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Native Oxide Growth on Wafer Surface During Final Rinse

Fuhe Li

Air Liquide - Balazs Analytical Services, 46409 Landing Parkway, Fremont, CA 94538, USA

Marjorie K. Balazs

SPWCC

1340 South DeAnza Blvd., Suite 207, San Jose, CA 95129-4644 USA

The effects of ambient and dissolved oxygen concentration in UPW on native oxide growth were studied at room temperature using a HF-cleaned silicon (100) surface. The studies were 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 SiO_2 equivalent thicknesses of the native oxides formed on those surfaces were then measured and compared. The results obtained indicate that the ambient and the dissolved oxygen concentration in UPW dramatically affect the growth rate of the native oxide on the silicon surfaces. Decreasing the dissolved oxygen concentration in UPW and using an inert and dry ambient for the ultra-cleaning may reduce or eventually prevent the native oxide from growing on silicon surfaces. The SiO_2 equivalent thicknesses of the native oxide formed on the silicon surfaces were characterized by a rapid acid extraction followed by a determination for extractable silicon in the acid. The determination of extractable silicon was accomplished by a high-resolution magnetic-sector mass spectrometer with inductively coupled plasma (ICP) as the ionization source. The analytical method developed has been demonstrated to be able to measure an oxide thickness on a silicon surface down to a monolayer range with a possible 0.1Å resolution.

Introduction

The presence of interfacial native oxide on a silicon surface has widely been recognized as an impediment to the formation of high-quality ultra-thin 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 the considerable efforts of studying the mechanism of the native oxide growth and developing new measuring techniques that are capable of detecting the ultra-thin native oxide formed on a silicon surface.

The objective of this paper is to extend our previous studies[4-5] of ultra-thin native oxide growth on a HF-cleaned silicon (100) surface and to refine the technique we used for the oxide thickness measurements. The previous studies dealt with the effects of the exposure time of a bare wafer to the UPW. The study showed that native oxide grows immediately during a UPW rinse. The growth rate was found to increase linearly with increasing exposure time during the first 10-minute 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-minute of the UPW rinse is still the focus. The authors believe that the initial surface oxidation may be closely related to the reaction mechanisms governing the initiation and kinetics of native oxide formation on silicon surfaces. The 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 ultra thin native oxide formed on silicon surfaces are essential. In this work, we have improved the procedure used to extract silicon in oxide form from silicon surfaces. We also utilized a double-focusing magnetic-sector based mass spectrometer with inductively coupled plasma (ICP) as the 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 has resulted 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 were studied.

Experimental

Analytical Instrumentation. All analyses were performed by a FinniganMAT Model ELEMENT2 HR-ICP-MS (ThermoFinnigan MAT, Bremen Germany), equipped with a 27 Hz 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, auxiliary flow rate of 0.98 L/min and nebulizer flow rate of 1.15 L/min. Following the calibration standards, sample solutions are directly introduced, through a state-of-the-art PFA self-aspiration micro-flow 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 and to produce high transmission for the ions from the ICP plasma. The ions produced in the plasma are extracted into the vacuum chamber of the mass analyzer through a Nickel (Ni) sampling and a skimmer cones. The ion beam then passes through the magnetic sector and the electrostatic deflection region (ESA), eventually reaching the secondary electron multiplier (SEM) located at the exit of the ESA, where the ions are 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 a R-7501 (0-1.0 PPM) and a R-7512 (1-12 PPM) CHEMets self-filling ampoules (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 the 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 matches with the sample solutions. Both p-type and n-

type wafers were used in this work. These wafers are polished 200 mm in size and with > 5 Ωcm resistivity. The crystal orientation of the wafers was all <100>.

Sample Preparation procedure. Experiments were designed to assess the ultra-thin native oxide growth on a 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 using ¼ inch clean and clear PVC (48 inch x 27 inch x 36 inch) by M. Braun, Newburyport, MA. It is 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 used was < 0.1%.

In practice, the samples were prepared in the following manner: Prior to each experiment, a wafer was chemically cleaned by immersion in diluted aqueous HF solution for 10 min. The wafer was taken out the HF bath, immersed in a clean UPW bath for few seconds to remove residue HF on the surface and any dissolved Si, then quickly transferred to another UPW bath or exposed to open air for the native oxide growth experiments. With diluted HF, the oxide layer formed during the UPW rinse or air exposure was quickly stripped off of the wafer and converted into an aqueous solution. The resultant solution was then directly introduced without any further chemical pre-treatment, into the ICP plasma for mass spectrometric measurement of silicon. The Si concentration obtained are converted into the SiO_2 equivalent film thicknesses in angstrom (Å) based on the assumption that the native oxides formed were completely SiO_2 and the density of the oxides was 2.2 gram/cm^3.

Data Evaluation and Processing

Silicon determination by HR-ICP-MS . In general, a conventional quadruple ICP-MS system offers superior detection limits than ICP-OES in most cases.[6] However, the application of the quadrupole ICP-MS to the low-level Si determination has somewhat been limited. This was due largely to its low resolution (one mass-unit separation) in acquired mass spectrum and the inability to spatially resolve the $^{28}Si^+$ signal from the common polyatomic interferences originated from molecular ions formed in the plasma, namely $^{12}C^{16}O^+$ and $^{14}N^{14}N^+$. 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 level by a quadruple based ICP-MS system leading to a detection limit that is similar to what the ICP-OES can offer with a much higher operating cost. 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 perhaps have further complicated the analysis. The resultant unstable high-backgrounds have subsequently increased the uncertainty of the measurements.

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 a HR-ICP-MS spectrum starting from 27.970 to 28.010 m/z acquired in a medium resolution with a resolving power around 4000. As can be seen, Si signal (m/z 27.97693) is baseline separated from the CO^+ (m/z 27.99491) and $N2^+$ (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 (3 times standard deviation) was found to be 0.3 ppb while spike recovery was 93%. The solution DL obtained corresponds to 0.003 Å in the SiO_2 equivalent thickness if the Si is stripped off from a 200-mm wafer surface. A practical quantitation limit (PQL) of 0.03 Å was calculated by multiplying the DL by a factor of 10. Modifying and specially cleaning the sample introduction and ion transportation systems may help further lower the BEC and improve the detection limit. However it is suggested that the PQL obtained at $\leq$ 0.1 Å 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 Figure 2. As can be seen, the curve is linear with 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 the enough information on the structure and density of the ultra-thin native oxide formed. The literature [7-9] has indicated that ultra-thin native oxide (10-100 Å) formed on a silicon surface is essentially a heterogeneous mixture of "SiO" and "SiO_2". At the interface of Si-SiO_2 structure, oxides thinner then 20 Å are not even fully stoichiometric, and there is a transition region in Si-SiO_2 structure

(See Figure 3). The XPS studies of the 2p electron spectral line of silicon atoms showed that the oxide has the form SiOx, with x increasing from 0 to 2 as the distance from the silicon surface increases to greater than at least 10 Å.[9]

Perhaps one way of estimating the thickness of the native oxide and being able to make direct comparison with others is to use SiO_2 equivalent thickness by assuming the oxides formed on a silicon surface to be complete SiO_2. The SiO_2 equivalent thickness can then be calculated using the volume of the diluted HF stripping solution, the wafer surface area, and the density of SiO_2. The density used in this study was 2.20 gm/cm^3 as other researchers have used[10] by assuming the native oxide to be fused or amorphous quartz. It should be kept in mind that the density of the native oxide with a thickness less than a monolayer might not be 2.2 gm/cm^3. Furthermore at the interface, the ultra-thin native oxide may have large quantities of =Si=H_3 and ≡Si-H bonds[11] and may have an average form of SiOx with x between 0 and 1, e.g. Si_2O, 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 O_2 Concentration in UPW. Figure 4 shows the SiO_2 equivalent film thicknesses measured on the silicon surfaces after the wafers were immersed in UPW bathes containing different amount of dissolved oxygen (DO) at a fixed exposure time (10 minutes). 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 formed for each condition and the average results reported. It can be seen that the 10-minute oxygenated UPW rinse produced a native oxide film with a SiO_2 equivalent thickness of approximately 1.3 Å on a silicon surface, which corresponds to an approximately half of a monolayer. The thickness of the native oxide became 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 O_2 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 prevented from growing during a UPW rinse if the dissolved O_2 concentration in UPW can be lowered.

It should be appointed out that the data shown in Figure 4 were resulted from the short-time UPW rinse. The dramatic effect of the dissolved O_2 concentration in UPW observed correlate well with what Ohmi and his co-works have found 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 O_2 concentration (< 0.5ppm). The filled nitrogen may directly or indirectly have contributed to the suppression of the native oxide growth. In fact, the slow decrease in the dissolved O_2 concentration in the UPW as a function of the duration of the UPW bath inside the nitrogen-purged glove box was observed.

Effect of Ambient. The SiO_2 equivalent film thicknesses produced by exposing the HF-cleaned silicon surface to open air and open nitrogen were also measured (see Figure 5). For the comparison purpose, the exposure time was kept constant at 10 minutes. There was no UPW rinse involved in this study. The room temperature was 23 °C and relative humidity in the open air approximately 40%. The results show that the growth of the native oxide in the open air is slower than that in the UPW rinse performed in atmosphere. The thickness of the native oxide produced by a 10-minute exposure was found less than 0.6 Å compared to 1.3 Å produced in the 10-minute UPW rinse. Since the 40% of the relative humidity corresponds to about 1% water content in the air,[1] the results seem to suggest that the UPW or H_2O 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 yields little or no native oxide on the silicon surfaces (see Figure 5 B). This seems to be 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 some kinetics work by exposing the wafers to a dry air where > 20% of oxygen was pesent[16]. Their work showed the native oxide hardly grew on silicon surfaces even with a seven-day exposure. These founding suggest that that the native oxide growth on the silicon surfaces requires the presence of water or H_2O molecule besides O_2 molecules. In previous section, we also demonstrated that the presence of molecular O_2 is necessary to the surface oxidation on a silicon surface during a UPW rinse. It appears that

our work have 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 O_2 and H_2O.[13] Yet our work was done during the initial stage and the first 10 minutes of the surface oxidation which may be more relevant to the elucidation of the growing mechanism of native oxide and the kinetics of surface oxidation. This can be attributed to the sensitivity and precision of the analytical method used din this work, which enables us to measure much thinner oxides. Because of the involvement of both the dissolved O_2 and H_2O 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 H_2O, while the dissolved O_2 or OH^- attacks the interior Si-Si bonds without breaking the Si-H bonds.[1,17]

P-type vs. N-type Wafer Surface. Seeing these results, a question arose as to whether all types of silicon wafers would grow native oxide at the same rate. Figure 6 shows the resultant rate of oxidation of P versus N type of doped wafer. 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 not protected from oxygen and moisture, these findings could have a significant difference on IC's during production.

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 the both N-type and P type wafers in an open air with 38% humidity continuously for 16 hours. The time dependence of native oxide film thickness formed on both types of wafers are shown in Figure 7. The results obtained seem to 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 step-like 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 angstroms of native oxide, the surface oxidation was slowed down before another rapid oxidation step takes place. This step-like surface oxidation has been obtained by an atomic force microscope and suggested by Morita as a reciprocal relationship, in which the native oxide forms one layer at a time.[1] Because of the sensitive and

reproducible oxide thickness measurement method used, we have been able to obtain the similar kinetic data for the first 60 minutes of surface oxidation which were missing from previously published literatures.

Conclusions

The results obtained in this work indicate that both the dissolved oxygen concentration and ambient dramatically affect the rate of the native oxide growth on the silicon surfaces. To reduce or prevent the native oxide growth during the UPW rinse and storage period, 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 SiO_2 equivalent thickness on a silicon surface after the rinse is, as a QC measure, an essential step to ensure the quality of the later 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 ultra-cleaning conditions so that a native oxide-free silicon surface can eventually be produced. The production of such an ideal interface shall help enhance the yields of the processes including but not limited to the high-quality ultra-thin 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 ultra-thin native oxide thickness measurement. It is more sensitive than the ICP-OES we used in our previous studies and more reliable than a conventional quadruple 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 ≤ 0.1Å for the SiO_2 equivalent thickness measurements. The method enables the precise and reliable measurements of the ultra-thin native oxides formed on a silicon surface within a monolayer range. As an independent method, it may also provide the data to correlate with the results produced by other techniques, such as ellipsometry in which the refractive index used is no longer a constant for the ultra-thin oxides being measured.[1]

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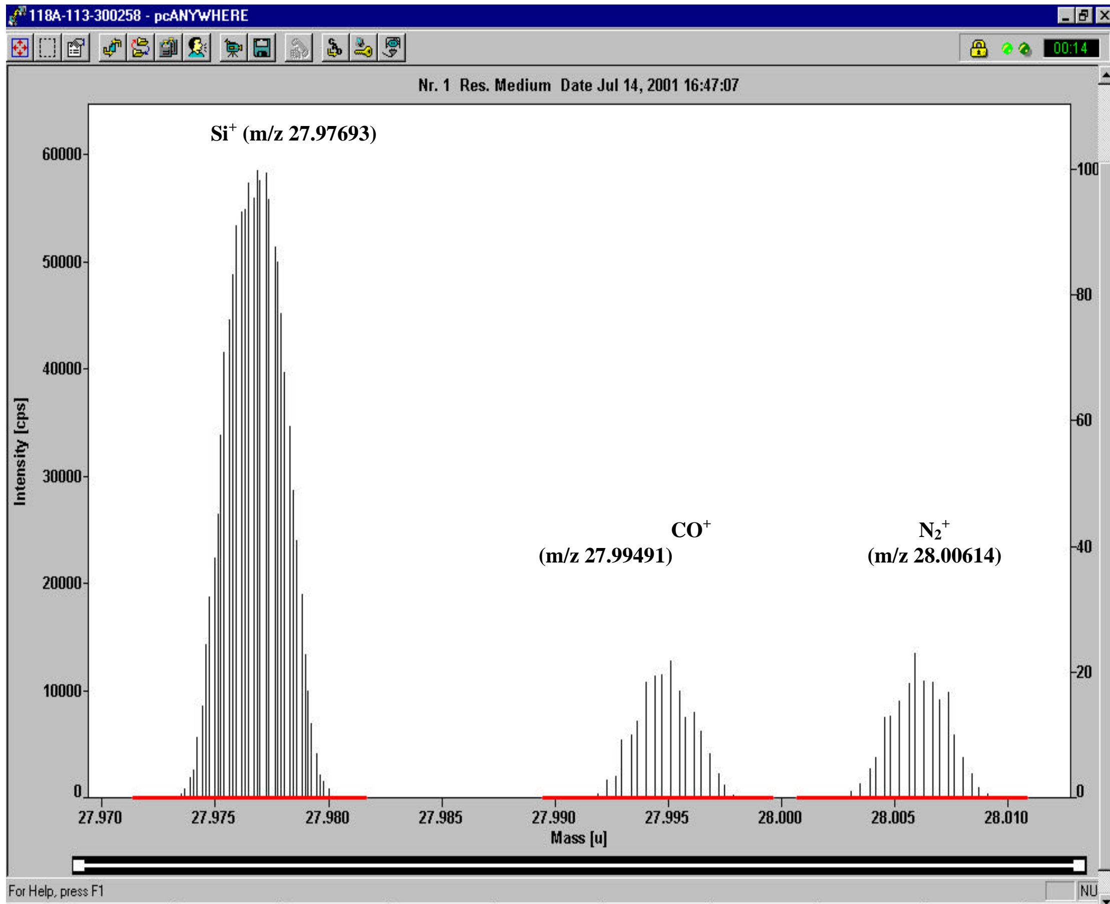

Figure 1. Spectrum acquired at medium resolution (MR) with 4000 resolving power using 10ppb Si standard.

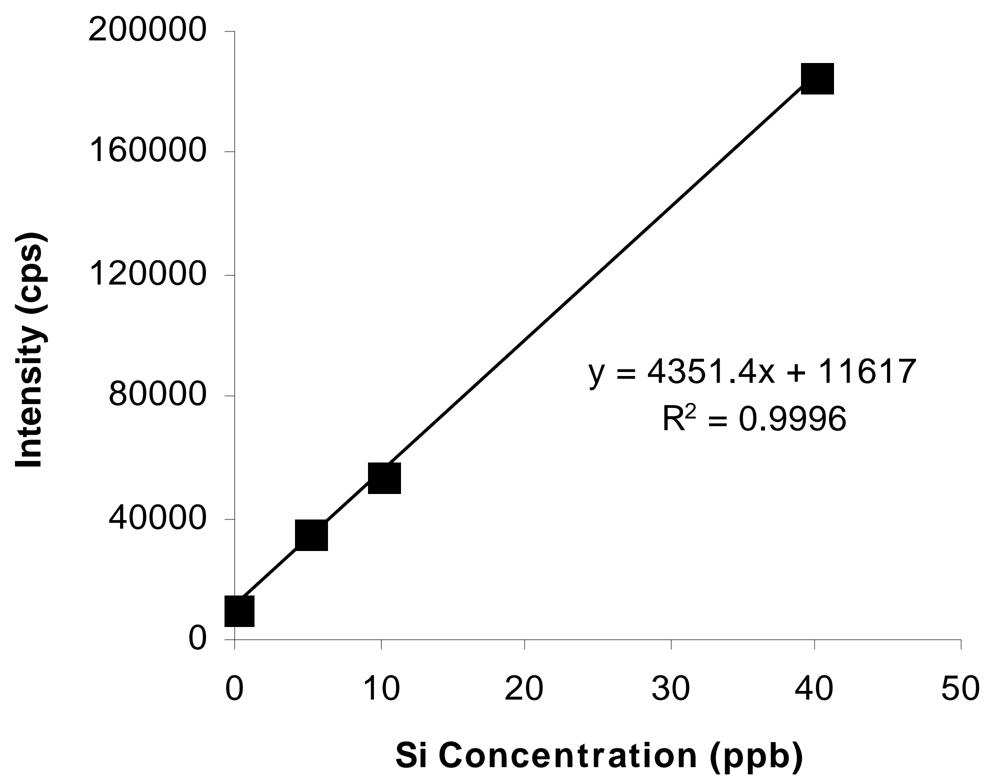

Figure 2. Calibration curve constructed for silicon (Si) at m/z 27.97693.

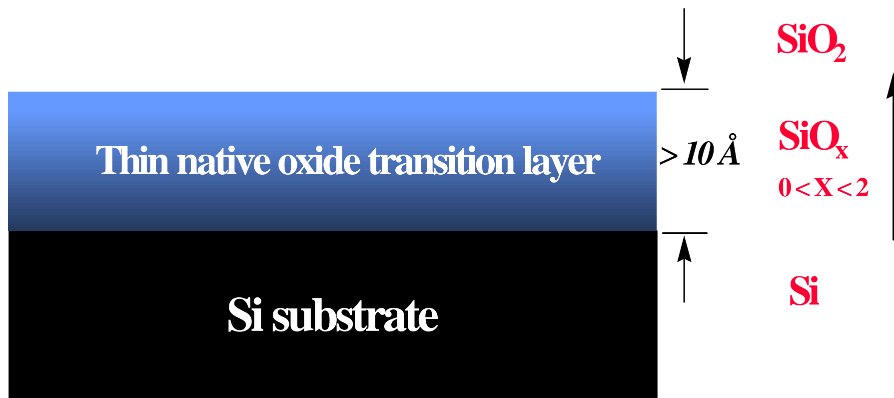

Figure 3. Computer-generated cross-sectional schematic diagram of Si-SiO_2 interface

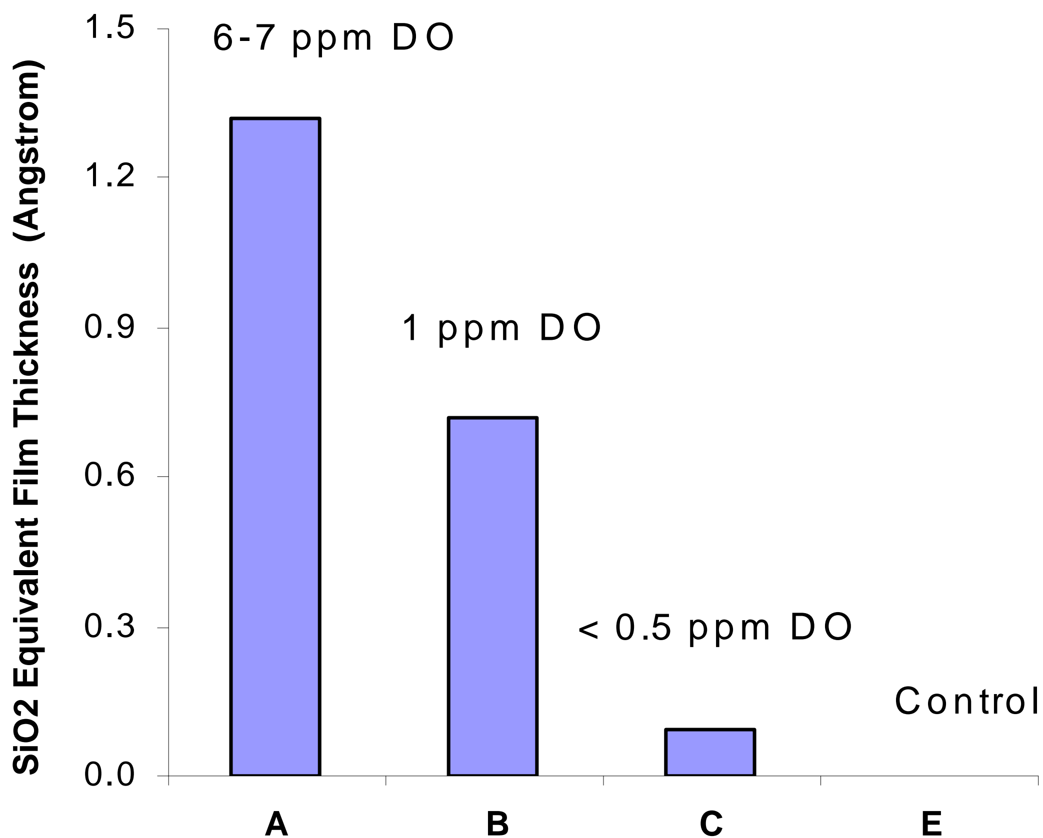

Figure 4. Averaged SiO_2 equivalent film thicknesses measured on HF treated silicon surfaces after the wafers were immersed in a UPW bath for 10 minutes. A). Oxygenated UPW bath contains 6-7 ppm dissolved oxygen; B). UPW bath contains 1 ppm dissolved oxygen; C). UPW bath contains < 0.5 ppm dissolved oxygen. E). Analytical Control.

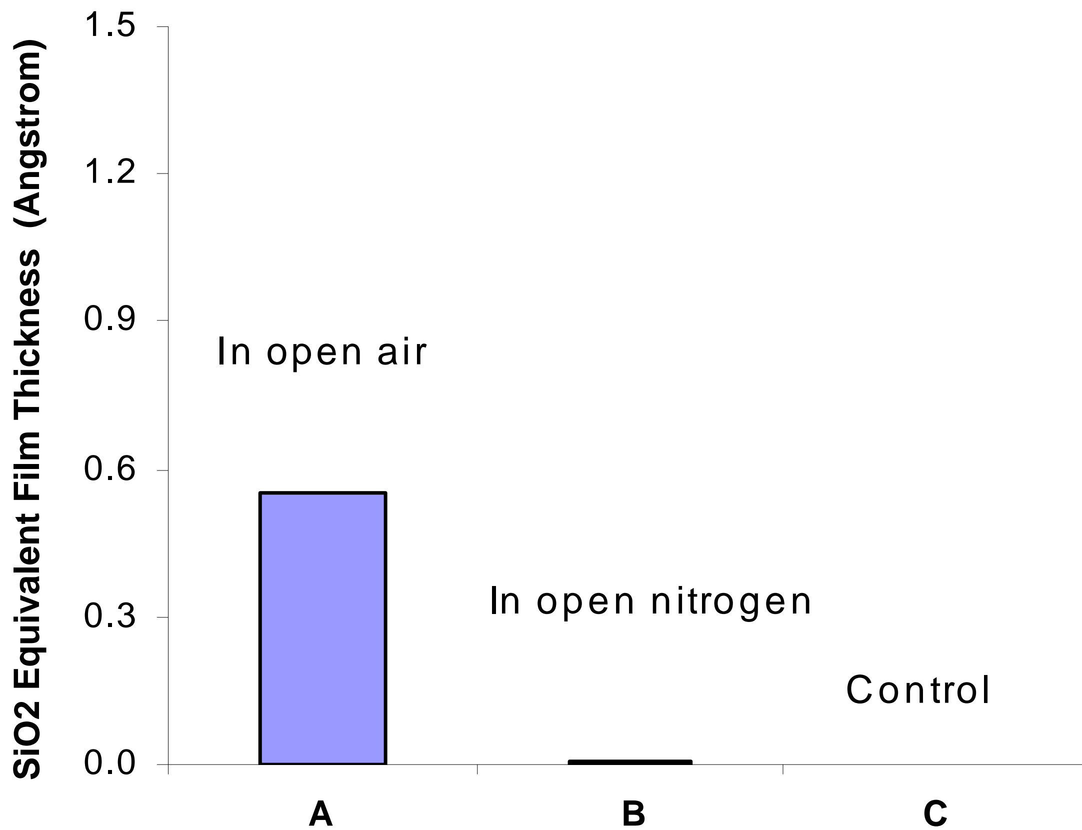

Figure 5. Averaged SiO_2 equivalent film thicknesses measured on HF treated silicon surfaces. A). After the wafers were exposed to open air for 10 minutes; B). After the wafers were exposed to open nitrogen for 10 minutes; C). Analytical control.

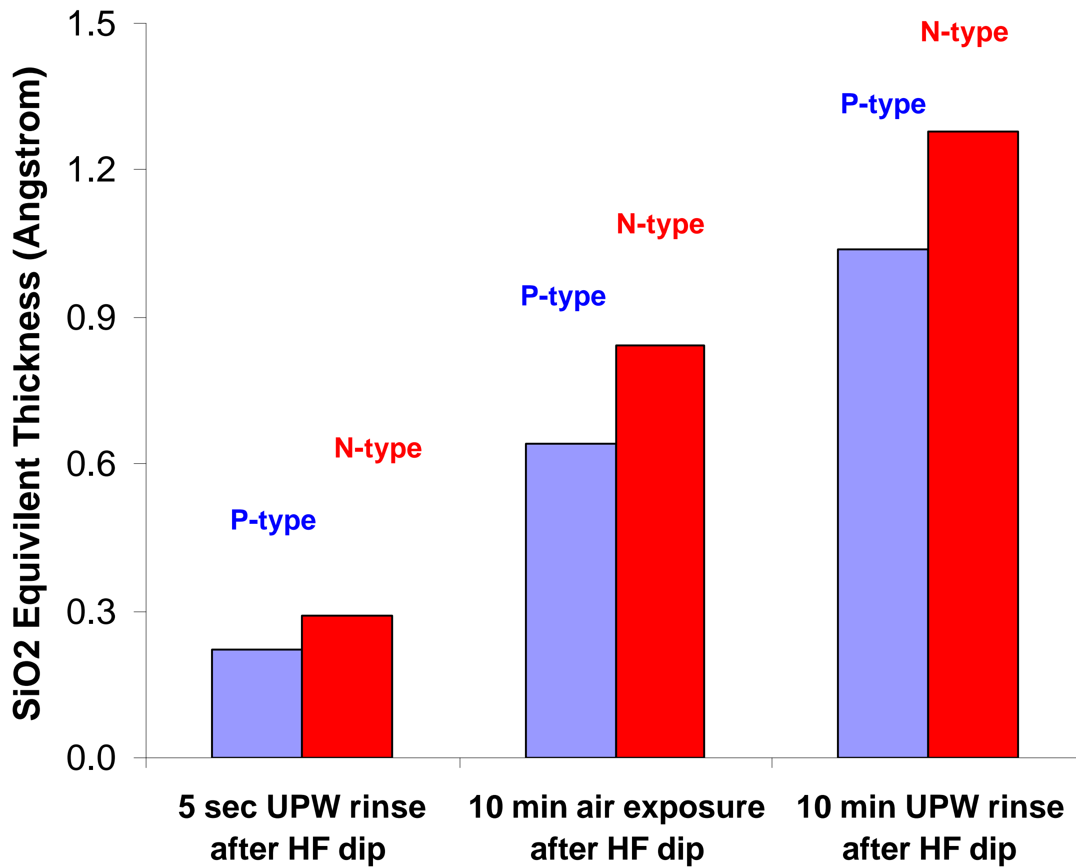

Figure 6. Comparison of oxidation on P-type versus N-type wafers in air exposure and UPW rinse.

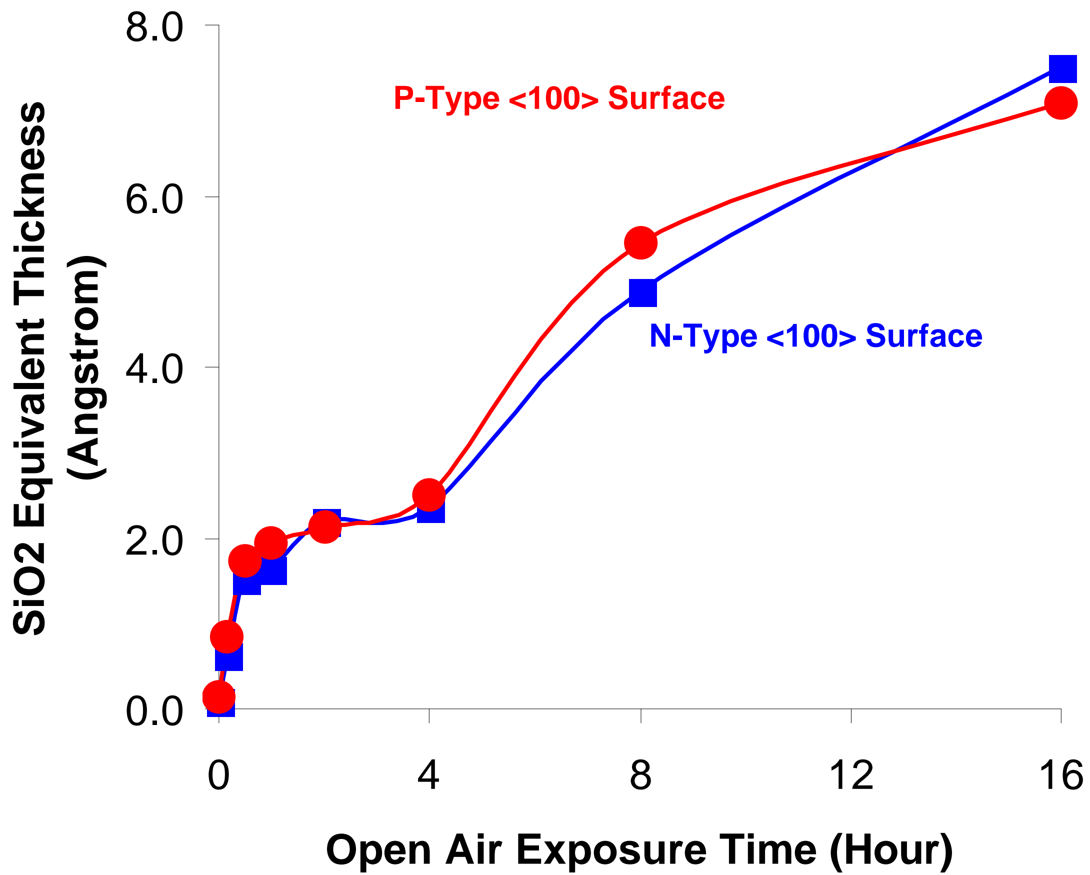

Figure 7. Oxidation of P-type versus N-type wafer surface after hours of exposure in open air at 66F and 38% Humidity.