at temperatures up to 400°C in an inert gas and were then injected onto the analytical column of the GC/MS for gas analysis.

#### **2.2. Analysis of outgassing from the plastic boxes**

Volatiles outgassing from the boxes for wafer storage were analyzed using head space gas chromatography-mass spectrometry (HS-GC/MS). All the boxes we analyzed are made of polypropylene, but each box includes several parts, such as a cassette, a lid, and packing material which are made of several kinds of plastics or thermoplastic elastomer materials. Plate specimens measuring 10×10×2 mm

were cut out of not only the box materials but also the parts of the boxes. Each of the specimens were heated to 100°C and then their gases vaporized were injected onto the analytical column of the GC/MS for gas analysis.

### **2.3. Removal of organic contamination by wet cleaning**

We next examined various wet cleaning solutions in terms of their ability to remove organic contaminants from the wafer surfaces. Both the as-received and post-cleaning surface organic contaminants were analyzed using TD-GC/MS to assess the relative removal efficiency of the various chemical treatments. In order to obtain a quantitative estimate of residual organic molecules per square centimeter on the wafers, the peak areas for each organic compound of resultant chromatograms were compared with those for standard samples whose organic concentrations had already been known.

### **2.4. Adsorption property of organic compounds after cleaning**

After removal of organic contamination, the silicon wafers were stored for one month in plastic boxes whose interior was continuously purged with nitrogen or oxygen. The atmosphere in the plastic box purged with purified nitrogen was kept at an oxygen concentration of < 0.5 ppm, and at a moisture level of < 10 ppm. Organic contaminants adsorbing on the silicon surfaces was then analyzed using TD-GC/MS. The silicon-surface composition and the native oxide growth on the substrate were also analyzed using the thermal desorption spectrometer (TDS) and X-ray photoelectron spectrometer (XPS), respectively.

## **3. RESULTS AND DISCUSSION**

### **3.1. Identification of organic contaminants adsorbing on the silicon wafers**

The typical gas chromatogram of organic contaminants adsorbing on the surface of the silicon wafers stored in plastic boxes shown in Fig. 1. Chemical structures of the organic compounds identified from the mass spectra are also shown in the figure. A large amount of 2,6-di-*t*-butyl-2,5-cyclohexadiene-1,4-dione and 2,6-di-*t*-butyl-4-methylene-2,5-cyclohexadiene-1-one, corresponding to the two adjacent peaks in the middle of the chromatogram as well as a large amount of dibutyl phthalate (DBP) were detected on this wafer.

Only aliphatic hydrocarbons were detected as outgassing from the box material itself (polypropylene) and the packing material (polyester elastomer), while two kinds of aromatic compounds, 2,6-di-*t*-butyl-4-methyl-phenol (BHT) and dibutyl phthalate (DBP), were detected in small quantities in addition to large quantities of various kinds of aliphatic hydrocarbons from the wafer cassette (polypropylene) and the lid (polycarbonate), as shown in Fig.2. BHT is an antioxidant or it can also be a decomposed product of certain anti-oxidants. DBP is a common plasticizer used in polymer formation.

The two organic compounds, 2,6-di-*t*-butyl-2,5-cyclohexadiene-1,4-dione and

2,6-di-*t*-butyl-4-methylene-2,5-cyclohexadiene-1-one, found on the wafer as shown in Fig.1 are known as oxidizing products of BHT. This suggests that BHT, which had outgassed from the boxes, would have adsorbed onto the wafer surface. The DBP detected on the wafer surface is therefore a result of the adsorption of DBP outgassing from the box material onto the wafer. It was found that major organic compounds adsorbing on the wafer surface are additives in plastic materials, such as antioxidants and plasticizers which outgas in small quantities, rather than aliphatic hydrocarbons, such as unpolymerized monomers and oligomers, which outgas in large quantities.

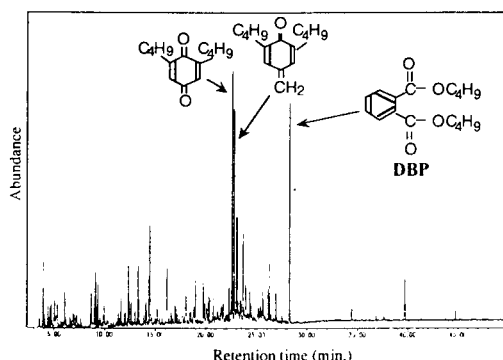


Fig.1. Typical gas chromatogram for organic contaminants adsorbing on the surface of a silicon wafer stored in a plastic box.

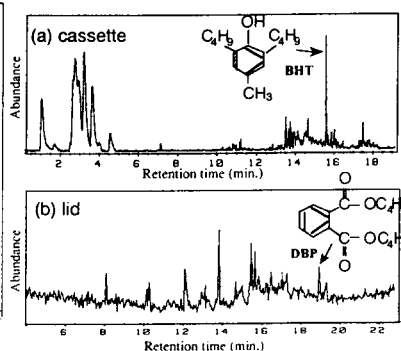


Fig.2. Typical chromatograms of gases from the two parts (the cassette and the lid) of a plastic box.

Organic additives such as BHT and DBP, with comparatively low vapor pressures and/or high dipole moments, have polar groups such as  $>C=O$  and  $-OH$ , thus, these additives are apt to adsorb on the surface of the native oxide on the silicon substrate which has polar groups such as  $-OH$  and  $-O$ , even if the quantity of these additives' outgassing is very small. On the other hand, aliphatic hydrocarbons do not have polar groups but have comparatively high vapor pressures, so they adsorb less easily onto the surface of the native silicon dioxide, although the quantity of outgassing is comparatively large. In other words, if the quantity of outgassing organics is small, this does not necessarily mean that the quantity of the organics adsorbing on the silicon surfaces will also be small.

### 3.2. Removal of the organic contaminants by wet cleaning

Fig.3 shows the amounts of the two kinds of typical additives, BHT and DBP, remaining as residues on the wafer surface after the wet cleaning. Both dilute HF and ozonized water completely removed both BHT and DBP. Ozonized water has the highest oxidation potential of the chemicals used, thus it was most effective at oxidatively degrading the organics.

Organic additives such as BHT, which have polar groups,  $-OH$  and  $=O$ , will adsorb on the native oxide surface due to strong hydrogen-bonding as shown in Fig.4. Therefore, the organic additives were not removed completely by  $H_2SO_4/H_2O_2$  and  $HNO_3$  (fuming nitric acid) because of their insufficient oxidation

potential for breaking such strong bonds. In contrast, dilute HF will be capable of removing the organics by lifting off the native oxide.

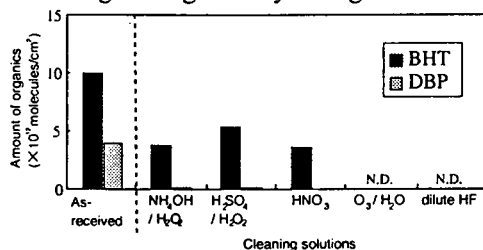


Fig. 3. Amounts of organic contaminants adsorbing on a silicon wafer before/after wet cleaning.

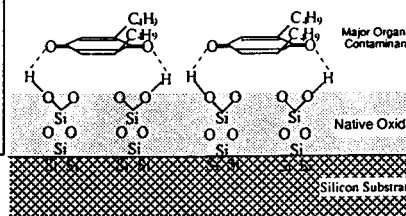


Fig. 4. Model for adsorption of organic contaminants on a silicon surface.

### 3.3. Organic adsorption on the silicon surface after wet-cleaning

The gas chromatograms of the organic compounds on the surface of the silicon wafers before and after storing in the nitrogen or oxygen purged box after dilute-HF cleaning are shown in Fig. 5. Only aliphatic hydrocarbons were detected on the wafer stored in the nitrogen purged box, while additives such as BHT and DBP, in addition to aliphatic hydrocarbons, were detected on the wafer exposed to ambient oxygen.

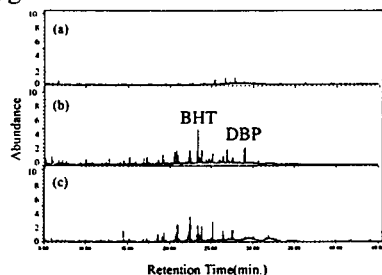


Fig. 5. Gas chromatograms of organic contaminants adsorbing on the surface of silicon wafers (a) just after DHF dipping, (b) stored in a plastic box purged with oxygen for one month after DHF dipping, and (c) stored in a plastic box purged with nitrogen for one month after DHF dipping.

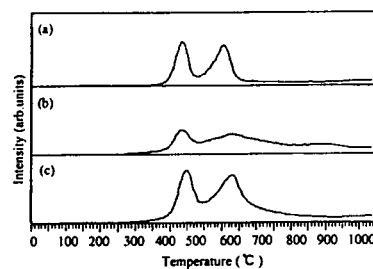


Fig. 6. Pyrograms of thermal desorption spectra for hydrogen on the surface of silicon wafers (a) just after DHF dipping, (b) stored in a plastic box purged with oxygen for one month after DHF dipping, and (c) stored in a plastic box purged with nitrogen for one month after DHF dipping.

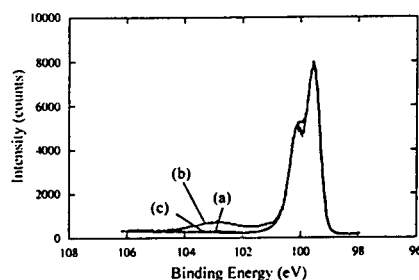


Fig. 7. Si 2p XPS spectral signature for Si(100) surfaces of wafers (a) just after DHF dipping, (b) stored in a plastic box purged with oxygen for one month after DHF dipping, and (c) stored in a plastic box purged with nitrogen for one month after DHF dipping.

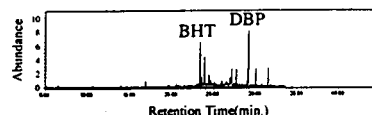


Fig. 8. Gas chromatogram for organic contaminants adsorbing on a silicon surface cleaned with ozonized water and stored in a plastic box purged with nitrogen.

The hydrogen desorption pyrogram and the XPS Si2p spectrum for the surface of wafers before and after storing in the nitrogen or oxygen purged box are shown in Figs.6 and 7, respectively. Figs.6 and 7 suggest that hydrogen termination was broken and a native-oxide layer grew on the silicon wafers stored in the oxygen atmosphere, while native oxides did not grow with hydrogen termination on the silicon wafer stored in the nitrogen atmosphere. The surface of the silicon wafers stored in the nitrogen atmosphere after oxide removal by DHF was non-polar due to the absence of a native oxide. Therefore, additives outgassing from the plastic box did not adsorb onto the silicon surface in the nitrogen atmosphere.

It should be emphasized that, after organic removal using HF, the regrowth of native oxide on the substrate of silicon can be avoided by using ambient nitrogen for the atmosphere inside the plastic box, if organics are to be prevented from adsorbing onto the silicon surface. For an ozonized-water-treated wafer, large quantities of adsorbed BHT and DBP on the surface of the silicon wafer were found even in the nitrogen atmosphere and were due to the presence of a chemical oxide[6] with polar groups on the surface, as shown in Fig.8.

#### 4. CONCLUSIONS

A very small quantity of additives in the plastic material are apt to adsorb onto the wafers more easily than the unpolymers monomers and oligomers outgassing in large quantities. Dilute HF as well as ozonized ultrapure water has been found to completely remove these organic contaminants adsorbing on the silicon surfaces. After wet cleaning, organic contaminants adsorb more easily on the ozonized water-treated silicon surface than on the dilute HF-treated surface. Adsorption of the organic additives on the silicon surfaces can be inhibited by preventing the native oxide growth in a nitrogen atmosphere after dilute HF cleaning.

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## INFLUENCE OF ORGANIC MOLECULE CONTAMINATION ON QUASI-BREAKDOWN OF ULTRATHIN GATE OXIDES

T. Yoshida, D. Imafuku, S. Miyazaki and M. Hirose\*

Dielectric degradation and quasi-breakdown of 3 to 5 nm thick gate oxides grown on wafers with and without organic contamination have been systematically studied under constant current Fowler-Nordheim stressing. Quantitative analysis of the tunnel current after oxide degradation has shown that the quasi-breakdown behavior is insensitive to a low level of organic molecule contamination in clean room air. A possible mechanism of the quasi-breakdown is discussed.

### 1. INTRODUCTION

The charge-to-breakdown  $Q_{BD}$  for 3-5 nm thick gate oxides is kept higher than  $1 \text{ C/cm}^2$  for electron injection from n<sup>+</sup>poly-Si gates [1], while it is dramatically enhanced for the substrate injection [2]. Also, it is known that the tunneling current is remarkably enhanced under constant-current or constant-voltage stress [3, 4]. In order to understand the origin of such quasi-breakdown, gate oxides were grown by changing the wafer surface microroughness, oxidation temperature and oxidation atmosphere. However, the breakdown behavior is almost independent of these parameters [1, 5]. In this paper we have investigated the influence of organic molecule contamination, which is now one of crucial problems in advanced superclean rooms, on the breakdown behavior of ultrathin gate oxides.

### 2. EXPERIMENTAL

Si wafers were cleaned by a modified SC-1 solution ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=0.15:3:7$  at  $80^\circ\text{C}$ ) followed by 0.1% HF +1%  $\text{H}_2\text{O}_2$  treatment. The wafers were immediately transferred to a horizontal oxidation furnace or exposed to clean room air for 20 min. The organic molecule contamination on Si surfaces was measured as a function of exposure time by high-resolution electron energy loss spectroscopy as shown in Fig. 1. The wafer surface is progressively contaminated with organic molecules with  $\text{CH}_x$  units by 15 to 30 min exposure to clean room air and it starts to be oxidized on the similar time scale. In case of heavy contamination with organic molecules, the wafer surface is also oxidized. Thus, it is not easy to discriminate the influence of the contamination on the quasi-breakdown from that of the native oxide formation. For this reason the wafer exposure time of 20 min was chosen. The oxidation was carried out in wet atmosphere at  $850^\circ\text{C}$ .

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\* Department of Electrical Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan

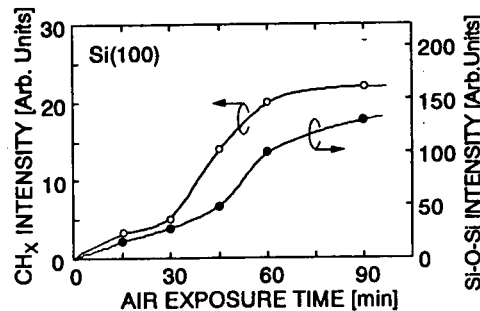


Figure 1. Surface coverage of organic molecules with  $\text{CH}_x$  units and surface oxidation state as probed by Si-O-Si bonds signal intensity measured as a function of wafer exposure time in clean room air.

### 3. RESULTS AND DISCUSSION

Local degradation of gate oxides after charge injection has been calculated by a model, in which a conducting filament extends into oxide within about 3 nm from the  $\text{SiO}_2/\text{Si}$  interface [5]. This model is supported by the TEM observation of a crystallized silicon filament produced by intrinsic breakdown [6]. Current-voltage characteristics for the gate oxides grown on the wafers with and without intentional organic contamination are compared in Fig. 2. The solid lines in the direct tunnel current region are calculated by a local wearout model [4, 5]. The quasi-breakdown current or the enhanced direct tunnel current component is explained by formation of the conducting filament with a areal size  $S_f$  of  $\sim 70 \times 70 \text{ nm}^2$  and a length of 3 nm extending from the  $\text{SiO}_2/\text{Si}$  interface and by the remaining oxide layer thickness above the filament being about 1.5 nm. As shown in Fig. 3 the remaining oxide layer thickness  $t_{\text{ox}}$  is constant for all tested MOS capacitors with different gate areas. Also, note that the organic contamination before oxidation does not cause any significant change in  $t_{\text{ox}}$  as indicated in the Fig. 3 (a). However, Weibull plot for the gate oxides with the organic contamination shows a little high cumulative failure at low injection levels compared to the case without the contamination as illustrated in Fig. 4, although  $Q_{\text{BD}}$  values of about  $5 \text{ C/cm}^2$  at 50 % cumulative failure

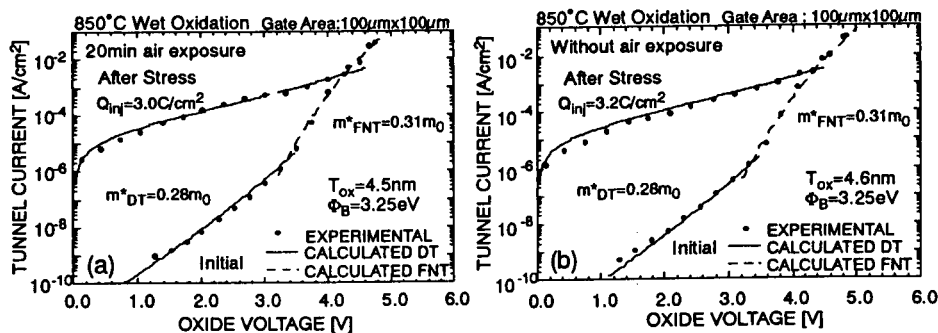


Figure 2. Tunnel current vs. oxide voltage or voltage drop in  $\text{SiO}_2$  before and after charge injection for MOS capacitors with (a) and without (b) air exposure before oxidation.

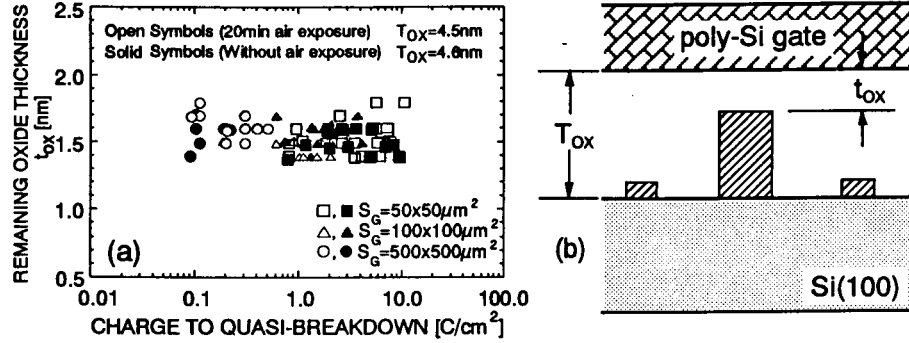


Figure 3. Remaining oxide layer thickness above the conducting filament for different gate areas  $S_g$  versus charge to quasi-breakdown (a), and a schematic illustration of a conducting filament formation in SiO<sub>2</sub> (b).

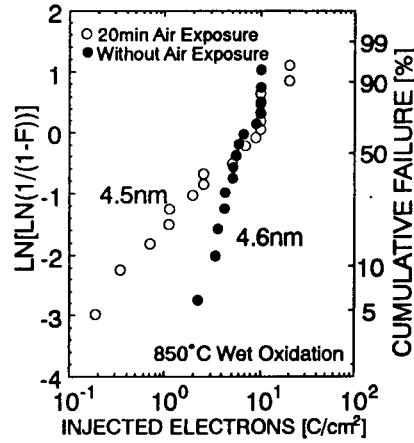


Figure 4. Weibull plot for MOS capacitors with and without air exposure before the oxidation.

is obtained for both types of MOS capacitors.

In order to reveal the kinetics of the conducting filament formation in SiO<sub>2</sub> under constant current stress, the areal size  $S_L$  normalized with the gate electrode area  $S_g$  is plotted as a function of charge to quasi-breakdown  $Q_{qbd}$  (Fig. 5). It is interesting to note that the empirical relation such as  $S_L = k Q_{qbd} S_g$  holds, where  $k$  is the constant. This relation indicates that the total electron dose  $Q_{qbd} S_g$  which causes quasi-breakdown determines the areal size of the conducting filament. This is because most of injected electrons from the n<sup>+</sup>poly-Si gate passes through the region where the progressive local oxide degradation or the filament growth takes place. It is likely that the total dose of injected electrons promotes the chemical reaction such as  $e^- + \text{Si-O-Si} \rightarrow \text{Si-Si} + \text{O}_2$  in the SiO<sub>2</sub> near the SiO<sub>2</sub>/Si interface to form the conducting path. This reaction is significantly enhanced by the existence of strained Si-O-Si bonds in SiO<sub>2</sub> near the interface [7] because hypervalent Si or five-fold coordinated Si is created by the compressive stress which distorts Si-O<sub>4</sub> tetrahedra [8]. The electron injection dissociates Si-O-Si bonds at the hypervalent silicon atom

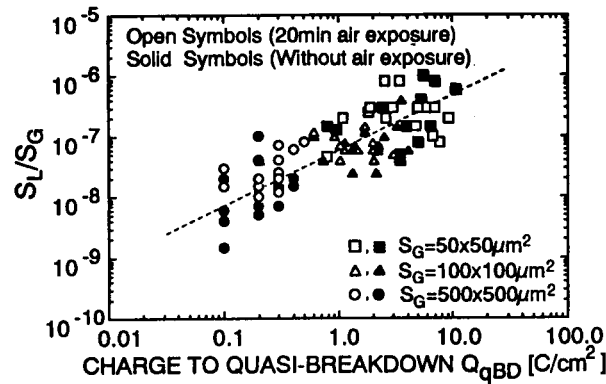


Figure 5.  $S_L/S_G$  versus  $Q_{qBD}$  for MOS capacitors with different gate areas.

sites, resulting in oxygen atom release and Si-Si bond formation in the  $\text{SiO}_2$  matrix. Since total volume of the conducting filament is given by  $S_L(T_{ox}-t_{ox})$  (see Fig. 3 (b)) and  $T_{ox}-t_{ox} \approx 3 \text{ nm}$  (Fig. 3 (a)), we obtain  $S_L(T_{ox}-t_{ox}) = k'Q_{qBD}S_G$  ( $k' = \text{constant}$ ). Physical meaning of this relation is that the total volume of the conducting filament is determined by the total injected charge into the region where oxygen molecule release and the Si filament formation simultaneously occur to reach the quasi-breakdown.

## SUMMARY

We have proposed a localized filament formation model for gate oxide degradation under constant current stress. This model can quantitatively explain the direct tunnel current component before and after the dielectric degradation. A possible chemical reaction which takes place in the oxide during electron injection is proposed and examined.

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## HYDROCARBONS IMPACT ON THIN GATE OXIDES

F. Tardif, G. Quagliotti, T. Baffert, L. Secourgeon

LETI (CEA - Technologies Avancées)

DMEL-CEA/G, 17 rue des Martyrs, 38054 Grenoble cedex 9, France

### 1. INTRODUCTION

The need for contaminant-free substrate surfaces for device fabrication has long been recognized in the semiconductor industry with major efforts in reducing particles and metallics. Until now, much less attention has been paid to organic contamination control. However, organics are suspected of inducing defects during critical fabrication steps<sup>[1],[2]</sup> such as : gate oxide, epitaxy, wafer bonding... First, the removal efficiency of hydrocarbons particularly difficult to eliminate is evaluated by IMS (Ion Mobility Spectroscopy). Then the hydrocarbons impact is here measured on gate oxides after a HFlast cleaning process. In the first test, the hydrocarbons are selected for their potential presence in the clean room. In the second test the toxicity of different hydrocarbon families is investigated.

### 2. EXPERIMENTS

The tests were performed at the Leti facilities on CZ (100) p type 14-22  $\Omega \cdot \text{cm}$  4" wafers. The hydrocarbons are intentionally deposited by injection of 5 ml of 2% organic material diluted in ethanol on the top of wafers previously treated in CARO (Sulphuric Peroxide Mixture) 2/1 at 160°C followed by a 2-minute 1%HF dip. Reference wafers are processed in the same way but without any intentional contamination in the ethanol. After contact, the wafers are individually rinsed and dried by the spin coating method. Measurement of residual hydrocarbons is performed by IMS (PCP : MMS 160 P) on 1  $\text{cm}^2$  of the wafer. Desorption is performed by temperature ramping from 20 to 250 °C with a rate of 40°C per min. Seven nm gate oxide is grown under wet conditions at 750°C without TCA or HCl. The time delay between HFlast plus hydrocarbon deposition and furnace is limited to less than 1 hour. All the thermal steps including wafer loading are performed under partial oxygen pressure. The test vehicle used is constituted by flat capacitors only (no lateral isolation). A previous silicon surface conditioning is performed in order to remove major crystalline defects due to oxygen precipitates by a 1100°C out-diffusion process.

### 3. HYDROCARBONS REMOVAL EFFICIENCY

Hydrocarbons deposit very fast on wafers and paradoxically faster in clean room than in a desk and faster in class 1 than in class 1000. The contamination caught by a wafer exposed under a laminar flow during 10' saturates the IMS! Fortunately this kind of contamination is rapidly removed by the commonly used oxidant cleanings such as CARO 2/1 10', SC1 [0.25,1,5] 10' and 6 ppm ozone in water. Nevertheless as this contamination is rapidly redeposited we rarely reached the low limit detection of the IMS. In order to discriminate between the performances of the different cleaning mixtures we chose to study 2 organic molecules : Hexadecane and Octylamine presenting a particularly high removal resistance and IMS peaks far from the parasitic ones brought by the ambient air. Figure 1 represent an example of IMS results obtained for Hexadecane removal by Ozone in water. The whole results are summarized in figure 2. SC1 is not able to remove all the types of organic contamination.

This work was carried out within the scope of the GRESSI Consortium between CEA-LETI and France Télécom-CNET

Caro due to its high process temperature enables the low limit detection of the IMS to be reached. Ozone gives good results as well but if carried out for a longer time. Better results would be obtained with higher Ozone concentrations as indicated by the drastic decrease of  $O_3$  when the contaminated wafers are dipped in the bath. In fact a simple calculation indicates that oxidation is actually limited by the number of Ozone molecules close to the wafer surface.

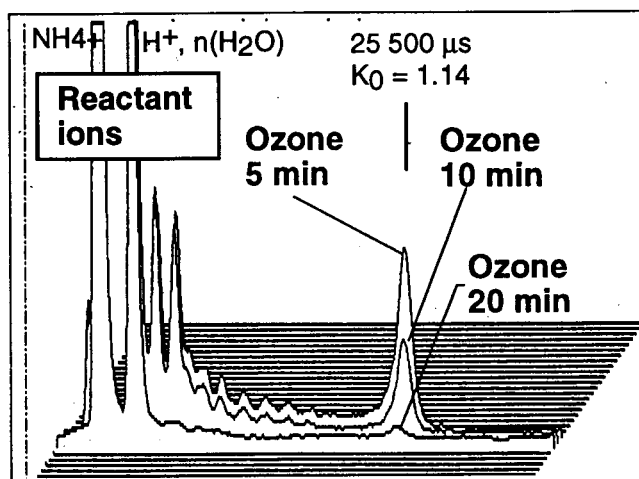


Figure 1 : IMS results for Hexadecane removal by Ozone in water

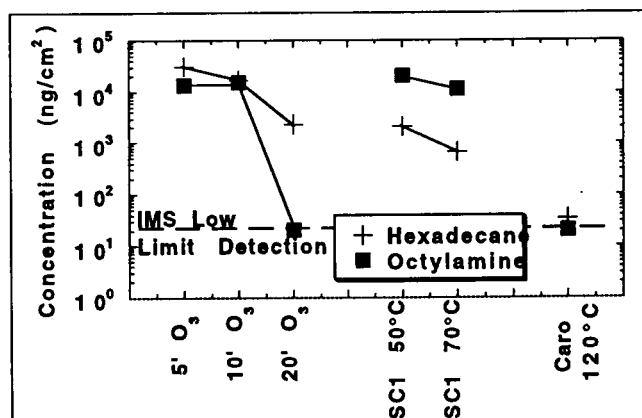


Figure 2 : Rough estimation of the residual carbonated contamination after different oxidant cleanings as determined by IMS.

#### 4. EFFECT OF HYDROCARBONS ON 7nm GATE OXIDES

In order to measure only the impact of hydrocarbons, the metallic contamination is checked by TXRF on several elements, all of them are under the arbitrary acceptable limit of  $5 \cdot 10^{10}\ atom/cm^2$ . The particles are monitored as well.

##### 4.1 Hydrocarbons present in clean room

The tested chemicals, commonly found in a clean room, are : Trichloro-ethylene (TCE), Acetone (ACE), the Posistrip EKC 830 (EKC), Ethylene glycol (EG),

Hexamethyl-disilazone (HMD) and the non-ionic surfactant NCW601A from Wako (NCW). Capacitor measurements were then performed in order to characterize what kind of defects might be generated by these organics.

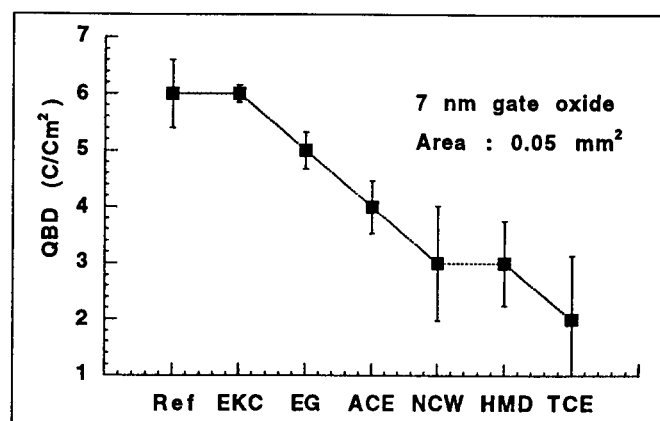


Figure 3 : Hydrocarbons impact on 7 nm gate oxide by QBD measurement on 0.05mm<sup>2</sup> capacitors.

All the tested organics, except EKC, are liable to drastically decrease the intrinsic defects of gate oxides grown after HFlast cleaning as shown by the Charge to breakdown (QBD) measurement in figure 3.

The capacitor infant breakdown yield drastically decreased only with EKC and TCE but the particle rate per cm<sup>2</sup> was higher for these two organics (figure 4). Therefore, no extrinsic defects are due to the organic chemicals.

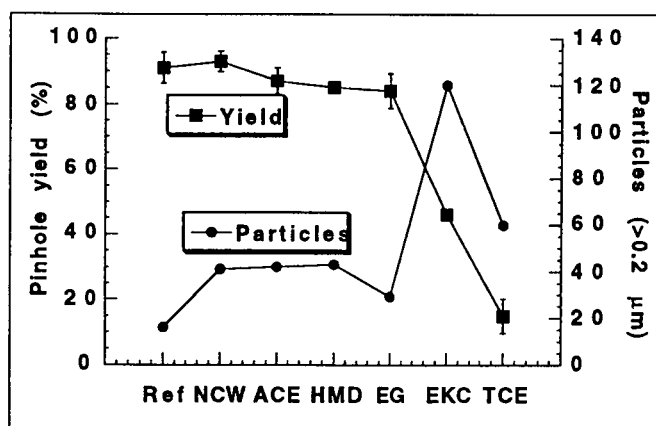


Figure 4 : Hydrocarbons impact on capacitor infant breakdown yield.

#### 4.2 Other hydrocarbons

In order to identify the most dangerous hydrocarbons, a more academic study is carried out. It could be imagined that the heavier the hydrocarbons are, the longer they are present on the silicon surface during furnace loading and consequently present a higher probability of interaction with the surface. 3 alkanes with different

boiling points were therefore tested : Octane (126°C), Decane (142°C) and Dodecane (170°C).

As represented in figure 5, these 3 chemical contaminants give rise to the same detrimental effects on 7 nm gate oxide.

We can also expect that certain organic functions may be more dangerous than others. So two alkenes : Octene and Decene, a cetone : 3-Octanone and an aromatic : Phenol all presenting a boiling point similar to Dodecane were tested.

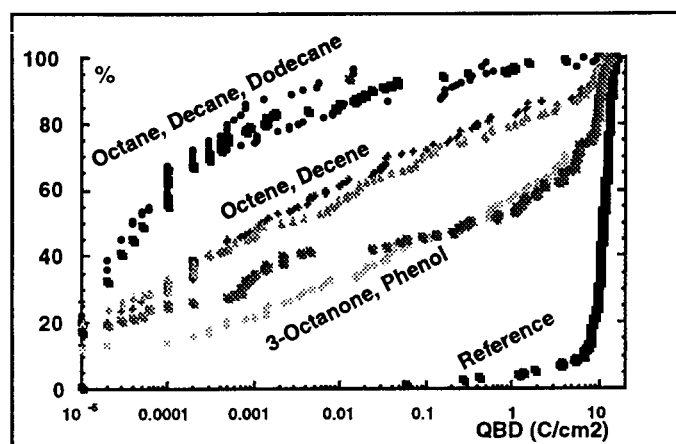


Figure 5 : 7 nm gate oxide QBD failure statistics due to deposition of different organics on HFlast treated wafers

Figure 5 shows important behaviour differences between the studied families of organics. However further investigations revealed that the amounts of organics deposited by our spin coating technique are different for the different hydrocarbon families. Indeed IMS measurements show that the less polar molecules represented by alkanes presenting a higher affinity with Silicon deposit about 10 times more than for the others.

Finally, the detrimental effects caused by hydrocabons on HFlast treated wafers before oxidation seem at first sight to be directly related to the amount of hydrocarbon rather than to other considerations.

## 5. CONCLUSION

CARO performed at 120 °C and 6 ppm of Ozone in water remove the most adherent tested hydrocarbons to a level below our IMS low limit detection. Nevertheless for the latter, a higher concentration is required to remove all the organics within an acceptable time.

Organics liable to be present in a clean room can seriously damage thin gate oxides especially after HF cleanings. The detrimental effects caused by organics seems to be more quantity-related than dependent on the type of chemical functions or on the thermal stability.

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## ON THE IMPACT OF GROWN-IN SUBSTRATE DEFECTS AND IRON CONTAMINATION ON GATE OXIDE INTEGRITY

J. Vanhellemont<sup>a</sup>, G. Kissinger<sup>b</sup>, K. Kenis<sup>a</sup>, M. Depas<sup>a</sup>, D. Gräf<sup>c</sup>, U. Lambert<sup>c</sup>  
and P. Wagner<sup>c</sup>

<sup>a</sup>IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>b</sup>Institute for Semiconductor Physics, D-15204 Frankfurt (Oder), Germany

<sup>c</sup>Wacker Siltronic AG, P.O. Box 1140, D-84479 Burghausen, Germany

### 1. INTRODUCTION

Small point defect clusters grown-in during Czochralski (Cz) crystal pulling can have an important impact on gate oxide integrity (GOI) for present day high quality silicon substrates. A pronounced effect of the crystal pulling conditions on GOI is indeed observed for gate oxide thicknesses between 10 and 100 nm [e.g. 1-2].

When the wafers are been cleaned e.g. using the SC1 clean in  $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$  mixtures, small etch pits develop on the wafer surface showing up in particle counters based on visible light scattering as localised light scatterers (LLS). As in this case they originate from the substrate they are also called Crystal Originated Particles (COP's) [3]. The use of infrared light has the advantage that the silicon substrate becomes transparent and a volume density of light scatterers can be obtained. Defect densities in the range  $10^5$ - $10^{10} \text{ cm}^{-3}$  can be measured. The size detection limit assuming  $\text{SiO}_2$  precipitates, was determined to be about 0.04  $\mu\text{m}$  [4].

In the present paper results will be presented of an ongoing study [5,6] of the impact of the silicon substrate on gate oxide quality as function of crystal pulling conditions, additional thermal treatments and the intentional introduction of metal contamination. Results obtained with visible and infrared scattering tools are correlated with those of electrical evaluation of the gate oxide quality.

### 2. EXPERIMENTAL

150 mm and 200 mm, p-type Cz substrates are studied obtained from crystals grown with different cooling ramps labelled A, B, C and D with decreasing cooling rate.

6.5 and 15 nm gate oxides are grown at 900°C on 150 mm wafers. The wafers are ramped-up in a 5%  $\text{O}_2$ /95%  $\text{N}_2$  atmosphere which is also used to grow the 6.5 nm oxides. The 15 nm oxides are grown in dry oxygen. 1, 4 and 16  $\text{mm}^2$  capacitors are fabricated using 500 nm phosphorus solid source doped polycrystalline silicon contacts patterned by wet etching. In a second experiment the effect of intentional surface contamination with  $10^{12} \text{ Fe cm}^{-2}$  before the 15 nm gate oxidation is evaluated.

The crystal defect density before and after gate oxidation is studied with infrared laser scattering tomography (LST). The metallic contamination before and after gate oxidation is monitored by total reflection x-ray fluorescence (TXRF). The carrier recombination lifetime in the substrates before and after gate oxidation is measured using micro wave absorption (MWA).

Gate oxide breakdown characteristics are studied by voltage to breakdown

(EBD) characteristics ramping up the voltage in steps of 0.1 V with a holding time of 10 ms ( $= 10 \text{ Vs}^{-1}$ ). Gate oxide defect densities are calculated assuming an intrinsic breakdown field of  $11 \text{ MVcm}^{-1}$ .

### 3. OBSERVATIONS AND DISCUSSION

#### 3.1 LST results

Average  $N_{\text{LST}}$  values for 150 mm wafers after gate oxidation, are given in Fig. 1. One can also obtain an idea of the size of the scattering centres by calibrating the instrument using samples with silicon oxide precipitates with known sizes [4]. With increasing cooling rate, the LST defect density increases while the average size of the defects decreases. After gate oxidation (70 min at  $900^\circ\text{C}$ ), the average size and apparent density of the LST defects increases but the size distribution has the same shape.

One can wonder if there exists a correlation between the surface and bulk LLS's observed by visible and near IR light, respectively. Taking for the typical size of the crystal originated particles (COP's) the value at the maximum density, a close correlation between the COP density and  $N_{\text{LST}}$  is indeed observed suggesting that both techniques reveal the same defect.

#### 3.2 Gate oxide integrity and substrate defects

When growing a gate oxide by thermal oxidation grown-in defects present in the silicon substrate are gradually incorporated into the oxide layer. The number of gate oxide defects therefore increases initially with increasing oxide thickness. It is assumed that a substrate defect which is incorporated in the oxide causes a weak spot with poorer dielectric properties leading to a smaller effective oxide thickness. An increase of the number of gate oxide defects, i.e. spots where the oxide breaks down for electrical fields smaller than the intrinsic breakdown field, is thus observed with increasing oxide thickness reaching a maximum defect density between 30 and 100 nm. This maximum is determined by the density of substrate defects and their average size. When the oxide thickness becomes larger than the typical defect size the midfield breakdown field shifts closer to the intrinsic level and the number of gate oxide defects will go down.

Figure 2 illustrates the strong impact of the substrate on the 15 nm gate oxide breakdown characteristics. The lines in the figure are cubic splines through the measurement points averaged over two wafers. The breakdown frequency has a maximum for electrical fields between 6 and  $8 \text{ MVcm}^{-1}$ . The maximum decreases with decreasing cooling rate while the corresponding breakdown field increases. For comparison results for epitaxial wafers are shown revealing no substrate effect and only intrinsic breakdown close to  $12 \text{ MVcm}^{-1}$ . One can expect that the electrical field at the maxima of midfield breakdown frequency correlates with the average size of the defects incorporated in the oxide as also suggested by Fig. 2.

In Figure 1 the calculated gate oxide defect density (per unit volume of consumed silicon) is given vs. the LST defect density measured on the same 150 mm wafer. Average values are given for two wafers each. The odd point for the highest defect density (A-wafer) is probably due to the small size of the scatterers in the substrate so that the majority of them is not detected by LST. Fig. 3 compares gate oxide defect densities with and without iron contamination for different types of

substrates. It is clear that for the Cz wafers the effect of the pulling conditions is larger than that of the  $10^{12} \text{ cm}^{-2}$  iron contamination:

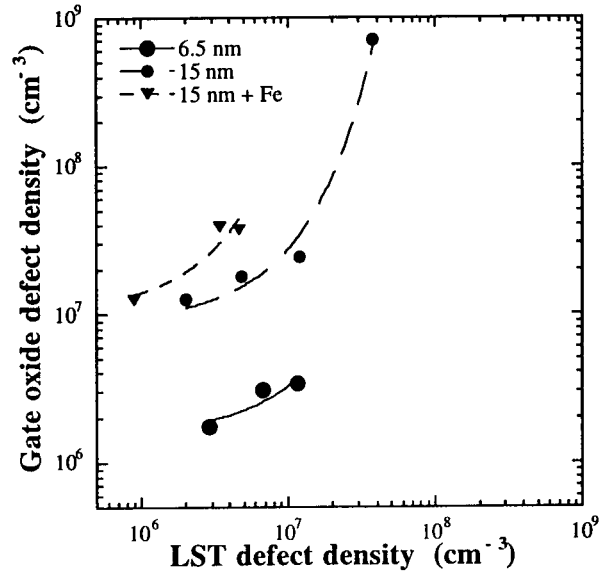


Figure 1. Gate oxide defect density vs. LST defect density for 150 mm wafers with 6.5 and 15 nm gate oxides with and without Fe contamination.

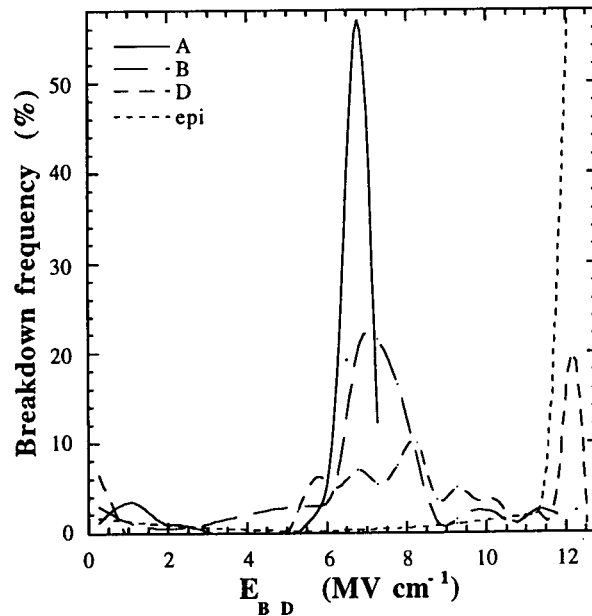


Figure 2. Breakdown frequency vs.  $E_{BD}$  for 15 nm gate oxides on 150 mm wafers.

It is shown that pulling and cooling rate during Czochralski growth of silicon single crystals strongly influence the number and size of grown-in microdefects. This distribution of microdefects not only determines the interstitial oxygen precipitation in subsequent thermal treatments but also has a prominent effect on thermal oxide break-down characteristics. A close correlation between the density of lattice defects detected by light scattering tools and gate oxide defect density is observed.

Iron contamination as high as  $10^{12} \text{ cm}^{-2}$  does not have a pronounced effect on 15 nm gate oxide integrity although the bulk lifetime of the substrates is strongly affected and reduced to a value of about  $1 \mu\text{s}$  (Fig. 4) in agreement with the expected bulk iron concentration [7].

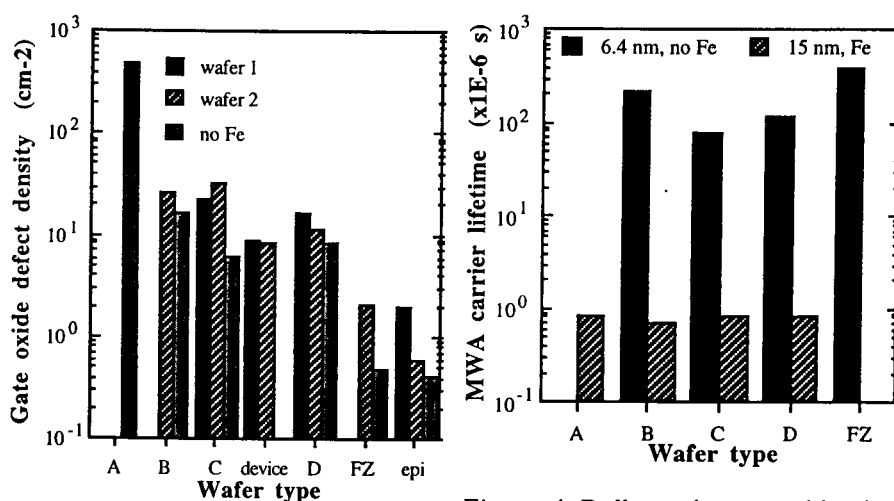


Figure 3. Gate oxide defect density for 15 nm gate oxides with and without  $10^{12} \text{ Fe cm}^{-2}$ .

Figure 4. Bulk carrier recombination lifetime measured by MWA after 6.4 and 15 nm gate oxidation without and with  $10^{12} \text{ cm}^{-2}$  Fe contamination, respectively.

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## SURFACTANTS IN WET PROCESSING OF SILICON

S. Raghavan,\* M.J. Kovach, P.D. Haworth, G. Li, C. Raghunath and J.S. Jeon.\*\*

*Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721.*

### 1.0 INTRODUCTION

In the fabrication of integrated circuits many steps involve the use of aqueous based chemicals. These chemicals include etchants such as buffered HF, photoresist developers based on tetramethyl ammonium hydroxide and alkaline cleaning solutions such as choline. Addition of surface active agents to these chemicals is known to offer many benefits during processing such as enhanced wetting of silicon<sup>(1-3)</sup>, reduced particulate contamination<sup>(4)</sup> and lowering of surface microroughness<sup>(3,5)</sup>. Even though non-ionic surfactants have enjoyed the most popularity, anionic surfactants are gaining increased attention.

Non-ionic surfactants based on alkylphenyl polyethylene oxide alcohol or alkylphenol polyglycidol are used in HF and buffered HF solutions for improved wetting of silicon and for effective penetration of chemicals into narrow hydrophobic trenches. Fundamental information on the interaction of the surfactants with silicon have not kept pace with process performance data on HF and BHF chemicals containing surfactants. In this paper, results of an investigation to characterize the interaction of a commercially available, high purity, polyglycidol type surfactant (OHS®) with silicon are reported. Specifically, the adsorption/desorption of the surfactant was investigated using Attenuated Total Reflection-Fourier Transform Infrared Radiation spectroscopy (ATR-FTIR) and wettability measurements. The effect of adsorbed surfactant was also probed using electrochemical techniques.

### 2.0 EXPERIMENTAL

#### 2.1 Materials

The non-ionic surfactant, OHS® (20% v/v aqueous solution), 100:1 HF and 20:1 BHF were supplied by Olin Microelectronic Materials. Deionized (DI) water was 18 MΩ-cm quality obtained from a Millipore Milli-Q four bowl system. All contact angle measurements were made on single side polished p(100) silicon wafers diced into 1.5 cm squares. The silicon internal reflection element, 50×20×1 mm single crystal parallelogram plate with 45° endcuts, was purchased from Harrick Scientific Corporation.

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\* To whom correspondence should be addressed.

\*\* Present address: Advanced Micro Devices, Sunnyvale, California.

## 2.2 Methods

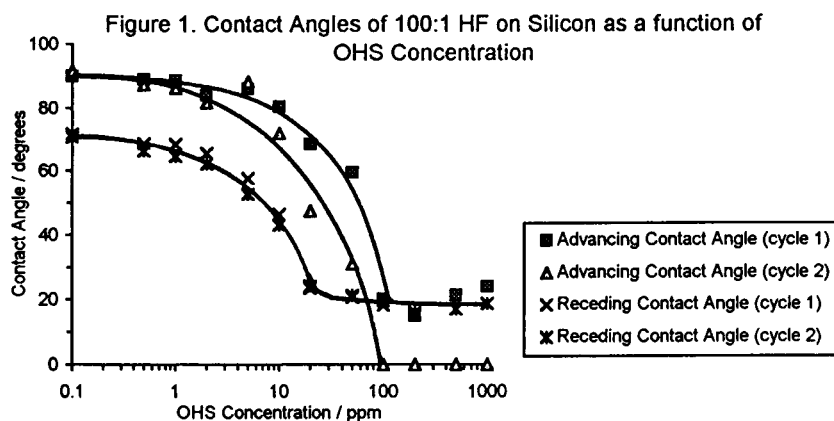
Two cycle advancing and receding contact angle measurements were made with a Cahn DCA-312 Dynamic Contact Angle Analyzer using the Wilhelmy plate technique at a sample immersion/emersion speed of  $64 \mu\text{m/sec}$ .

The removal of adsorbed surfactant by DI water was studied using an overflow rinse technique. Silicon wafer samples were immersed into and withdrawn from 100:1 HF and 20:1 BHF containing OHS at  $64 \mu\text{m/s}$  using the DCA apparatus. The samples were then rinsed with DI water in the overflow cell (volume 185 ml) and the advancing and receding contact angles of DI water on the silicon were measured after various rinse times.

Adsorption and desorption measurements were performed with a Perkin-Elmer Model 1725 FTIR spectrophotometer equipped with an MCT detector. The silicon IRE was sealed in the teflon liquid flow cell (volume  $\approx 2\text{ml}$ ) with Viton O-rings. The cell was installed in a twin parallel mirror reflection attachment. Pure 100:1 HF was drawn into the cell with a syringe and allowed to equilibrate for 10 minutes and the IR spectrum of the HF was then recorded. The 100:1 HF solution containing OHS<sup>®</sup> was then drawn into the cell. Spectra were recorded at various time intervals between 1 and 60 minutes to characterize the adsorption kinetics of OHS<sup>®</sup>. DI water was then pumped through the cell at a rate of 5 ml/min using a peristaltic pump and the spectra were recorded at various times between 1 and 60 minutes to characterize the kinetics of surfactant desorption.

## 3.0 RESULTS AND DISCUSSION

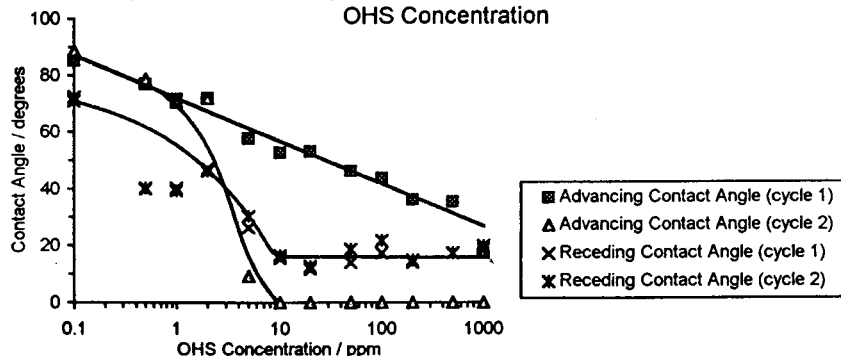
The first and second cycle contact angles of 100:1 HF and 20:1 BHF on silicon are plotted as a function of OHS<sup>®</sup> concentration in figures 1 and 2. Each measurement was performed at least three times, the associated errors were approximately  $\pm 2^\circ$ .



The first and second cycle advancing contact angles of 100:1 HF remain

approximately  $90^\circ$  as the OHS<sup>®</sup> concentration is increased to 5 ppm; the value then decreases rapidly as the OHS<sup>®</sup> concentration is increased to 100 ppm. When the surfactant concentration is increased further the first cycle advancing angle remains constant at approximately  $20^\circ$ . On the second cycle the 100:1 HF completely wets the silicon surface at OHS<sup>®</sup> concentrations of 100 ppm and above. The wetting of silicon by 20:1 BHF containing surfactant displays some differences to the corresponding measurements in 100:1 HF. As the OHS<sup>®</sup> concentration is increased from 0 to 1000 ppm the first cycle advancing contact angle decreases linearly from  $90^\circ$  to  $20^\circ$ . In contrast, the second cycle advancing contact angles decrease rapidly as the surfactant concentration is increased, and the silicon is completely wet by the 20:1 BHF at OHS<sup>®</sup> concentrations of 10 ppm and higher.

Figure 2. Contact Angles of 20:1 BHF on Silicon as a function of OHS Concentration



The trends displayed by the contact angles of 100:1 HF and 20:1 BHF on silicon correlate very closely to the behaviour of OHS<sup>®</sup> in these solutions. The critical micelle concentration (CMC) of OHS<sup>®</sup> was measured as 100 ppm in 100:1 HF and 20 ppm in 20:1 BHF, and these values correspond very well to the surfactant concentration where each solution most effectively wets the silicon surface.

The rinsing of OHS<sup>®</sup> from silicon was also studied. Silicon wafer samples were dipped into 100:1 HF and 20:1 BHF solutions containing the surfactant. The contact angle of DI water on the silicon surface was measured at various rinse times in the overflow cell. These values provide an insight into the hydrophobic-hydrophilic nature of the silicon surface. This information was interpreted to gain a qualitative understanding of the removal of adsorbed surfactant from the silicon. The DI water flow rates studied were 100 and 200 ml/min. For all solutions studied the OHS<sup>®</sup> was more effectively rinsed from the silicon surface by the flow rate of 200 ml/min rather than the lower flow rate; for example, the contact angle of DI water on silicon exposed to 100 and 500 ppm OHS<sup>®</sup> in 100:1 HF recovered to the contact angle value measured on pure silicon after 60 seconds rinsing in DI water at a flow rate of 200 ml/min. The results also indicated that OHS<sup>®</sup> was easier to rinse from silicon when adsorbed from 100:1 HF rather than 20:1 BHF. However, OHS<sup>®</sup> adsorbed from 20:1 BHF at lower concentrations was easier to rinse than that adsorbed from higher concentration solutions in 20:1 BHF.

The technique of Attenuated Total Reflection-Fourier Transform Infrared Radiation (ATR-FTIR) spectroscopy was used to follow the kinetics of adsorption of the surfactant onto silicon from 100:1 HF, and the subsequent desorption when rinsed with DI water. The amount of surfactant adsorbed onto the silicon IRE was calculated from the  $2875\text{ cm}^{-1}$  peak in the aliphatic stretching region ( $2800\text{--}3050\text{ cm}^{-1}$ ) of the IR spectrum of OHS<sup>®</sup>. This region was chosen because the silicon IRE absorbs infrared radiation below approximately  $1500\text{ cm}^{-1}$ , whilst water has strong absorbance above  $3050\text{ cm}^{-1}$ . The absorbance spectrum due to the adsorbed surfactant layer was measured by subtracting the background spectrum of pure 100:1 HF from the recorded spectrum. The amount of surfactant adsorbed onto the silicon IRE was calculated from the following equation. It is based on a step type concentration profile at the solid/liquid interface<sup>(2)</sup>.

$$\frac{A}{N} = \epsilon_s C_s d_{es} + \epsilon_s \left( \frac{2d_{es}}{d_{ps}} \right) (C_i t)$$

In the above equation,  $A$  is the measured absorbance,  $N$  is the number of solution sensing reflections in the IRE,  $\epsilon_s$  is the molar absorptivity ( $\text{m}^2/\text{mol}$ ) of OHS<sup>®</sup> at  $2875\text{ cm}^{-1}$  measured by IR transmission,  $C_s$  is the bulk surfactant concentration ( $\text{mol}/\text{m}^3$ ),  $d_{ps}$  is the depth of penetration of the evanescent wave ( $\text{m}$ ),  $d_{es}$  is the effective depth of penetration of the wave ( $\text{m}$ ),  $t$  is the thickness of the adsorbed surfactant layer ( $\text{m}$ ) and  $C_i$  is the concentration of the surfactant at the interface ( $\text{mol}/\text{m}^3$ ). The adsorption density, measured in  $\text{moles}/\text{cm}^2$ , of the surfactant is then  $(C_i t)/10000$ .

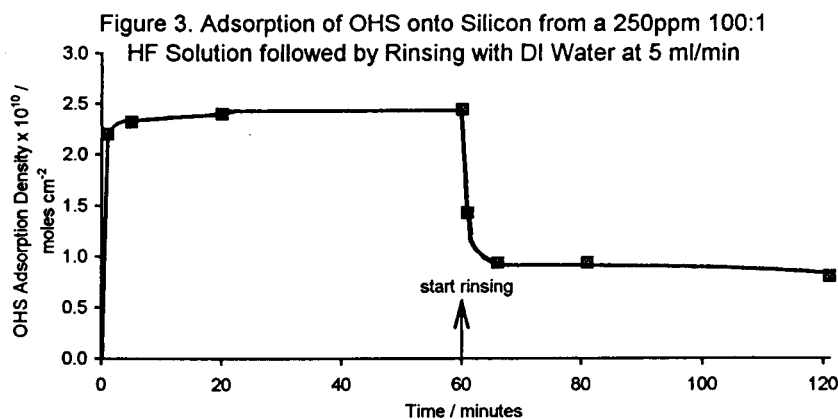
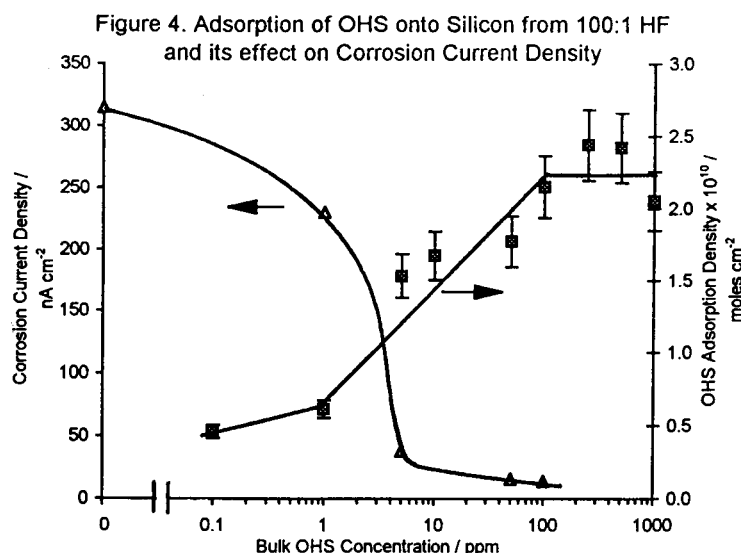


Figure 3 is a plot of the kinetics of adsorption of OHS<sup>®</sup> onto silicon from a 250 ppm solution in 100:1 HF. It is clear that the OHS<sup>®</sup> adsorbs onto the silicon surface quickly, and most of the adsorption takes place in the first minute of contact between the silicon and the surfactant solution. Also plotted is the desorption of OHS<sup>®</sup> when DI water is pumped through the cell at a rate of 5 ml/min. Again the OHS<sup>®</sup> is quickly removed. However, the residual surfactant after 60 minutes rinsing remains approximately  $7 \times 10^{-11}\text{ moles cm}^{-2}$ .



The adsorption/desorption experiment was repeated for OHS<sup>®</sup> concentrations in the range 0.1-1000 ppm in 100:1 HF and in each case similar kinetics were measured. The residual OHS<sup>®</sup> after 60 minutes rinsing with DI water at 5 ml/min remained reasonably constant at approximately  $7 \times 10^{-11}$  moles  $\text{cm}^{-2}$  when adsorbed from OHS<sup>®</sup> solutions in the concentration range 10-1000 ppm. The desorption kinetics and residual surfactant were also measured when rinsing with 100:1 HF at 5 ml/min. The results agreed closely with the corresponding values for the DI water rinse. This indicated that the OHS<sup>®</sup> was adsorbed onto the silicon surface rather than trapped in an oxide which may have formed during the DI water rinse.

The OHS<sup>®</sup> adsorption density on the silicon IRE after 60 minutes contact time is plotted against the bulk surfactant concentration in figure 4. The adsorption density increases rapidly as the OHS<sup>®</sup> concentration is increased from 1 ppm and reaches a maximum value in the region of the CMC of OHS<sup>®</sup> in 100:1 HF. As can be seen from figure 1 this corresponds to the concentration range of OHS<sup>®</sup> which brings about the largest decrease in the contact angle of 100:1 HF on silicon.



The effect of adsorbed surfactant on the electrochemical properties of silicon in 100:1 HF was investigated using DC polarization techniques. Anodic and cathodic polarization curves were obtained in solutions of different OHS<sup>®</sup> concentrations. The corrosion current density of silicon was calculated from these curves.

Figure 5 displays the polarization curves for n(100) silicon in 100:1 HF under illumination from a 100 watt lamp. The anodic polarization curve represents the dissolution of silicon and the cathodic polarization curve most likely represents the reduction of hydrogen ions. It can be seen from these data that the open circuit potential ( $E_{\text{ocp}}$ ) of silicon becomes more noble upon addition of surfactant. The values of the corrosion current density calculated from the cathodic polarization curve are tabulated in table 1. The addition of surfactant at a level of 10 ppm

decreased the corrosion current density from 315 to 38 nA/cm<sup>2</sup>. Based on the OHS<sup>®</sup> adsorption data presented in figure 4 the inhibition of the corrosion of silicon can be attributed to surfactant adsorption.

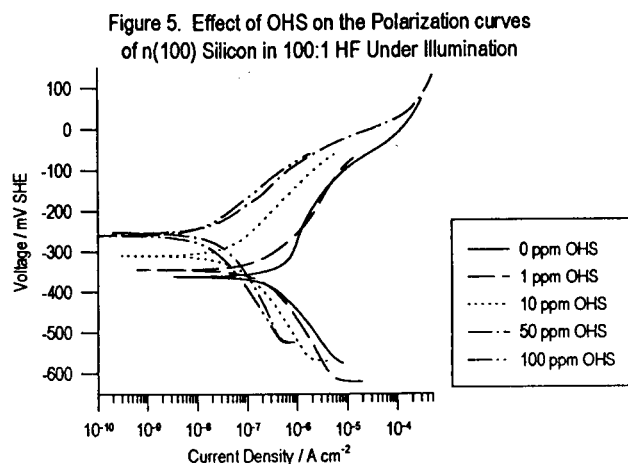


Table 1. Corrosion of n(100) silicon in 100:1 HF under illumination.

| OHS <sup>®</sup> Conc. / ppm | $i_{\text{corr}}$ / nA cm <sup>-2</sup> | $E_{\text{ocp}}$ / V vs. SHE |
|------------------------------|-----------------------------------------|------------------------------|
| 0                            | 315                                     | -0.365                       |
| 1                            | 230                                     | -0.345                       |
| 10                           | 38                                      | -0.309                       |
| 50                           | 16                                      | -0.253                       |
| 100                          | 14                                      | -0.257                       |

#### 4.0 CONCLUSIONS

A polyglycidol type surfactant (OHS<sup>®</sup>) is very effective in rendering hydrogen terminated silicon surfaces hydrophilic in HF and BHF solutions. ATR-FTIR studies have shown that the adsorption of this surfactant onto silicon occurs rapidly from dilute HF solutions. The desorption of the surfactant during HF or DI water rinsing is also rapid, but a small amount ( $\approx 7 \times 10^{-11}$  moles/cm<sup>2</sup>) of residual surfactant remains on the silicon surface even after extended rinsing. Addition of OHS<sup>®</sup> to HF reduces the corrosion of silicon.

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## A Model of Particle Deposition on Si surfaces in DHF in Terms of Surface Zeta Potential

H. Aoki and N. Aoto

ULSI Device Development Laboratories, NEC Corporation  
1120, Shimokuzawa, Sagamihara, Kanagawa 229, Japan

### 1. INTRODUCTION

This study proposes a mechanism for depositing polystyrene (PSL) particles on Si surfaces in diluted-HF (DHF) and diluted-HCl solutions in terms of the zeta potential of Si substrate surfaces and particles. In previous papers, the particle deposition on surfaces has been discussed through the zeta potential measurement for different types of particles, substituted for the zeta potential of surfaces and particles. For example, PSL particle deposition on Si surfaces was discussed using zeta potential data for PSL particles and Si particles.<sup>1-4)</sup> In contrast to previous works, we directly measured the zeta potential of Si substrate surfaces as well as those of particles. We found that the zeta potential of Si substrate surfaces is clearly different from those of Si and PSL particles in DHF, but they are close in diluted HCl. These results can explain the larger number of depositing PSL particles in DHF than in diluted HCl. We explained the phenomena by means of the calculated surface charge densities and the calculated thickness of the electrical double layer.

### 2. EXPERIMENT

The zeta potential was measured for Si substrate surfaces, Si particles of 0.1  $\mu\text{m}$  diameter and polystyrene (PSL) particles of 0.5  $\mu\text{m}$  diameter, in diluted-HF (DHF) and diluted-HCl solutions of pH 3 - 5. We used a zeta potential measuring apparatus (Otsuka electronics: ELS-800) in which the surface zeta potential is analyzed with the measured distribution of electrophoresis velocity of particles<sup>5)</sup> in the DHF and diluted-HCl solutions.

### 3. RESULTS

Figure 1 shows the pH dependence of the number of PSL particles that deposit on bare-Si substrates dipped for 10 minutes in DHF solutions of pH 3 - 5 (1.5 % -  $1.5 \times 10^{-2}$  %) and in diluted-HCl solutions of pH 3 - 5 ( $3.6 \times 10^{-3}$  % -  $3.6 \times 10^{-5}$  %), with PSL particles intentionally dispersed ( $10^5$  particles/ml) in the solutions. The number of PSL particles deposited is larger in DHF than in diluted HCl, and increases with decreasing pH. The pH dependence of zeta potential in DHF solutions is shown in Fig. 2 for Si substrate surfaces, Si particles, and PSL particles. It is shown that the zeta potential in DHF for Si substrate surfaces is clearly different from that for Si particles. The zeta potential has a negative value for both Si particles and PSL particles in DHF of pH 3-5 but positive values for Si substrate surfaces at a pH of lower than 4.5. Thus the PSL particle deposition on Si substrates, shown in Fig. 1, cannot be explained by the conventional zeta potential of Si and PSL particles, but can be explained by the polarity difference between the zeta potentials of Si substrate surfaces and PSL particles. Figure 3 shows the pH dependence of zeta potential in diluted-HCl solutions. At pH 3 - 5, the zeta potential of Si substrate surfaces and that of Si particles are close and have

negative values. The zeta potential of PSL particles has negative values at pH 3.5 - 5. At pH 3, the surface zeta potential becomes positive and has different polarity from those of PSL and Si particles. Such pH dependence of zeta potential can qualitatively explain the results shown in Fig. 1 as follows. The PSL particle deposition in diluted HCl is lower than in DHF because the polarity of the zeta potentials of Si substrate and PSL particles is the same at pH 3.5 - 5. The PSL particle deposition at pH 3 is greater than at higher pH values in diluted HCl, because the polarity of the zeta potential of Si substrate and PSL particles becomes different at pH 3.

#### 4. DISCUSSION

The zeta potential difference can be explained by the difference in surface charge densities. Figure 4 shows a model of surface charge distributions for (a) a Si substrate, and (b) a Si particle, in a solution of a defined  $H^+$  concentration. The electrical double layer on the Si substrate surface was regarded as a planer capacitor and that of the Si particle surface as a spherical capacitor. Thus the surface charge density on the Si substrate surface is expressed as

$$\sigma_{sub} = C_{sub} \psi_0 / S = \epsilon_0 \epsilon_r \psi_0 / d \quad \dots \text{Eq. (1)}$$

where  $\psi_0$ : Si surface potential,  $\epsilon_0$ : permittivity in vacuum,  $\epsilon_r$ : dielectric constant of solution, S: area of Si substrate, and d: thickness of electrical double layer. The surface charge density on a Si particle surface is expressed as

$$\sigma_{par} = C_{par} \psi_0 / 4\pi r^2 = \epsilon_0 \epsilon_r \psi_0 / d (1 + d/r) \quad \dots \text{Eq. (2)}$$

where r: radius of the particle. The relation between the thickness of the electrical double layer and the ionic strength (ion concentration) is known to be

$$d \approx 0.3 / Z M^{1/2} \quad (\text{nm}) \quad \dots \text{Eq. (3)}$$

where Z: ionic charge and M: ionic strength. By using Eqs. (1), (2) and (3), the surface charge densities depending on pH ( $H^+$  ion concentration) are calculated as shown in Fig. 5, with the  $\epsilon_r$  values of 84 for HF and 12 for HCl, and a Z value of 1 for both HCl and HF. The induced charges are negative in both HF and HCl solutions. Figure 5 indicates that the difference in the surface charge density between the substrate surfaces and the particles is small in diluted HCl but large in DHF. This tendency is in good agreement with the zeta potential difference between Si substrates and Si particles shown in Figs. 2 and 3.

There is another factor that influences the pH dependence of particle deposition shown in Fig. 1. This is the thickness of the electrical double layer given by Eq. (3). Figure 6 shows the pH dependence of the thickness of the electrical double layer calculated from Eq. (3). The thickness decreases drastically as the pH value decreases. When the layer is thin, the van der Waals force enhances the particle deposition. Therefore the number of depositing PSL particles is thought to increase with decreasing pH, as shown in Fig. 1.

#### 5. CONCLUSION

We succeeded in measuring the zeta potential of Si substrate surfaces instead of that of Si particles in DHF and diluted-HCl solutions. The fundamental characteristics of PSL particle deposition on Si substrate surfaces can be explained by the measured zeta potential, the calculated surface charge densities, and the calculated electrical double layer thickness. Such evaluation and analysis using zeta potential of both substrates and particles can be applied effectively to developing a new cleaning technology.

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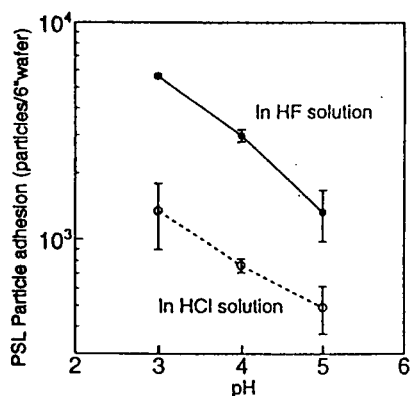


Fig. 1 Number of PSL particles depositing on Si substrates in DHF and HCl solutions with intentionally dispersed PSL particles depending on its pH.

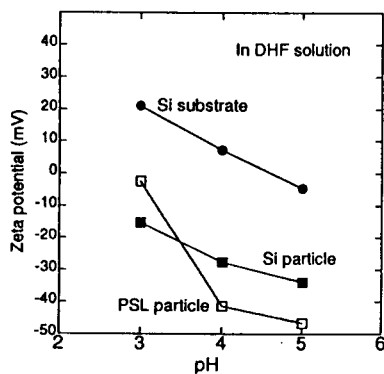


Fig. 2 Zeta potential for Si substrate surfaces, Si particles, and PSL particles in DHF solutions depending on pH.

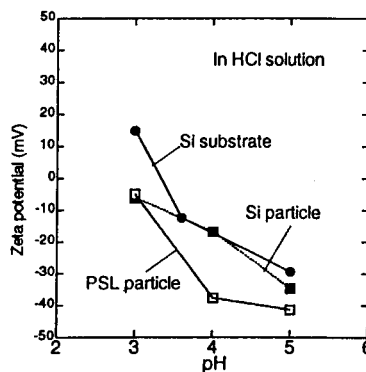


Fig. 3 Zeta potential for Si substrate surfaces, Si particles, and PSL particles in HCl solutions depending on pH.

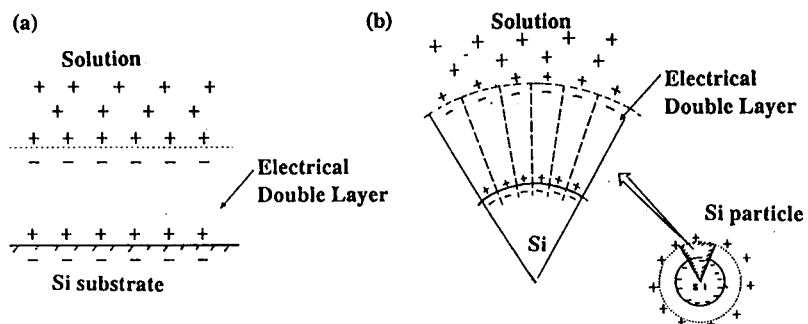


Fig. 4 A model of charge distributions.  
 (a) on a Si substrate surface: as a planer capacitor,  
 (b) around a Si particle surface: as a spherical capacitor.

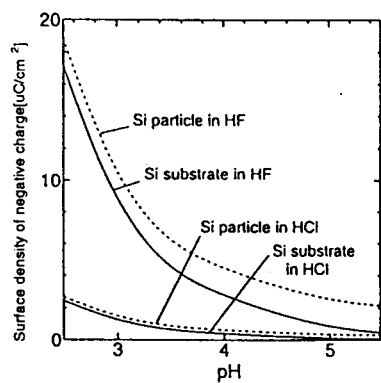


Fig. 5 Calculated surfaces charge density in DHF and HCl solutions for Si substrate and Si particles, depending on pH.

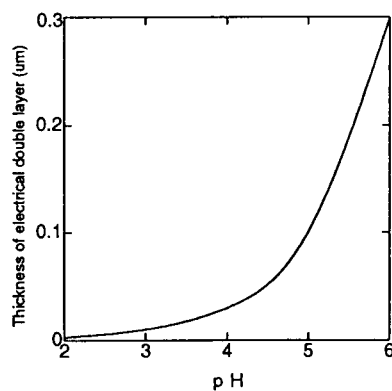


Fig. 6 Calculated thickness of the electrical double layer depending on pH.

## The optimization of Buffered Hydrogen Fluoride composition to control wet process

H.Izumi\*, M.Miyashita\*, T.Yabune\*, K.Tsuru\*, K.Yamane\*,  
H.Kikuyama\*, and T.Ohmi\*\*

**Abstract**—The variation of chemical composition in BHF has been investigated. We found that the composition of BHF with low HF concentration is not stable, and  $\text{NH}_4\text{F}$  concentration affects to the variation of the composition strongly. BHF having low  $\text{NH}_4\text{F}$  concentration(LA-BHF) is more stable compared with BHF having high  $\text{NH}_4\text{F}$  concentration. Furthermore, LA-BHF have excellent etching characters.

### 1. Introduction

The wet process is one of the essential technology to produce semiconductor devices with high density and functionality. The chemicals used for the wet processes shows a rapid progress in point of a impurity. On the other hand, high yield production is required because DRAM fell in a price, i.e., fluctuation-free manufacturing is required. In wet processes, the stability of chemicals will become to important to eliminate fluctuations. In our previous research, LA-BHF has better characterizations than it having high  $\text{NH}_4\text{F}$  concentration [1,2]. We present more advantages of LA-BHF. It has been found that  $\text{NH}_4\text{F}$  concentration in BHF having low etch rates affects to the chemical stability of BHF solution strongly. Furthermore, we found that LA-BHF can etch silicon dioxide uniformly.

### 2. Experimental

The variation of chemical composition in  $\text{HF-NH}_4\text{F-H}_2\text{O}$  system with standing time was analyzed by the titration using 0.1N-NaOH. The weight of sample solutions, the temperature and the surface area were 500g, 25°C and 78.5cm<sup>2</sup> respectively. Thermal silicon dioxide was used for measurement of etch rate.

In the investigation of etching uniformity, 6 inch wafers having thermal silicon dioxide(1000nm thick) were used. 25 wafers (1 cassette) were etched with BHF for 1 minute at 25°C, and rinsed with DIW. The transportation time from BHF bath to DIW bath is 10 seconds. And then, the etched depth was measured (121 points a wafer) by the optical-type film thickness meter.

Multiple internal reflection infrared measurement were used for the investigation of residual surfactant on silicon prism surface with Fourier transform infrared spectroscopy (FTIR), and liquid flow type cell was used in this measurement [3]. The silicon prism used here were prepared for double side polished p-type Si(100) wafers. The sample size was 0.5×20×50 mm<sup>3</sup> with 45° bevels on each of the short edges.

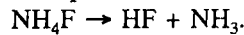
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\* Hashimoto Chemical Corporation : 227, 7-cho, Kaisan-cho, Sakai-City, Osaka 590 Japan.

\*\* Department of Electronics, Faculty of Engineering, Tohoku University : Aza-Aoba, Aramaki, Sendai 980 Japan.

### 3. Results and discussion

In Fig.1, HF concentration after 70 hours is plotted as a function of  $\text{NH}_4\text{F}$  concentration for two HF concentrations. HF concentration after 70 hours is measured after adding  $\text{H}_2\text{O}$  to initial weight. It is clearly seen that HF concentration rise as increase of  $\text{NH}_4\text{F}$  concentration, and the rising rate of 0.1wt%HF-BHF is larger than 0.2wt%HF-BHF. The increase of HF concentration caused by the decomposition of  $\text{NH}_4\text{F}$  itself as follows,



Especially,  $\text{NH}_4\text{F}$  decomposes easily in BHF having high  $\text{NH}_4\text{F}$  concentration. So, we should use LA-BHF, because only adding  $\text{H}_2\text{O}$  is effective to keep BHF composition.

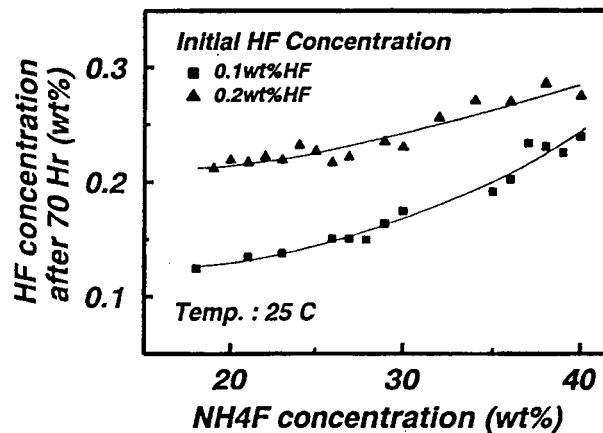


**Fig.1.** The variation of HF concentration in BHF. Initial HF concentration are 0.1 and 0.2wt%. The  $\text{NH}_4\text{F}$  concentration is from 18 to 40wt%. Standing time and relative humidity are 70 hours and 40%.

Figure 2 shows the variation of etch rate as a function of standing time. HF and  $\text{NH}_4\text{F}$  concentration are 0.08wt% and 40wt%, respectively. Initial etch rate is 1.6nm/min, and the etch rate changes to 4.2nm/min after 70 hours.

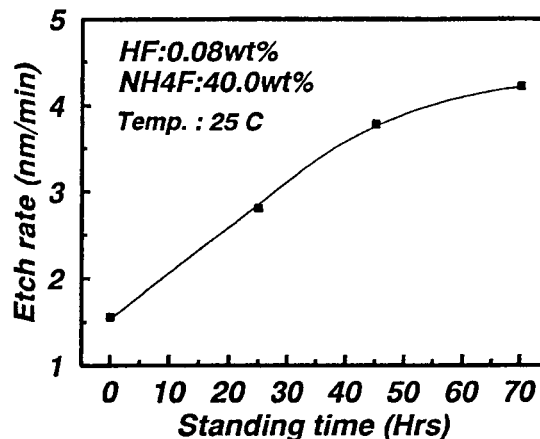


**Fig.2.** The variation of etch rate of BHF against thermal silicon dioxide as a function of standing time. Relative humidity is 40%.



In Fig.3, evaporation quantity is plotted as a function of standing time for two humidities of ambience. Evaporation quantity are calculated as follows.

$$\text{Evaporation Quantity (wt\%)} = (\text{evaporation weight}) / (\text{initial weight}) \times 100$$

HF and  $\text{NH}_4\text{F}$  concentrations are 0.1wt% and 20wt%, respectively. We can clearly see that the ambience affects to the evaporation of BHF strongly. Most of the evaporation element is moisture, so HF concentration increase with increase of evaporation quantity. The addition of  $\text{H}_2\text{O}$  to BHF bath is very effective to control wet process, but we should use BHF having low etch rate at high humidity ambience to realize more accurate wet process.

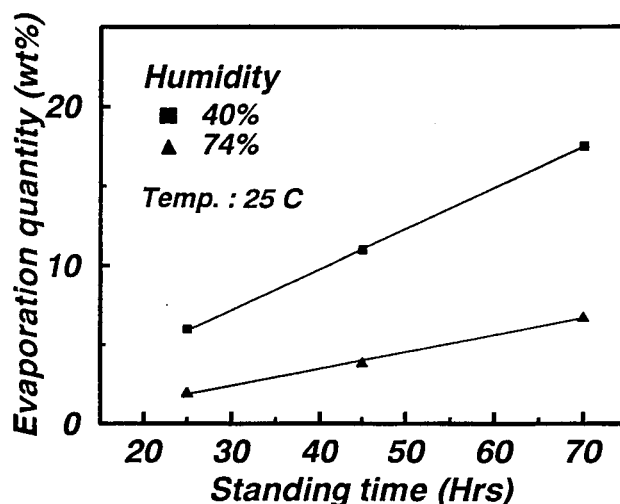


Fig.3. The relationship between standing time and evaporation quantity of BHF. HF and  $\text{NH}_4\text{F}$  concentration are 0.10 and 20.0wt%.

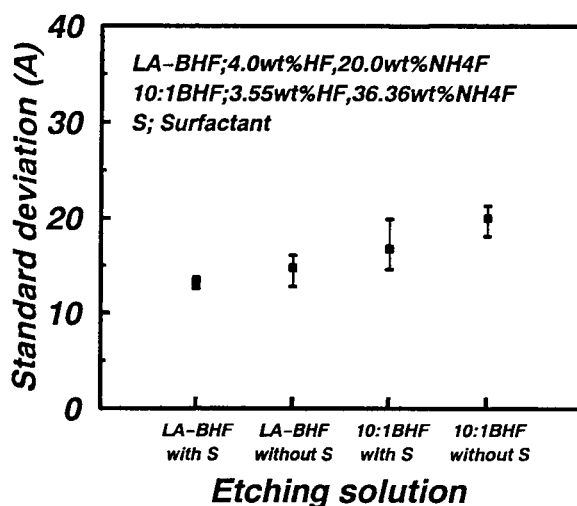
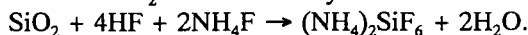


Fig.4. The comparison of the standard deviation of etching uniformity with 4 type BHF solutions.

Figure 4 shows the standard deviation of the etching quantity with 4 type BHF solutions. LA-BHF is better than BHF having high  $\text{NH}_4\text{F}$  concentration. The reaction of BHF and  $\text{SiO}_2$  is described by



It is well known that the solubility of  $(\text{NH}_4)_2\text{SiF}_6$  increase as decrease  $\text{NH}_4\text{F}$  concentration in BHF. So,  $(\text{NH}_4)_2\text{SiF}_6$  produced at interface of the solution and wafer surface solve immediately in LA-BHF, and it can etch  $\text{SiO}_2$  surface uniformly. In addition, LA-BHF with surfactant have more excellent etching uniformity. We believe that the addition of the surfactant protects the adhesion of gas bubbles because surfactant added BHF has high wettability.

It is clearly seen in Fig.4. that surfactant added BHF has high performance compared with conventional BHF. But, there is a fear of the residue of surfactant on silicon surface. Figure 5 indicates FTIR spectra of silicon surface which were treated with 0.5wt%HF and surfactant added BHF. These spectra were measured after DIW rinsing for 10 minutes. In Fig.5, there is not a difference between 0.5wt%HF treated surface and surfactant added BHF treated it in aliphatic stretching region ( $2800\text{--}3000\text{cm}^{-1}$ ), so we speculate that the residual surfactant is nothing or very little on silicon surface treated by surfactant added BHF after DIW rinsing.

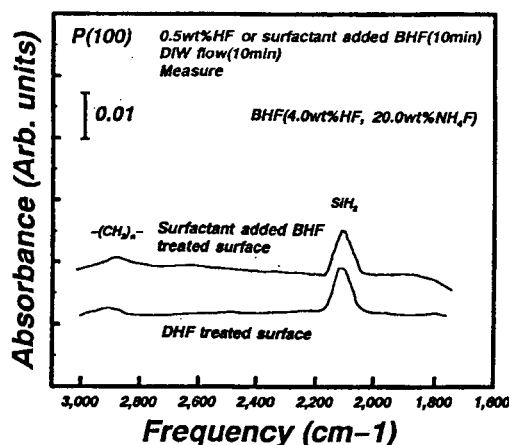


Fig.5. FTIR spectra of DHF or surfactant added BHF treated silicon surface after DIW rinsing.

#### 4. Conclusion

The variation of chemical composition in BHF has been investigated. We found that the composition of BHF with low HF concentration is not stable, and  $\text{NH}_4\text{F}$  concentration affects to the variation of the composition strongly. LA-BHF is more stable compared with BHF having high  $\text{NH}_4\text{F}$  concentration, and is controlled chemical composition easily. Furthermore, LA-BHF have excellent etching characters.

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## Post CMP Cleans Based On Anionic Surfactant Solutions

**Mike Jolley, Semitool, Kalispell Mt.  
Bob Johnson and Ole Ahlstrom, IDT, Hillsboro Or.**

### Introduction

A key step in modern IC processing is Chemical Mechanical Polishing (CMP). Oxide and metal layers are planarized using this method. After polish residual slurry needs to be removed from the wafers. One common method of removal is brush scrubbing<sup>1</sup>. Another common method is based on high pH chemical solutions<sup>2</sup>.

Dilute hydrofluoric and buffered hydrofluoric solutions in water or glycol have been used for removing surface metals after a scrubbing clean. These mixtures work well for surface metals removal, but suffer from particle deposition due to electrostatic attraction between the particle and the wafer surface.

Recent work has shown that adding anionic surfactants to acidic solutions can help reduce particle deposition through control of Zeta potentials of the surface and particles<sup>3,4</sup>. In low pH solutions this results in electrostatic repulsion instead of attraction. This work extends this concept to see if adding anionic surfactants to fluoride solutions can be used to enhance particle removal.

### Experimental

The chemical cleans were all performed in a Teflon spray processor made by Semitool. Particle counts were done on a Tencor 6420 and oxide etch rates determined with a Prometrix spectrophotometer or an Thermawave Optiprobe. Several polishing slurry types were used. The oxide slurries were high pH colloidal silica suspensions. The tungsten slurries were low pH solutions with alumina as the abrasive. A variety of oxides were used on both 150 mm and 200 mm wafer sizes. The surfactant used in all cases was a commercial anionic surfactant from 3M, FC93. The typical dilution of surfactant was 1 cc of FC93 working solution to 250 cc of cleaning solution. Silicon wafers with an oxide layer were either dipped in polishing slurry or they were given an actual polish process and then cleaned in surfactant solutions. The clean consisted of an initial rinse in DI followed by the surfactant clean and a final DI rinse and dry.

### Results and Discussion

1) Slurry Dip Tests. These tests were performed on oxide wafers dipped into polishing slurries and then cleaned using dilute HF with and without surfactants.

Table One  
150 mm Wafers with 80 Å Thermal Oxide. 500:1 HF, 10 Å Etch

| Treatment                           | Tungsten Slurry Rinse and Dry Only | Tungsten Slurry. HF with no surfactant | Tungsten Slurry. HF with surfactant | Oxide Slurry. HF with surfactant | Dried Tungsten Slurry. HF/Surfactant |
|-------------------------------------|------------------------------------|----------------------------------------|-------------------------------------|----------------------------------|--------------------------------------|
| Post Dip Particle Count > 0.2 $\mu$ | 140188                             | 31799                                  | 24                                  | 19                               | 24                                   |

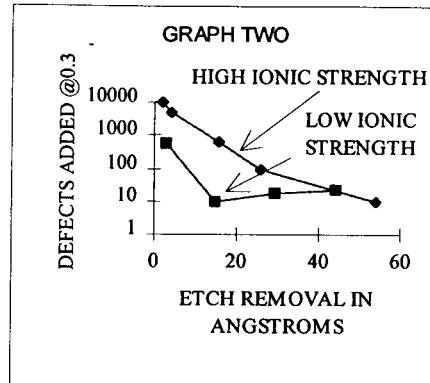
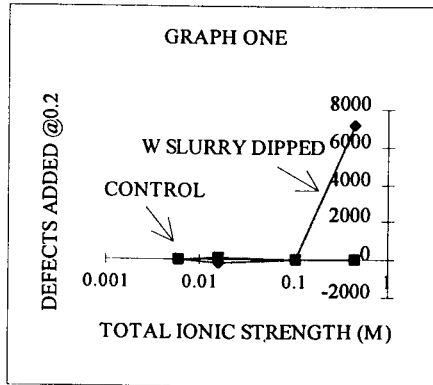


Table One shows the dramatic effect of adding surfactants to the cleaning mixture. Graph's One and Two show the effect of solution ionic strength. All testing was done on 150 mm wafers with thermal oxide on them. The slurry used in all cases was WA355, a solution of ferric nitrate and alumina. The surfactant concentration was 1 part in 250 by volume. Graph One shows the effect of adding KCL to a 500:1 DI:HF solution at 40 °C. In each trial one wafer was dunked in the slurry and the control wafer was not. Both received the clean with its 10 Å etch removal target. The increase in particle counts on the slurry dunked wafer between 0.1 M and 0.45 M is in agreement with other authors published works\*. Graph Two shows the added particle counts after slurry dunk and clean as a function of etch removal in the clean step. Two different solutions were used @ 40 °C with a 250:1 surfactant dilution. The weak ionic solution was a 500:1 HF mixture. The strong ionic solution was a 15:1 dilution of DI and ammonium fluoride. The HF solution only required around 15 Å of etch for effective particle removal, while the ammonium fluoride solution requires around 40 to 50 Å etch.

2) Polished Wafers Testing: Several hundred 150 mm wafers were processed through the final polish step by a captive wafer manufacturer. After polish these wafers were given a rinse/dry cycle only. Three cleaning splits were performed. The first was based on HF w/surfactant and SC1, the second was HF only and SC1, and the final based on SC1 and Piranha.

| Clean Treatment | Average | STD DEV | Wafer Count |
|-----------------|---------|---------|-------------|
| HF Surfactant   | 13.90   | 10.19   | 73          |
| HF/SC1          | 42.18   | 18.14   | 65          |
| Pir/SC1         | 162.89  | 22.28   | 64          |

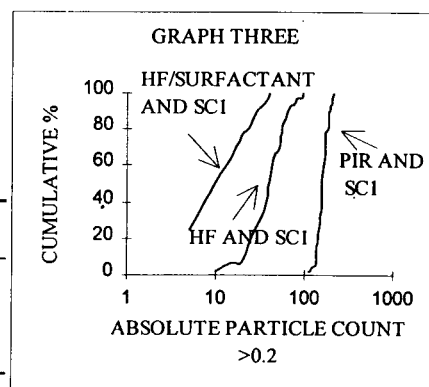


Table Two shows the summary statistics of the particle counts after clean. Graph Three is a plot of the distribution after clean. The surfactant aided clean produced the lowest final particle count.

3) Oxide CMP Characterization: This experiment was conducted at IDT's 200 mm wafer fabrication facility in Hillsboro Or. A fractional factorial experiment was run to look at the effects of HF concentration, surfactant concentration, etch temperature and etch removal. Two micron thick TEOS wafers were given a touch polish using colloidal silica slurry on an IPEC polisher. Around 200 Å of oxide was removed in this step. After a final buffing step on the polisher the wafers were transferred to a Semitool Spray Acid tool for cleaning in the HF/surfactant mixture. The factors and the experimental set points are tabled below along with two graphs showing the statistically significant effects.

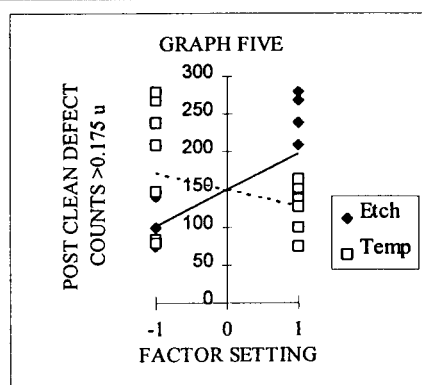
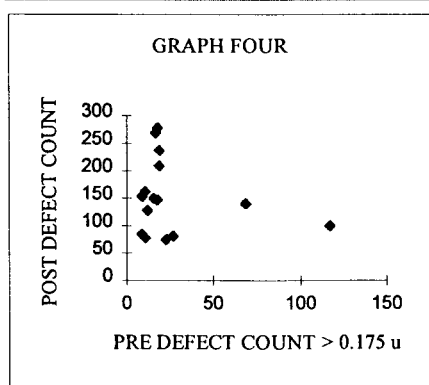
The data analysis was done using the method of multiple linear regression. The dependent variable was final particle counts and the independent variables were the experimental factors. The starting particle count was added to the analysis because of the significant effect on the results. The factor settings and regression results are found in Table Three

Table Three

| Factor                                        |         |         |
|-----------------------------------------------|---------|---------|
|                                               | +       | -       |
|                                               | Setting | Setting |
| HF Concentration (fraction by volume)         | 0.004   | .001    |
| HF Temp (°C)                                  | 45      | 35      |
| Surfactant Concentration (fraction by volume) | .005    | .001    |
| Etch Removal in Angstroms                     | 150     | 50      |
| Starting Particle Count >0.175 $\mu$          | 117     | 9       |

| Regression Statistics |       | Factor     | Coefficients | Standard Error | t Stat |
|-----------------------|-------|------------|--------------|----------------|--------|
| Multiple R            | 0.90  | Intercept  | 297.50       | 82.42          | 3.61   |
| R Square              | 0.82  | HF         | -7915.66     | 7111.51        | -1.11  |
| Adjusted R Square     | 0.72  | Surfactant | 1711.06      | 4736.12        | 0.36   |
| Standard Error        | 36.12 | Temp       | -7.09        | 2.07           | -3.43  |
| Observations          | 15    | Etch       | 1.25         | 0.21           | 5.81   |
|                       |       | Pre Count  | 0.89         | 0.41           | 2.19   |



One of the concerns with adding surfactant to cleaning solutions is the possibility of residual surface contamination. To evaluate this wafers were given a touch polish and a 100 Å etch in a 500:1 mixture of DI and HF at 40 °C. Samples with and without the surfactant were surface analyzed by Charles Evans and Associates. TXRF was used for surface metal's and ESCA was done to study the amount of C, F, C, O and Si on the surface.

TXRF Results (Units of  $10^{10}$  Atoms/sq. Cm)

|                        | K   | Ca | Ti | Cr | Mn | Fe  | Ni | Cu | Zn |
|------------------------|-----|----|----|----|----|-----|----|----|----|
| Control TEOS           | <20 | <8 | <5 | <3 | <1 | 0.9 | <1 | 4  | 5  |
| Polish + HF Only       | <20 | <8 | <5 | <3 | <1 | 0.9 | <1 | <1 | <3 |
| Polish + HF/Surfactant | <20 | <8 | <5 | <3 | <1 | 1.5 | <1 | <1 | <3 |

ESCA Results- Atomic Concentration in %

|                        | C   | O    | N    | F    | Si   |
|------------------------|-----|------|------|------|------|
| Polish + HF Only       | 5.6 | 64.4 | <0.1 | <0.1 | 29.9 |
| Polish + HF/Surfactant | 5.3 | 65.5 | <0.1 | <0.1 | 29.1 |

### Conclusion

Adding anionic surfactants to dilute mixtures of hydrofluoric acid and other oxide etching chemistries improves their ability to clean silicon wafers after exposure to CMP polishing slurries. Trials done with both a caustic colloidal silica slurry and an acidic alumina based slurry indicate the ability to clean silicon oxide surfaces back to starting level particle counts. The clean also removes dried slurry from silicon oxide surfaces. The cleaning efficiency is thought to be a result of the surfactant's ability to control the Zeta potential of both the slurry particle and the oxide surface to the same polarity. This results in electrostatic repulsion of a slurry particle as it is lifted off the surface during the etch step. This repulsion prevents the liberated particle from adhering again to the surface. Cleaning efficiency is affected by ionic strength. Higher ionic strengths limit the range over which the electrostatic repulsion is effective and this results in lower cleaning efficiencies. The process is dependent on temperature and etch removal amount, but less affected by acid and surfactant concentration. Adding FC93 surfactant does not appear to leave a surface residue or increase metallic contamination.

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## PARTICLE REMOVAL CLEANINGS FOR BACKEND PROCESSES

F. Tardif\*, P. Patruno\*\*, T. Lardin\*, A.S. Royet\*

O. Demoliens\*, J. Palleau\*, J. Torres\*

\* LETI (CEA-Technologies avancées)

DMEL-CEA/G, 17 rue des Martyrs, 38054 Grenoble cedex 9, France

\*\* SGS-Thomson, rue Jean Monet Crolles, France

### 1. INTRODUCTION

Today, interconnections represent one of the major potential causes of IC manufacturing yield loss. Particle detrimental effect is easy to imagine as it can induce shorts and discontinuities in the conductive lines. For advanced  $0.18\ \mu\text{m}$  technology, the commonly measured  $0.2\ \mu\text{m}$  particles are very close to the line width and thus potentially very dangerous. Furthermore, CMP steps which are increasingly used in backend processes leave large amounts of residual slurries. From our experience, scrubbing alone does not give enough final stable results when starting from billions of particles. Therefore, it is necessary to set up wet pre-cleaning recipes which furthermore have to be compatible with the conductive line presence. Using our knowledge in front end surface engineering field, non-organic wet diluted chemistries are here designed for backend applications.

### 2. GENERAL TRENDS AND METHODOLOGY

Figure 1 represents an example of advanced backend surface configuration. The surfaces to be cleaned are mainly composed of  $\text{Si}_3\text{N}_4$  and oxides with the presence of W, Cu, Al/Cu, Ti, TiN, ...

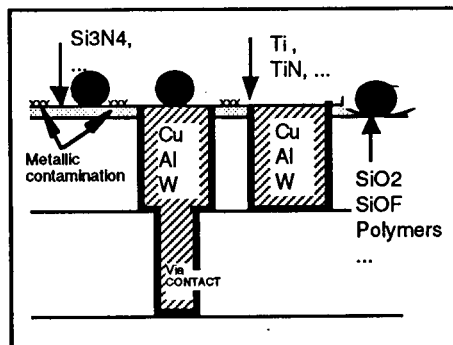


Figure 1 : Example of backend surface materials

Two types of particles were tested :  $\text{Al}_2\text{O}_3$  ( $0.8\ \mu\text{m}$ ) and  $\text{SiO}_2$  ( $1.2\ \mu\text{m}$ ) for their opposite property in terms of Zeta potential and also because they are both used as CMP colloids. In order to remove particles by underetching mechanism, different non-oxidant solutions covering the whole pH scale were adjusted in order to remove 5 nm of PECVD TEOS oxide (chosen as the backend reference material) in  $10'$ . These solutions are based on mixtures of HF, BOE and ammonia. The ammonia solution used is in fact a conventional SC1 without the oxidant species  $\text{H}_2\text{O}_2$  which is not necessary in the case of a thick oxide and could be dangerous for metal lines. Nevertheless the wafer backside has to be protected as well. As shown in figure 2 the etching rate of PECVD  $\text{Si}_3\text{N}_4$  is in the same order of magnitude as for silicon oxides. So both cases can be treated simultaneously.

These diluted cleaning recipes were then tested in terms of compatibility with the above described metals (arbitrary criterion : etching rate < 1 nm/min). Ti, TiN, and W present an acceptable etching rate whatever the pH. For Al/Cu (not dealt with here), the use of organic mixtures including corrosion inhibitors seems to be more suitable.

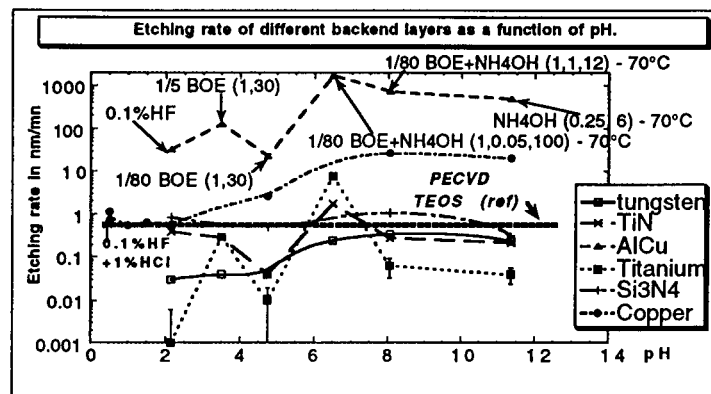


Figure 2 : Etching rate of different backend materials in diluted mixtures

### 3. PARTICLE REMOVAL

About 300 particles were intentionally deposited on 4" wafers by dipping in a spiked Di water bath. The wafers were then cleaned during 10' in the different selected mixtures. The new experimental data of figure 3 confirm that previously obtained [1], [2] and [3]. It shows the behaviour of the Zeta potential of the main backend surface material and studied particles as a function of the pH.

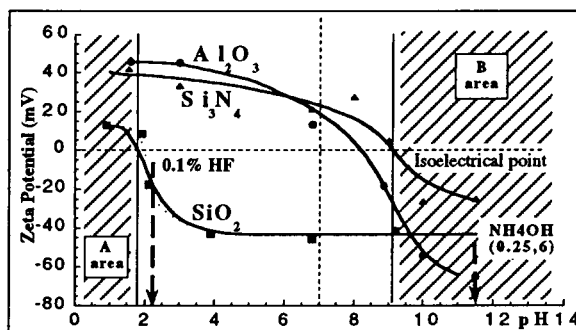


Figure 3 : Zeta potential of  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$  vs pH as measured by Zetameter

It can be seen that for electrostatic reasons, only the most acidic and alkaline tested cleanings are favourable to remove all types of particles. Indeed, at  $\text{pH} < 1.8$  or  $\text{pH} > 9$  particles are repulsed (same electrostatic sign) from the substrates after their separation by underetching mechanism.

#### 3.1 Silicon oxide cleaning (PECVD TEOS oxide)

On silicon oxide, the most potentially difficult particles to remove are represented by the very electropositive alumina. On Silicon it is usually assumed that a 2 nm etching is necessary to remove the particles. According to figure 4, a 4 to 5 nm etching seems to be more appropriate for oxide cleaning. The optimal removal efficiency does not depend on the etching rate.



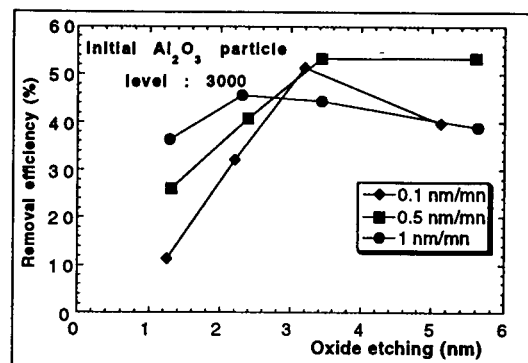


Figure 4 : Removal efficiency of alumina particles in HF based chemistry

Figure 5 shows that as expected from Zeta potentials, removal of  $\text{Al}_2\text{O}_3$  particles on silicon oxide is favoured by high pH values. For low pH the apparent positive particle charge can be shifted to more negative ones using an anionic surfactant. Indeed, we verify that the poor efficiency of acidic cleaning solution can be increased by introduction of 50 ppm of Mercryl sulfate surfactant until a pH is reached corresponding to the isoelectrical point ( $\text{pH} = 8$ ).

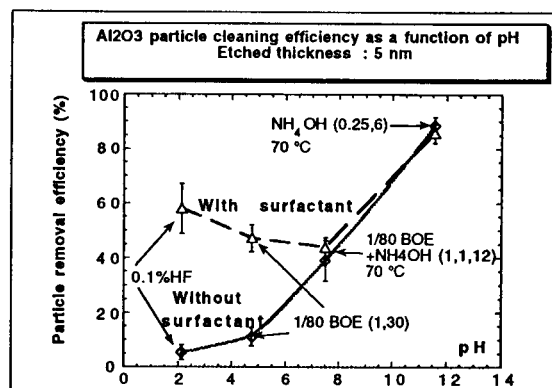


Figure 5 :  $\text{Al}_2\text{O}_3$  particle removal on silicon oxide (etched thickness : 5 nm)

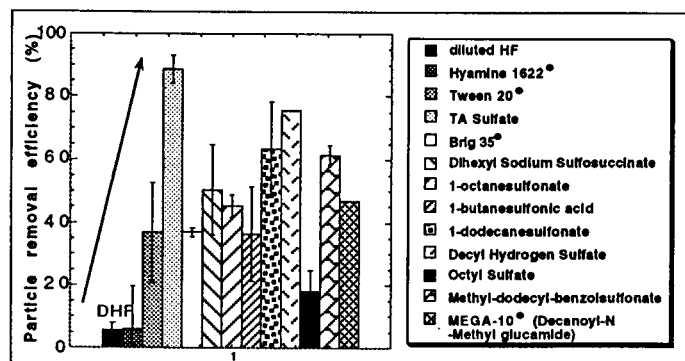


Figure 6 : Performances of different anionic and non-ionic surfactants in 0.1% HF to remove  $\text{Al}_2\text{O}_3$  particles deposited on oxide.

As shown in figure 6, certain surfactants injected at the Critical Miscellaneous Concentration level even enable here the same good performances obtained with alkaline media. Acidifying the 0.1%HF with traces of a strong acid enables the area "A" of figure 3 to be reached and in addition enables the results to be improved.

### 3.2 Silicon nitride cleaning

Figure 7 shows that both alumina and SiO<sub>2</sub> particles are satisfactorily removed from silicon nitride layers in [0.25,6] NH<sub>4</sub>OH since the underetching is about 3 to 4 nm.

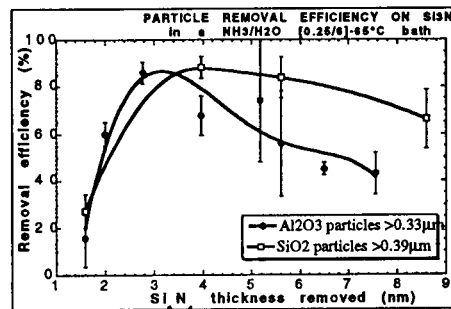


Figure 7 : SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> particles removed from Si<sub>3</sub>N<sub>4</sub> by diluted NH<sub>4</sub>OH

Figure 8 shows that as expected, particle removal can be improved by lowering the pH by increasing the HF concentration or adding traces of HCl in 0.1%HF. SiO<sub>2</sub> particles deposited on silicon nitride can also be removed at intermediate pH.

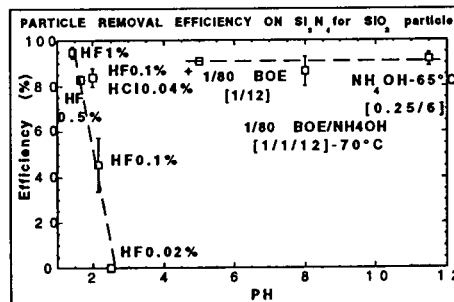


Figure 8 : SiO<sub>2</sub> particles removed from a Si<sub>3</sub>N<sub>4</sub> surface (4 nm etched)

## 4. CONCLUSION

This work opens up one of the possible ways for backend cleaning. Particles can be satisfactorily removed from silicon oxides and nitride layer by diluted mineral chemistries without any damage for the outcropping metals except for Aluminum alloys.

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## The Selective Strip Of Defective Layers:Cleaning Semiconductor Substrate For The Chemical Mechanical Polishing Process

H. Park\*, J. Song\*, Y. Cho\*, Y. Koh\*, and M. Lee\*

A new chemical solution(phosphoric acid+fluoroboric acid mixture) was used for post W-CMP cleaning to replace scrubbing and/or diluted HF dip. Its oxide selectivity over metals and particle removing power was good enough for the cleanup process after CMP.

### 1. INTRODUCTION

As the minimum feature size of semiconductor devices is getting close to 0.25  $\mu\text{m}$  or below, the planarization of thin film including interlevel dielectric(ILD) is getting more important than ever to provide good process margin for photolithography work. One of the ways to achieve a good planarity for oxide layers is chemical mechanical planarization(CMP), which can also be applied to metals such as tungsten(W) for the multilevel metal interconnects.[1] Since it utilizes slurry and pad, CMP process is considered to be a dirty process and people/engineers are, in some cases, reluctant to adopt this process even though its benefits have been recognized throughout the semiconductor device manufacturing world. In addition, the process cost itself is to be higher than conventional processes such as the etch back process. However, confronted with the technological limitations of conventional processes, the introduction of the CMP process seems to be inevitable, even in the DRAM business.

To make the CMP process successful, it is important to establish a good post-CMP cleaning process: removing not only slurry and particles but also metallic impurities from the polished wafer surface and in some cases removes the damaged top surface layer if necessary. One popular method for the cleanup is to scrub the polished surface with diluted chemical solution such as ammonia hydroxide( $\text{NH}_4\text{OH}$ ), which removes particles very effectively.[2] However, it is not clear whether it is enough to employ only the scrubbing process. Some companies are known to incorporate the diluted HF dip after the scrubbing to remove top oxide layers with metallic contaminants which means the Cost of Ownership(CoO) of the CMP process may be expensive: it requires polisher, scrubber, and/or HF wet bath as well as consumables such as slurry and pad. One of the way to reduce the process cost is to replace the scrubbing plus dipping with the conventional wet cleaning process. *We have developed a new chemical solution for the post CMP cleaning process.*

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\* Semiconductor R&D Center, Samsung Electronics Co., Ltd., Kiheung, Korea.

In this paper, we will show the results of our new chemical solution, *the mixture of phosphoric acid( $H_3PO_4$ ) and fluoroboric acid( $HF_4$ )*, employed to post W-CMP cleaning process.

## 2. EXPERIMENTAL

A Wetstech Model 372 chemical-mechanical planarizer was used for polishing, postpolish buffing and so on. Wafers with tungsten plug pattern were polished with alumina slurry and scrubbed along with the diluted ammonia hydroxide spray. For the split, some wafers went through the diluted HF dip after the scrubbing. Some polished wafers were cleaned in our new chemical solution bath for different mixing conditions and cleaning time. The chemical bath was operated at room temperature. Details of the split conditions are listed in *Table 1*.

*Table 1.* The experimental conditions for the post-CMP cleaning splits

| Split | Buffing | Scrubbing | DHF dip | PFM Dip* |
|-------|---------|-----------|---------|----------|
| A     | Yes     | Yes       | No      | No       |
| B     | Yes     | Yes       | Yes     | No       |
| C     | Yes     | Yes       | No      | Yes      |
| D     | Yes     | No        | No      | Yes      |
| E     | No      | No        | No      | Yes      |

\*PFM Dip: (Phosphoric acid+Fluoroboric Acid Mixture) Dip

For the W-plug pattern, the contact size was  $0.5\mu m$  with an aspect ratio of 2. The oxide layer was PE-TEOS or PE-SiH<sub>4</sub>, and the barrier metal layer of Ti/TiN was employed. DOE splits for the PFM Dip process were done to find an optimum process condition. The atomic force microscopy(AFM) measurement for the surface roughness and the vertical scanning electron microscopy(V-SEM) observation for the profiles of the W-plug patterned wafers were done before and after the cleaning process.

## 3. RESULTS AND DISCUSSION

### 3.1. Results of the DOE splits

Our preliminary test results showed that Ti started to react to phosphoric acid above  $70^\circ C$ , and that the etch selectivity between oxide and metals was high enough to remove oxides without etching metals for the W-plug structure with Ti/TiN barrier layer at certain conditions. To find an optimum condition, we applied *3 factor Box-Behnken method* to our chemical splits with 3 factors including  $H_3PO_4$  concentration, temperature, and the mixing ratio of  $H_3PO_4$  and  $HF_4$ . *Figure 1* shows the Pareto chart for the etch rate of PE-SiH<sub>4</sub> oxide,

and the mixing ratio turned out to be a dominant factor with temperature. To meet the requirements for post-CMP cleaning application, it is necessary to have a chemical solution with high etch selectivity at low operating temperature. We found the optimum condition range for the solution from the DOE splits.

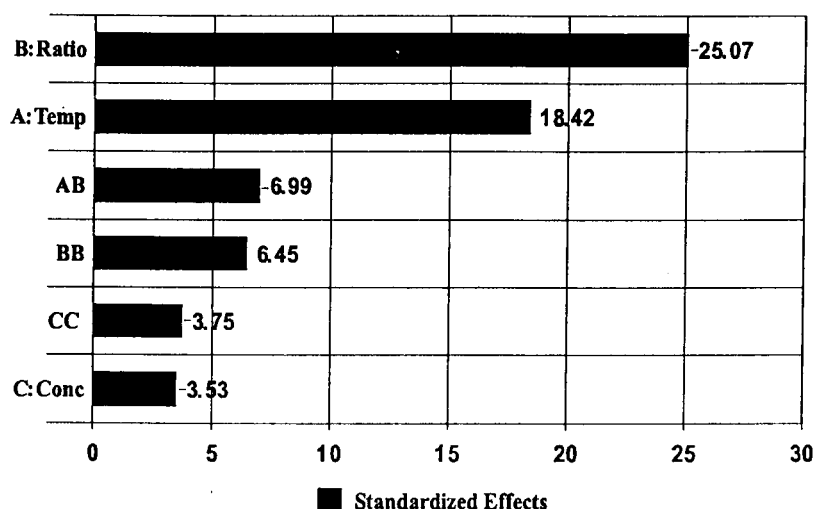


Figure 1. The Pareto chart for the etch rate of PE-SiH<sub>4</sub> oxide

### 3.2 Profiles of W-plug patterned wafers for the cleaning splits

Figure 2 shows the profiles of the W-plug patterned wafers before and after the cleaning splits. Figure 2(a) and (b) are for the split A and B respectively. Since our plug pattern has Ti barrier metal layer which is very reactive to chemical solutions, plug lifting can happen when the Ti layer is exposed to the HF during the dip after the scrubbing(split B). On the other hand, the split D did not produce the plug lifting even at higher etching conditions. Figure 2(c) and (d) show the profiles of W-plug patterned wafers at different etch rates of split D. As shown in the figure, none of the splits produced the plug lifting. Our initial assumption was that phosphoric acid might give some protecting layer on the top surface even for the metal layer and that under certain conditions Ti could be stable with phosphoric acid. Our etch rate data seemed to agree with our assumption showing that Ti was stable up to about 50°C under certain conditions. However, Ti showed much less stability with diluted phosphoric acid as expected.

### 3.3 Slurry/Metallic contamination/Particles

When the wafers were polished for the experiment, aluminar slurry was used.

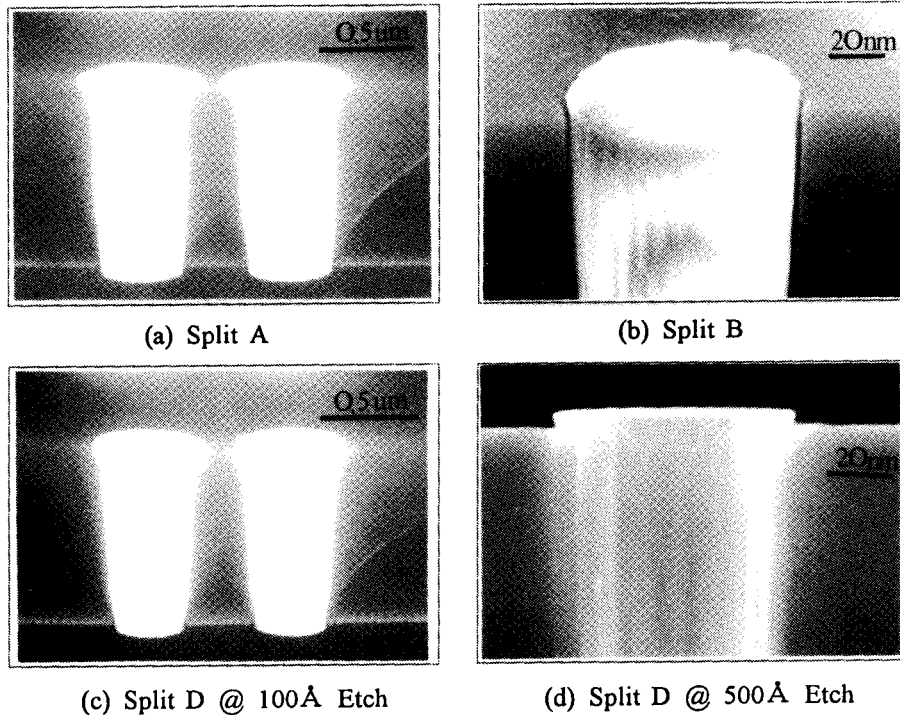


Figure 2. The profiles of W-plug pattern after the clean splits

Our early finding that *alumina was soluble to phosphoric acid* motivated us to use phosphoric acid for the post-CMP cleaning solution. The TXRF results on the oxide surface after the cleaning was done and no visible amounts of Al and other metallic contaminants were found after the PFM clean. Particle removal after the clean were examined. Wafers were initially exposed to dirty room air and went through our modified PFM clean which had new ingredient-anionic surfactant. We found that the modified PFM clean could remove over 70% of particles from the surface.

#### 4. CONCLUSION

A new chemical solution, (Phosphoric acid+Fluoroboric Acid Mixture), was examined for the post-CMP cleaning to replace the scrubbing and/or dipping. It showed a high oxide selectivity over metals and a good removing power against slurry, particles, and metallic contaminants.

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## PARTICLE-SURFACE INTERACTIONS IN CHEMICAL MECHANICAL POLISHING\*

M.T. Dugger<sup>+</sup>, J.S. Jeon<sup>++</sup>, S. Raghavan<sup>++</sup>, C.L.J. Adkins<sup>+</sup>, P.J. Resnick<sup>+</sup>

<sup>+</sup>Sandia National Laboratories, Albuquerque NM USA 87185

<sup>++</sup>Dept. of Materials Science and Engr., Univ. of Arizona, Tucson AZ USA 85721

### 1.0 INTRODUCTION

Material removal in chemical mechanical polishing (CMP) occurs by a pressure accentuated chemical attack of the surface. The polishing slurry typically consists of abrasive particles and reactive chemicals that may or may not include an oxidant. Post-CMP cleaning processes must remove both the ionic contaminants and any remaining polishing slurry particles. Central to the effectiveness of a clean is the use of conditions that will minimize the binding force between the residual particles and the wafer surface. The morphology and composition of the particle, the surface from which it must be removed, and the environment surrounding the wafer will determine the magnitude of forces that hold a particle to the wafer surface. At the Sandia/SEMATECH Center for Contamination Free Manufacturing, two techniques -- atomic force microscopy (AFM) and electrokinetic deposition -- are being used to explore these interactions for CMP of both oxide and tungsten surfaces. A basic understanding of particle-surface interaction forces and how they are affected by the chemical/physical environment of the particle and surface is the objective of this task. Modification of the binding forces between particles and wafer surfaces may be used to maximize post-CMP cleaning effectiveness.

### 2.0 APPROACH

The focus of the AFM work to date has been investigation of conditions relevant to oxide polishing and post-CMP cleaning. The probe tip is used to simulate a slurry particle because its shape, radius of curvature (on the order of 10 nm) and composition approaches that of slurry particles. Using an atomic force microscope in the force versus distance mode, data can be collected that show the attractive or repulsive nature of the wafer/tip interaction in various liquid chemistries. In lateral force mode, information can be obtained about the friction coefficient between the wafer and tip under various contact pressures. In both of these modes, the effect of addition of a nonionic surfactant was investigated and a series of experiments was performed to determine the effects of pH and ionic strength on particle binding forces.

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The electrokinetic deposition studies were performed using LPCVD tungsten films. Two kinds of alumina particle dispersions were used in this study: (1) a dispersion made from high purity alumina particles; and (2) a commercially available alumina slurry used in tungsten CMP. The effects of a nonionic surfactant and the addition of hydrogen peroxide on alumina deposition on the tungsten have also been investigated.

### 3.0 RESULTS AND DISCUSSION

The role of adsorbed surfactants on particle binding forces was explored with Triton X-100. The binding force between an oxide probe and a thermal oxide film, polished and etched in dilute HF to remove organic contamination, was measured in deionized water (DIW) and DIW with 1000 ppm of Triton. The results are shown in Figure 1. The attractive force observed on approach in DIW is suppressed in the presence of the surfactant. However, once contact is made, the surfactant does not significantly alter the adhesive force of the probe. Suppression of the attractive force on approach is attributable to steric hindrance. The probe is apparently able to displace the surfactant under sufficient pressure, so that van der Waals attraction dominates. Nanoscale friction measurements using lateral force microscopy, as well as bulk friction and wear measurements, indicate no effect of the addition of Triton to surface sliding forces or material removal rates.

Measurements under a variety of pH and ionic strength conditions show that repulsive forces are generated between oxide surfaces in high pH environments, consistent with the zeta potential of these surfaces. These results indicate that reduced particle levels may be realized by maintaining a pH such that electrostatic repulsion prevails throughout the polishing and cleaning steps. Control of the ionic strength appears to be a secondary effect modulating the attractive/repulsive forces. The extent of the electrostatic double layer is inversely proportional to the ionic strength. At very high ionic strength, the double layer can be small enough to permit short-range van der Waals attraction of particles to the wafer surface.

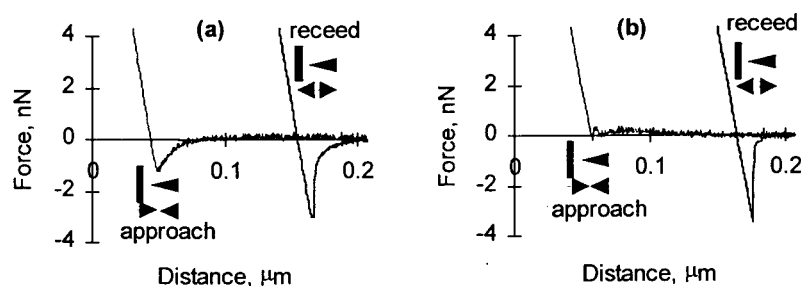


Figure 1. Force versus distance in DIW (a) and DIW+1000 ppm Triton (b).



Measurements of probe forces in DIW containing 200 ppm of Triton indicate attractive force between the probe and wafer of approximately 1 nN magnitude, which is similar to that observed with DIW alone. High concentrations of surfactant are apparently required to provide steric repulsion in neutral water. In KOH solutions of pH 10, repulsive force between the probe and wafer was observed. This observation is consistent with electrostatic repulsion of similarly-charged surfaces, beyond the extent of any adsorbed surfactant.

Figure 2(a) shows the results of zeta potential measurements carried out on high purity alumina powder, alumina particles in a commercial CMP slurry, and a CVD tungsten wafer. Differences in composition as well as shape may contribute to the differences in zeta potential for high purity alumina and slurry particles. Interestingly, the profile of zeta potential vs. pH for alumina particles in the diluted slurry shows a flat region of small negative zeta potential in the pH range of 4 to 6. The tungsten wafer zeta potential was negative at pH 4. It may be concluded from this figure that the high purity alumina particles will adhere to tungsten at pH values less than 8 and the alumina in the commercial slurry would exhibit a weak tendency to adhere to tungsten below a pH of 4.

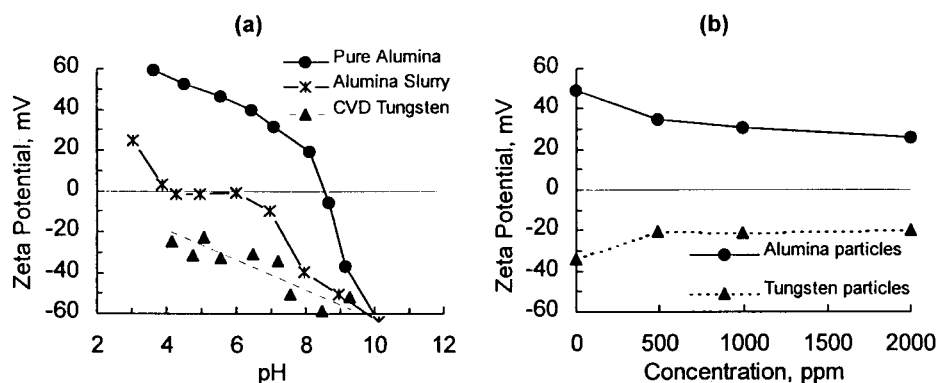


Figure 2. Zeta potential in a 0.001 M KCl solution versus pH (a), and zeta potential versus OPEO ( $n=9.5$ ) concentration at a pH of 4.5 (b).

The importance of electrostatic interactions between alumina particles and tungsten surfaces in particulate contamination during CMP was investigated by carrying out controlled deposition experiments in the absence or presence of an applied potential. Experiments under an applied potential were carried out to create a "worst-case scenario" for particle deposition/adhesion. Additionally, application of an anodic bias during deposition allowed the simulation of contamination on  $WO_x$ , which is known to form on tungsten in the presence of an oxidant. Under cathodic bias, the surface of W was covered with positively charged alumina particles in a dispersion maintained at a pH of 4, and these particles were difficult to remove by a DI rinse. Under anodic bias significantly less contamination was observed, indicating a lack of attraction between the positively charged surfaces. Thus, one strategy to reduce alumina contamination

on W would be to add an additive to the slurry that would provide a zeta potential of the same sign to both the surface and the particles.

The feasibility of controlling particle adhesion by steric repulsion of adsorbed layers on the particles and the W surface was investigated using nonionic surfactants. Of the surfactants investigated, octylphenol polyethylene oxide (OPEO) with a ethylene oxide chain length between 9 and 10 was found to be effective in controlling particle deposition. As shown in Figure 2(b), the surfactant did not reverse the zeta potential of alumina from positive to negative; the beneficial effect was mainly due to steric repulsion.

#### 4.0 CONCLUSIONS

Particle/wafer attraction and particle deposition were found to be consistent with electrostatic attraction forces for both oxide and tungsten wafers. Both AFM and electrokinetic techniques can be used to study the origins and magnitudes of particle/wafer interactions relevant, at the laboratory scale, to CMP processing. Electrostatic interactions are important in the adhesion of particles during CMP operations. It is possible to influence particle deposition by modifying the electrostatic charge characteristics of wafer or particle surfaces, or by introduction of a non-ionic surfactant. The processing implications of this work are: (1) the oxide polish/rinse/clean process should be maintained at high pH in order to minimize particle deposition (this has been observed experimentally [3]); (2) the effectiveness of nonionic surfactant additions to prevent particle deposition in polishing/cleaning solutions is dependent on the zeta potential of surfaces in the system at the working pH, and may require concentrations greater than 1000 ppm. These laboratory findings are being tested on full-scale polishing equipment.

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