



Effects of Ambient and Dissolved Oxygen Concentration in Ultrapure Water on Initial Growth of Native Oxide on a Silicon (100) Surface

Fuhe Li,* Marjorie K. Balazs,* and Scott Anderson

Air Liquide—Balazs Analytical Services, 46409 Landing Parkway, Fremont, California 94538, USA

The effects of ambient and dissolved oxygen concentration in ultrapure water (UPW) on native oxide growth were studied at room temperature using a silicon (100) surface. Studies focused on the initial stage of the surface oxidation immediately after the HF cleaning. The silicon surfaces were exposed at a fixed duration to the UPW with different dissolved oxygen concentrations, open air, and dry nitrogen, respectively. The SiO₂ equivalent thicknesses of the native oxides formed were then measured and compared. Results indicate that the ambient and the dissolved oxygen concentration in UPW dramatically affect the growth rate of the native oxide. Decreasing the dissolved oxygen concentration in UPW and using an inert and dry atmosphere for the ultracleaning is shown to reduce or eventually prevent the native oxide from growing on silicon surfaces. The SiO₂ equivalent thicknesses of the native oxide formed on these surfaces were characterized by a rapid acid extraction followed by a determination for extractable silicon. The extractable silicon was determined by a high-resolution magnetic-sector ICP mass spectrometer. This analytical method has been demonstrated for measurement of an oxide thickness on a silicon wafer surface down to a monolayer range with a possible 0.1 Å resolution.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1946487] All rights reserved.

Manuscript submitted July 30, 2004; revised manuscript received March 9, 2005.

The presence of interfacial native oxide on a silicon surface has widely been recognized as an impediment to the formation of high-quality ultrathin gate, atomic layer epitaxy, and small metal contacts on the surfaces.¹⁻³ Suppressing oxide growth during the surface cleaning and precisely controlling the interface prior to the advanced ULSI processes have become absolutely critical. This recognition has led to considerable efforts of studying the mechanism of the native oxide growth and developing new measuring techniques that are capable of detecting the ultrathin native oxide formed on a silicon surface.

The objective of this paper is to extend our previous studies^{4,5} of ultrathin native oxide growth on an HF-cleaned silicon (100) surface and to improve the technique used for oxide thickness measurements. Previous studies dealt with the effects of UPW exposure time on a bare wafer and showed that native oxide grew immediately during a UPW rinse. The growth rate was found to increase linearly with increasing exposure time during the first 10 min of the rinse.^{4,5} The emphasis of this paper is, however, placed on the effects of the ambient and the dissolved oxygen concentration in UPW. The initial stage of the surface oxidation during the first 10 min of the UPW rinse is still the focus. It is the authors' belief that the initial surface oxidation may be closely related to the reaction mechanisms governing the initiation and kinetics of native oxide formation on a silicon wafer surface. This study of the initial surface oxidation is thereby of practical importance to better understand the mechanisms and to find the solutions to suppress the growth of native oxide during UPW rinse and storage processes.

In order to carry out such a study, reliable measurements of the ultrathin native oxide formed on silicon surfaces are essential. In this work, we have improved the procedure used to extract silicon in an oxide form from the silicon surface. We also utilize a double-focusing magnetic-sector based mass spectrometer with inductively coupled plasma (ICP) as an ionization source (HR-ICP-MS) for the determination of extractable silicon instead of the ICP optical emission spectroscopy (ICP-OES) used previously. The combination of these two improvements results in a 100-fold enhancement in analytical sensitivity. With the new procedure, the effects of the ambient and the dissolved oxygen concentration in UPW on initial surface oxidation can be clearly shown.

Experimental

Analytical instrumentation.—All analyses were performed on a FinniganMAT Model ELEMENT2 HR-ICP-MS (ThermoFinnigan MAT, Bremen, Germany), equipped with a 27 MHz argon inductively coupled plasma (ICP) source and a double-focusing magnetic-sector based mass analyzer with a reverse Nier-Johnson geometry. The optimized operating parameters for the HR-ICP-MS include a forward RF power of 1.15 kW, a reflected power <5 W, an argon coolant flow rate of 15 L/min, an auxiliary flow rate of 0.98 L/min, and a nebulizer flow rate of 1.15 L/min. Following the instrument calibration with standards, sample solutions are directly introduced, through a state-of-the-art PFA self-aspiration microflow nebulizer (Elemental Scientific Inc., Omaha, Nebraska), into the ICP plasma where the analytes are atomized, excited, and ionized.

During the analysis, a grounded platinum (Pt) electrode (GuardElectrode™) was placed between the quartz ICP torch and the RF coil to prevent the so-called capacitive-coupling responsible for argon based mass interferences and to produce high transmission for the ions from the ICP plasma. The ions produced in the plasma were extracted into the vacuum chamber of the mass analyzer through nickel (Ni) sampling and skimmer cones. The ion beam then passed through the magnetic sector and the electrostatic analyzer (ESA), eventually reaching the secondary electron multiplier (SEM), where the ions were counted. The silicon concentrations in the sample solutions were determined at mass *m/z* 27.97693. The amount of dissolved oxygen in the UPW was determined colorimetrically using an R-7501 (0–1.0 PPM) and an R-7512 (1–12 PPM) CHEMets self-filling ampoule (CHEMetrics, Inc., Calverton, VA).

Reagents, standards, and wafers.—Hydrofluoric acid (HF) used throughout this work was of MB electronic grade (Ashland Chemicals, Columbus, OH). The UPW with 18.2 MΩ resistivity was produced by a Milli-Q Element final polisher (Millipore Corp., Bedford, MA) fed with in-house high-purity deionized water. The concentration of dissolved oxygen in the UPW was found to be 6–7 ppm. A 10000-ppm (μg/ml) single-element standard of silicon (NIST, Gaithersburg, MD) was used as the stock standard solution. Calibration standards were prepared by serial dilution of the stock standard and by adding the appropriate amount of HF so that the final concentration of HF in the standards matched that in the sample solutions. Both *p*-type and *n*-type wafers were used in this work. These wafers were polished 200 mm in size and with >5Ω cm resistivity. The crystal orientation of all wafers was <100>.

* Electrochemical Society Active Member.

Sample preparation procedure.—Experiments were designed to assess the ultrathin native oxide growth on an HF-treated silicon surface in different ambient environments and under different cleaning conditions. A glove box was used in this study to isolate atmosphere and to produce various ambient conditions. The box was made with $\frac{1}{4}$ inch clean and clear PVC (48 inch \times 27 inch \times 36 inch) by M. Braun, Newburyport, MA. It was equipped with an antechamber flange and an oxygen/humidity monitor. The typical oxygen content in the nitrogen filled box, unless otherwise noted, was 0.5%. The water content in the nitrogen was $<0.1\%$.

In practice, the samples were prepared in the following manner: Prior to each experiment, all test wafers were chemically cleaned by immersion in dilute aqueous HF (1–5%) solution for 10 min. The wafers were pulled out of the HF bath, immersed in a clean UPW bath for a few seconds to remove residue HF, and dissolved Si from the surface, then quickly immersed in another UPW bath or exposed to open air for the native oxide growth experiments. With dilute HF, the oxide layer formed on the wafer surfaces during UPW rinse or air exposure was quickly stripped off and converted into aqueous solutions. The resulting solutions were then directly introduced without any further chemical pretreatment into the ICP plasma for mass spectrometric measurements of silicon. Silicon concentrations were converted into the SiO_2 equivalent film thicknesses in angstroms (\AA) based on the assumption that the native oxides were completely SiO_2 and the density of the oxides was 2.2 g/cm^3 .

The dilute HF used for stripping silicon dioxide off wafer surfaces contains dissolved oxygen. When in contact with silicon wafers, the HF solution can also etch the surface. Fortunately, the etch rate of the silicon surface in HF under the chosen conditions was found to be so slow that the amount of silicon contributed from the surface was insignificant compared to the Si from the dissolution of silicon dioxide. Because the SiO_2 equivalent film thickness from the Si surface was consistent under the chosen etch conditions, it was subtracted as an analytical blank from all thickness results measured using this method.

Data Evaluation and Processing

Silicon determination by HR-ICP-MS.—In general, a conventional quadrupole ICP-MS system offers superior detection limits over ICP-OES.⁶ However, the application of the quadrupole ICP-MS to the low-level Si determination has been somewhat limited. This is due largely to its low mass resolution (one mass-unit separation) and the inability to spatially resolve the $^{28}\text{Si}^+$ signal from the common polyatomic interferences formed from molecular ions in the plasma, namely $^{16}\text{C}^{16}\text{O}^+$ and $^{14}\text{N}^{14}\text{N}^+$. The analyte and interference signals are essentially superimposed onto each other. This isobaric spectral overlap presents a considerable impediment for the reliable analysis for Si at low concentrations by quadrupole based ICP-MS systems. In addition, different amounts of dissolved molecular CO_2 , organic, HNO_3 , and/or dissolved N_2 species present in the calibration standards and sample solutions can further complicate this analysis.

Using a double-focusing magnetic-sector based mass analyzer, HR-ICP-MS provides a resolving power up to 10000 allowing almost interference-free measurements. Figure 1 shows an HR-ICP-MS spectrum starting from 27.970 to 28.010 m/z acquired in medium resolution mode with a resolving power around 4000. From the figure, it can be seen that the Si signal (m/z 27.97693) is baseline separated from the CO^+ (m/z 27.99491) and N_2^+ (m/z 28.00614) interfering signals. The removal of interfering signals not only reduces the Si background equivalent concentration (BEC), but also improves the analytical reliability. The detection limit of Si was evaluated by analyzing eight independent samples spiked with 1-ppb Si standard. The DL (three times standard deviation) was found to be 0.3 ppb while spike recovery was 93%. The solution DL obtained corresponds to 0.003 \AA in the SiO_2 equivalent thickness if the Si is stripped off from a 200-mm wafer surface with a 314 cm^2 surface area. A practical quantitation limit (PQL) of 0.03 \AA was

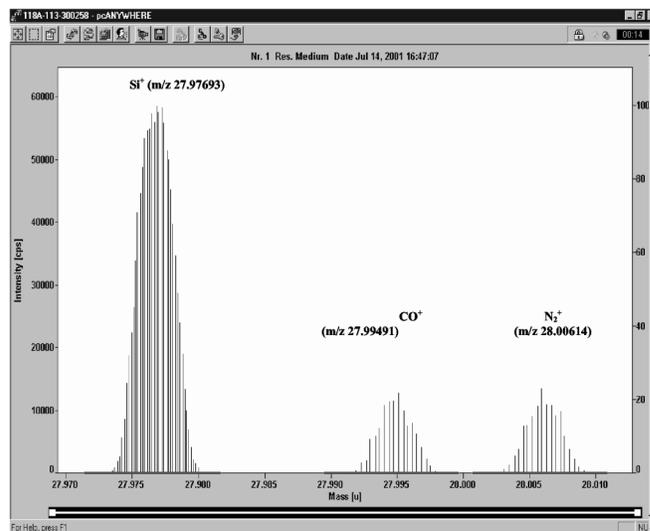


Figure 1. Spectrum acquired at medium resolution (MR) with 4000 resolving power using a 10 ppb Si standard.

calculated by multiplying the DL by a factor of 10. Although excessive cleaning of the sample introduction and ion transportation systems may help further lower the BEC and improve the detection limit, it is suggested that the PQL obtained at $\leq 0.1 \text{ \AA}$ with this method is perhaps sensitive enough for the purpose of monitoring native oxide thickness on a silicon surface. The calibration curve constructed using low-level Si standards is shown in Fig. 2 with both good linearity and the typical correlation coefficient being 0.999 or better.

Conversion of silicon concentration to oxide thickness.—The conversion of extractable Si concentration to oxide thickness was found to be difficult due to the lack of information on the structure and density of the ultrathin native oxide formed. Previous literature⁷⁻⁹ has indicated that ultrathin native oxide ($10\text{--}100 \text{ \AA}$) formed on a silicon surface is essentially a heterogeneous mixture of “ SiO ” and “ SiO_2 .” At the interface of the Si– SiO_2 structure, oxides thinner than 20 \AA are not even fully stoichiometric, and there is a transition region in Si– SiO_2 structure (see Fig. 3). The X-ray photoemission spectroscopy studies of the $2p$ electron spectral line of silicon atoms showed that the oxide has the form SiO_x , with x increasing from 0 to 2 as the distance from the silicon surface increases to greater than at least 10 \AA .⁹

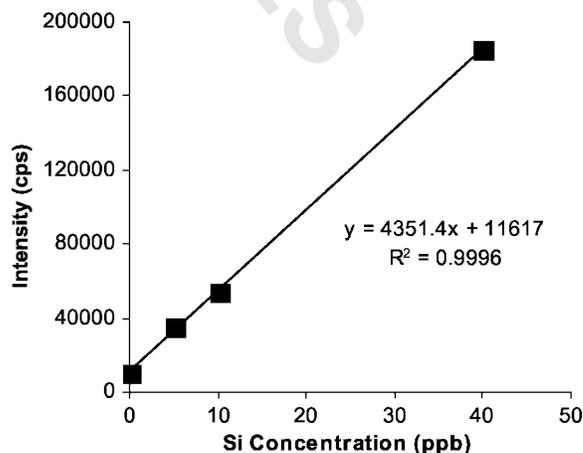


Figure 2. Calibration curve constructed for silicon (Si) at m/z 27.97693.

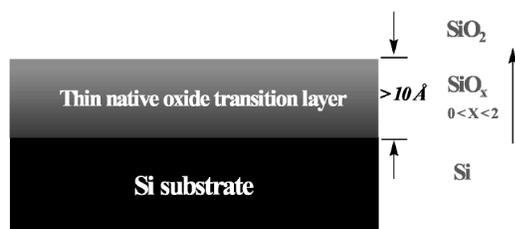


Figure 3. Computer-generated cross-sectional schematic diagram of Si-SiO₂ interface.

One way of estimating the thickness of the native oxide and being able to make direct comparisons is to assume the oxides formed on a silicon surface to be complete SiO₂. The SiO₂ equivalent thickness can then be calculated using the volume of the diluted HF stripping solution, the wafer surface area, and the density of SiO₂. The density used in this study was 2.20 g/cm³ as other researchers have used¹⁰ by assuming the native oxide to be fused or amorphous quartz. It should be noted that the density of the native oxide with a thickness less than a monolayer might not be 2.2 gm/cm³. Furthermore, at the interface, the ultrathin native oxide may have large quantities of =Si=H₃ and ≡Si-H bonds¹¹ and may have an average form of SiO_x with *x* between 0 and 1, without considering the hydration. This is further supported with the early study done by Deal and Kao using a pulsed laser atomic probe.¹²

Results and Discussion

Effect of dissolved O₂ concentration in UPW.—Figure 4 shows the SiO₂ equivalent film thicknesses measured after the wafers were immersed in UPW baths containing different amounts of dissolved oxygen (DO). All experiments were conducted at a fixed exposure time of 10 min. The study was essentially focused on the short-time frame of a UPW rinse that is also typical for wafer cleaning today. The UPW rinse was done in atmosphere for (a) and (b) and in the nitrogen-purged glove box for (c). Duplicate etching and analyses were performed for each condition and the average results reported. It can be seen that the 10-min oxygenated UPW rinse produced a native oxide film with a SiO₂ equivalent thickness of approximately 1.3 Å on a silicon surface. This thickness corresponds to approximately $\frac{1}{2}$ of a monolayer. The thickness of the native oxide became

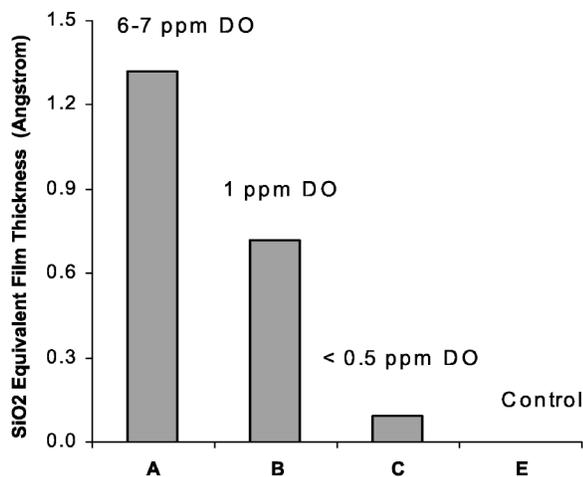


Figure 4. Averaged SiO₂ equivalent film thicknesses measured on HF treated silicon surfaces after the wafers were immersed in a UPW bath for 10 min. (a) Oxygenated UPW bath contains 6–7 ppm dissolved oxygen; (b) UPW bath contains 1 ppm dissolved oxygen; (c) UPW bath contains <0.5 ppm dissolved oxygen; (d) analytical control.

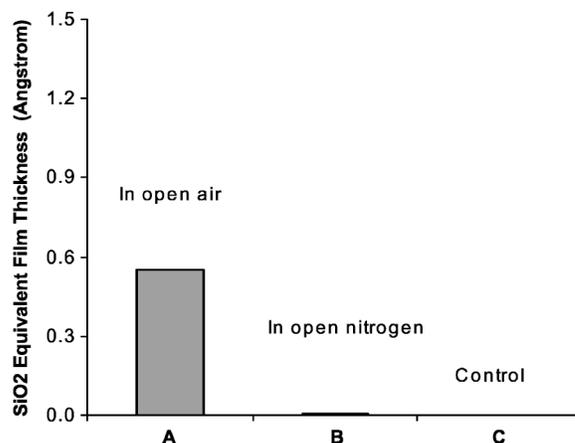


Figure 5. Averaged SiO₂ equivalent film thicknesses measured on HF treated silicon surfaces. (a) After the wafers were exposed to open air for 10 min; (b) after the wafers were exposed to open nitrogen for 10 min; (c) analytical control.

thinner, however, as the dissolved oxygen concentration in UPW decreased. When the dissolved oxygen concentration in the UPW was less than 0.5 ppm, the thickness of the native oxide formed was found to be less than 0.1 Å. The presence of the dissolved O₂ in the UPW is apparently a key to the growth of the native oxide on a wafer surface. The results suggest that the native oxide may be minimized during a UPW rinse if the dissolved O₂ concentration in UPW can be lowered.

The data shown in Fig. 4 were obtained from the short-time UPW rinse. The dramatic effect of the dissolved O₂ concentration in UPW appears to correlate well with the data that Ohmi and his co-workers have reported in their long-time rinse studies.^{13–15} The glove box was used in this study to produce and maintain a UPW bath with a low dissolved O₂ concentration (<0.5 ppm). The nitrogen inside the glove box may have directly or indirectly contributed to the suppression of the native oxide growth in UPW due to the low dissolved O₂ concentration in the UPW bath. In fact, the slow decrease in the dissolved O₂ concentration in the UPW bath inside the nitrogen-purged glove box was observed, which may be due to the gradual replacement of the dissolved O₂ in the UPW by dissolved N₂ by equilibrium.

Effect of ambient atmosphere.—The SiO₂ equivalent film thicknesses produced by exposing the HF-cleaned and UPW rinsed silicon surfaces to open air and open nitrogen were also measured (see Fig. 5). To allow a direct comparison, the exposure time was kept constant at 10 min as well. Prior to the exposure, the HF-cleaned silicon wafers were only immersed in UPW for 2–3 s to remove possible HF dissolved Si on the surfaces. The room temperature was 23°C and relative humidity in the open air approximately 40%. The results showed that the growth of the native oxide in the open air was slower than the UPW rinse performed in atmosphere. The thickness of the native oxide produced by a 10-min exposure was found less than 0.6 Å compared to 1.3 Å produced in the 10-minute UPW rinse. Because the 40% relative humidity corresponds to about 1% water content in the air,¹ the results seem to suggest that the UPW or H₂O molecule also plays an important role in the native oxide growth on a wafer surface.

As expected, the exposure of bare wafers to inert and relatively dry nitrogen produced little or no native oxide on the silicon surfaces (see Fig. 5b). This is easily understood because the oxygen content in the glove box was only 0.5% while the water content in the nitrogen used was <0.1%. Morita and Ohmi have previously conducted kinetics work in this area by exposing the wafers to a dry air where >20% of oxygen was present.¹⁶ Their work showed the native oxide hardly grew on silicon surfaces even with a seven-day

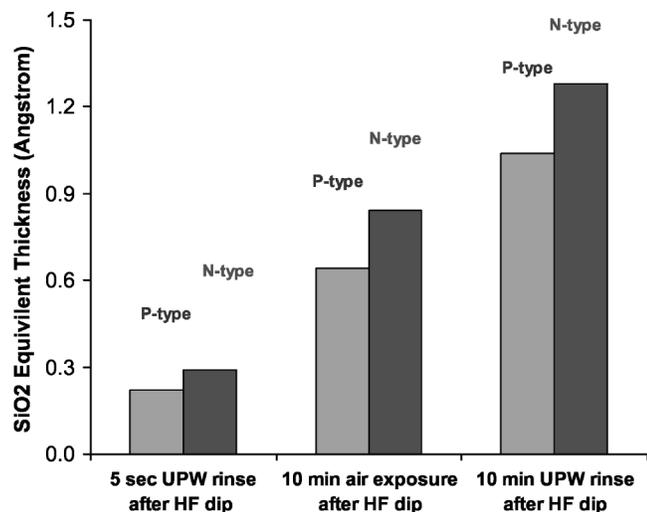


Figure 6. Comparison of oxidation on *p*-type vs. *n*-type wafers in air exposure and UPW rinse.

exposure. These findings suggest that the native oxide growth on silicon surfaces requires the presence of water or H₂O molecules in addition to O₂ molecules. In the previous section, we have demonstrated that the presence of molecular O₂ is necessary to the surface oxidation on a silicon surface during a UPW rinse. It appears that our work has further confirmed the theory described by Morita, Ohmi, and their co-workers that the native oxide growth on a silicon surface requires the coexistence of O₂ and H₂O.¹³ Yet our research work was essentially conducted during the initial stage, and the first 10 min of the surface oxidation may be more relevant to the elucidation of the growth mechanism of native oxide and the kinetics of surface oxidation. The ability to study the initial-stage native oxide growth was attributed to the sensitivity and precision of the analytical method used in this work because much thinner oxides can now be measured. Because of the involvement of both the dissolved O₂ and H₂O in the surface oxidation, it is possible that Si-H bonds on the hydrogen-terminated surface, after the HF cleaning, are easily converted into Si-O-Si or Si-OH in the presence of H₂O, while the dissolved O₂ or OH⁻ attacks the interior Si-Si bonds without breaking the Si-H bonds.^{1,17}

The test wafers used in this ambient study were not as dry as processed silicon wafers found in industrial fabrication processes. Although the HF-last surfaces are hydrophobic and do not have any obvious water marks, there will still be residue water on the surface. Such water residue is compensated in industrial processes by utilizing a vapor dryer such as an isopropyl alcohol (IPA) dry to completely remove any water that remains on the surface. Therefore, the rates of native oxide growth on wafer surfaces measured in this study could be slightly different from those in the real-world fabrication process due to the involvement of the residue water on the test wafers. The relative growth rates obtained by exposing identical test wafers to UPW, open air, and dry nitrogen, however, should remain the same.

p-type vs. *n*-type wafer surface.—In observing these oxidation results, a question arose as to whether all types of silicon wafers would grow native oxide at the same rate. Figure 6 shows the rate of surface oxidation of *p*- vs. *n*-type doped wafers. It reveals a definite difference between the two during the initial stage of the surface oxidation with *n*-type wafer growing slightly more native oxide on the surface in both open-air exposure and UPW rinse. Considering the fact that native oxide will immediately grow on any wafer surfaces not protected from oxygen and moisture, these findings could have a significant difference on integrated circuits during production.

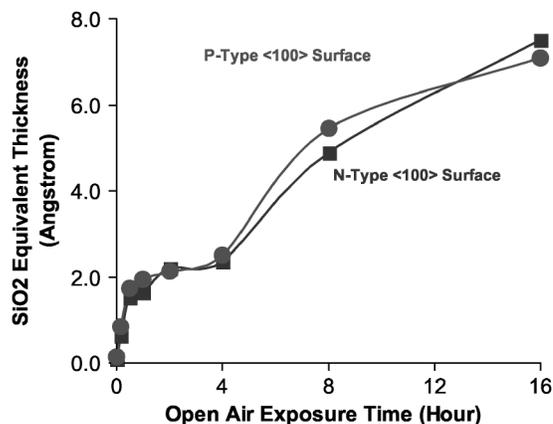


Figure 7. Oxidation of *p*-type vs. *n*-type wafer surfaces after hours of exposure in open air at 19°C and 38% humidity.

A long-term kinetics study was also performed to examine the long-term growth rates of native oxide on both *n*-type and *p*-type wafers. The study was accomplished by exposing both *n*-type and *p*-type wafers in open air with 38% humidity for 16 h. The time dependence of native oxide film thickness formed on both types of wafers is shown in Fig. 7. The results suggest that the long-term oxidation rates on these two types of wafers are similar in spite of the apparent rate difference observed during the initial surface oxidation. However, the results also show a steplike surface oxidation pattern. For example, after the HF cleaning, both *n*- and *p*-type wafer surfaces are oxidized immediately and rapidly. After forming approximately 2 Å of native oxide, the surface oxidation was slowed before another rapid oxidation step takes place. This steplike surface oxidation has been observed by atomic force microscopy and suggested by Morita as a reciprocal relationship where the native oxide forms one layer at a time.¹ Because of the sensitive and reproducible oxide thickness measurement method used here, we have been able to obtain similar kinetic data for the first 60 min of surface oxidation that was missing from previously published work.

Conclusions

The results obtained in this work indicate that both the dissolved oxygen concentration and ambient atmosphere dramatically affect the rate of the native oxide growth on silicon surfaces. To reduce or prevent the native oxide growth during the UPW rinse and storage periods, it is necessary to keep the dissolved oxygen concentration in the UPW as low as possible. It is also desirable to clean wafers in an inert and dry ambient such as a closed nitrogen environment. Perhaps the routine monitoring of the SiO₂ equivalent thickness on a silicon surface after the rinse is, as a QC measure, an essential step to ensure the quality of the subsequent ULSI processes on the surfaces. The thickness data generated using the analytical method described in this work may help the continuing efforts of modifying and optimizing the ultracleaning conditions so that a native oxide-free silicon surface can eventually be produced. The production of such an ideal interface should help enhance the yields of processes including but not limited to the high-quality ultrathin gate formation, the atomic-layer epitaxy deposition by ALCVD, and small metal contact-holes formation.

The HR-ICP-MS was found to be a better tool for the low-level extractable Si determination and the ultrathin native oxide thickness measurement. It is much more sensitive than the ICP-OES used in our previous studies and more reliable than a conventional quadrupole based ICP-MS. By coupling the rapid acid-etching process developed in our laboratory with HR-ICP-MS, one can now provide a resolution of ≤ 0.1 Å for the SiO₂ equivalent thickness measurements. The method enables the precise and reliable measurements of the ultrathin native oxides formed on silicon surfaces within a

monolayer range. As an independent method, it can also provide the data to correlate with the results produced by other techniques, such as ellipsometry in which the refractive index is no longer a constant for the ultrathin oxides being measured.¹

Air Liquide America L. P. assisted in meeting the publication costs of this article.

References

1. M. Morita, *Native Oxide Films and Chemical Oxide Films, Ultraclean Surface Processing of Silicon Wafers*, p. 543, T. Hattori, Editor, Springer, New York (1998).
2. K. Yamada, M. Morita, C. M. Soh, H. Suzuki, and T. Ohmi, *J. Electrochem. Soc.*, **140**, 371 (1993).
3. M. Hirose, T. Yasaka, M. Takakura, and S. Miyazaki, *Solid State Technol.*, **34**, 43 (1991).
4. F. Li, M. K. Balazs, and B. E. Deal, *18th Annual Semiconductor Pure Water and Chemicals Conference Proceedings*, p. 125, Santa Clara, CA (1999).
5. F. Li, M. K. Balazs, and B. E. Deal, *Solid State Technol.*, **43**, 87 (2000).
6. A. Montaser and D. W. Golightly, *Inductively Coupled Plasma in Analytical Atomic Spectrometry*, p. 552, VCH Publishers, Inc., New York (1992).
7. R. A. Clarke, R. L. Tapping, M. A. Hopper, and L. Young, *J. Electrochem. Soc.*, **122**, 1347 (1975).
8. Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrow, *J. Vac. Sci. Technol. A*, **7**, 2104 (1989).
9. M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and K. Suma, *Appl. Phys. Lett.*, **55**, 562 (1989).
10. K. Vepa, K. Buker, and L. W. Shive, *Proceedings of Cleaning Technology in Semiconductor Device Manufacturing IV*, p. 358, R. E. Novak and J. Ruzyllo, Editors, The Electrochemical Society, Pennington, NJ (1995).
11. G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.*, **56**, 656 (1990).
12. B. E. Deal and D. B. Kao, in *Proceedings of Tungsten and Other Refractory Metals for VLSL Applications*, p. 27, E. K. Broadbent, Editor, Materials Research Society, Pittsburgh (1987).
13. T. Ohmi, H. Kuwabara, S. Saito, and T. Shibata, *J. Electrochem. Soc.*, **137**, 1008 (1990).
14. M. Morita, T. Ohmi, E. Hasegawa, and A. Teramoto, *Jpn. J. Appl. Phys., Part 2*, **29**, L2392 (1990).
15. T. Ohmi, *Proceedings of the 15th SPWCC Conference*, p. 157, M. K. Balazs, Editor, Balazs Analytical Laboratory, Sunnyvale, CA (1996).
16. M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and K. Suma, *Appl. Phys. Lett.*, **55**, 562 (1989).
17. Y. B. Kim, M. Tuominen, I. Raaijmakers, R. De Blank, R. Wilhelm, and S. Haukka, *Electrochem. Solid-State Lett.*, **3**, 346 (2000).