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Citation: *Journal of Applied Physics* **103**, 044104 (2008); doi: 10.1063/1.2832430

View online: <http://dx.doi.org/10.1063/1.2832430>

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In situ observation of wet oxidation kinetics on Si(100) via ambient pressure x-ray photoemission spectroscopy

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(Received 28 September 2007; accepted 13 November 2007; published online 20 February 2008)

The initial stages of wet thermal oxidation of Si(100)-(2×1) have been investigated by *in situ* ambient pressure x-ray photoemission spectroscopy, including chemical-state resolution via Si 2*p* core-level spectra. Real-time growth rates of silicon dioxide have been monitored at 100 mTorr of water vapor. This pressure is considerably higher than in any prior study using x-ray photoemission spectroscopy. Substrate temperatures have been varied between 250 and 500 °C. Above a temperature of ~400 °C, two distinct regimes, a rapid and a quasisaturated one, are identified, and growth rates show a strong temperature dependence which cannot be explained by the conventional Deal-Grove model. © 2008 American Institute of Physics. [DOI: [10.1063/1.2832430](https://doi.org/10.1063/1.2832430)]

I. INTRODUCTION

A precise control of silicon oxide, or alternative gate oxide, growth at atomic scales is a major issue in the semiconductor industry as the gate thicknesses in metal-oxide-semiconductor transistors shrinks down to ~10 Å. The importance of intermediate oxidation states and the structure of the interface between crystalline Si and amorphous SiO₂ has become fundamental in many processing steps and in general in device fabrication. An extensive number of studies have thus been devoted to understanding oxygen-based as well as water-based oxidation. In both of these processes, a key role is played by the kinetics of the initial stages: how oxygen molecules in dry oxidation and water molecules in wet oxidation react at the Si surface and promote the formation of the oxide layer. In classic early studies, Deal and Grove¹ proposed a model to explain the kinetics of the oxide growth, which is based on diffusion of the oxidant through the oxide layer, and reaction at the interface between the silicon substrate and the oxide layer. This Deal-Grove (DG) model explains experimental results fairly well for oxide thicknesses above 20 nm. However, in the case of thinner layers, it has been shown that the DG model needs to be modified; several models have been proposed to explain much faster growth rates in the early stages of oxidation.^{2,3} A complete understanding of oxidation kinetics in the fast regime still remains a challenging problem to be solved.⁴

From an experimental point of view, the difficulty of identifying the growth mechanism in the early stages of oxidation arises from the lack of high-precision tools for monitoring growth rates *in situ* at pressures that are realistic from a technological point of view. As one nondestructive, chemical-state, and surface-sensitive analytical tool, x-ray photoelectron spectroscopy (XPS) has been widely utilized to provide important information on Si oxidation such as interfacial chemical states,⁵ interfacial bonding structures,⁶ and initial growth rates with very high precision.⁷ However, due to the short inelastic scattering length of emitted electrons and the need to maintain the electron spectrometer at high-vacuum conditions, standard XPS measurements are usually carried out in ultrahigh vacuum (UHV) or near-UHV environments, which radically differ from typical oxide formation conditions. As prior examples, for the case of dry oxidation, the initial kinetics has been studied in real time using XPS at an oxygen pressure up to 10⁻⁵ Torr or less,⁸ but there have been no equivalent *in situ* studies of wet oxidation by XPS at these lower pressures. By *ex situ* XPS measurements, in which surfaces are prepared in one chamber and then transferred to another for measurement, it has been pointed out that the presence of surface hydrogen bonding (Si-H) and initial growth rates at elevated temperatures are closely related phenomena.⁹ It is thus clear that only real-time and *in situ* measurements can provide direct information on the dynamics of all the oxidation states while the oxide growth is in progress and thus consequently assist in unveiling critical information on the interfacial oxide formation processes at the atomic scale.

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II. EXPERIMENTAL SETUP

In this work, we apply XPS *in situ*, in real time, and at much higher ambient pressures, which we term ambient pressure XPS (APXPS), to the initial stages of the wet thermal oxidation process on Si(100)–(2×1) using a specially designed system that is located at beamline 9.3.2 at the Advanced Light Source of the Lawrence Berkeley National Laboratory, and described in detail elsewhere.¹⁰ Briefly, this system consists of an Al foil window to separate the beamline from the sample chamber, and a PHI electron analyzer equipped with a specially designed differentially pumped electrostatic lens in order to permit measuring spectra with the local ambient sample pressures from UHV to several Torr. Si 2*p* core-level spectra have been recorded while the chamber pressure was held at 100 mTorr of water vapor pressure or $\sim 10^4$ times higher than in prior XPS studies of Si oxidation. The samples were cut from commercially available Si(100) wafers,³ cleaned in a boiling solution of H₂SO₄/H₂O₂ for 10 min, rinsed in deionized water, and dipped in a 50% HF solution for 30 s. A thin oxide layer passivating the surface is then grown by immersing the sample in HCl:H₂O₂:H₂O=1:1:4 at 80 °C for 10 min. The oxide layer is removed after transferring the sample inside the chamber by repeated cycles of direct current flow heating the surface up to 1000 °C. Once a clean surface is achieved, as verified by high-resolution Si 2*p* spectra, and the temperature adjusted, water vapor is introduced in the chamber via a metal leak-valve controller and the pressure is kept constant at 100 mTorr throughout the experiment. Continuous acquisition of the Si 2*p* core-level range monitors in real time the formation of chemically shifted oxidation states on the initially clean silicon surface. The incoming photon energy was set to 350 eV. The overall instrument resolution in real-time measurement was estimated to be ~ 400 meV, which is small compared to the typical chemical shifts of about 1 eV per unit change in the oxidation state. The scanning time of a single spectrum for such real-time measurements was 18 s, with this acquisition speed being selected in order to have sufficient count rates in the least amount of time so as to better follow oxidation dynamics. The temperature was controlled by a feedback system with a resistive button heater underneath the sample and a thermocouple attached to its surface. Higher-resolution XPS spectra requiring longer acquisition times were collected at the beginning and end of each set of measurements, before admitting and after pumping out the water vapor in the chamber. All spectra were analyzed by subtracting a Shirley background, due to inelastic scattering, and deconvoluting each spectrum into six doublets: elemental silicon 2*p*(Si⁰), three intermediate oxidation states (Si¹⁺, Si²⁺, Si³⁺), stoichiometric Si oxide (Si⁴⁺), and an additional component located next to the Si⁰ state that has been attributed to Si-H (X).⁶ Each doublet was considered as a Voigt function with a free Gaussian width, a fixed Lorentzian width of 85 meV, a spin-orbit splitting of 600 meV, and a spin-orbit branching ratio set constant to 0.5. The positions and widths of our resulting oxide and Si-H bonding components agree with previously published work.⁶

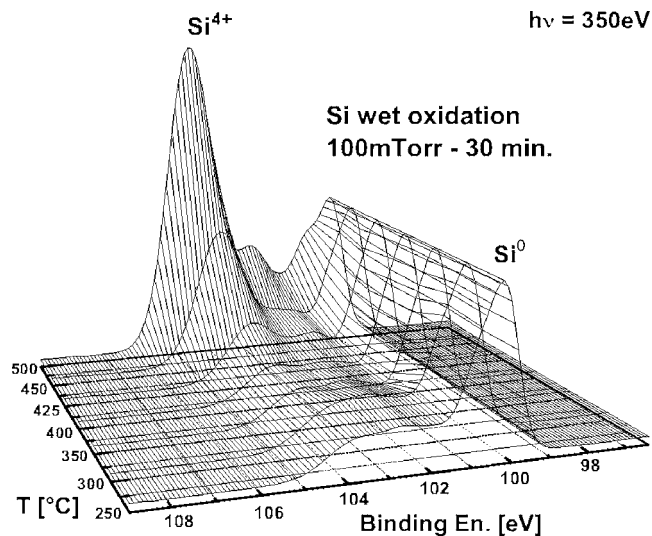


FIG. 1. Comparison of Si 2*p* spectra after a 30 min oxidation at 100 mTorr, normalized to the Si⁰ peak intensity. Both a strong oxidation enhancement and a slight Si⁴⁺ peak shift to higher binding energy can be observed above 400 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows a collection of spectra acquired after exposing the clean silicon surface to water vapor for 30 min at temperatures between 250 and 450 °C, and Fig. 2 shows high-resolution spectra after oxidation at two different temperatures. To permit easier visualization in Fig. 1, the fitted

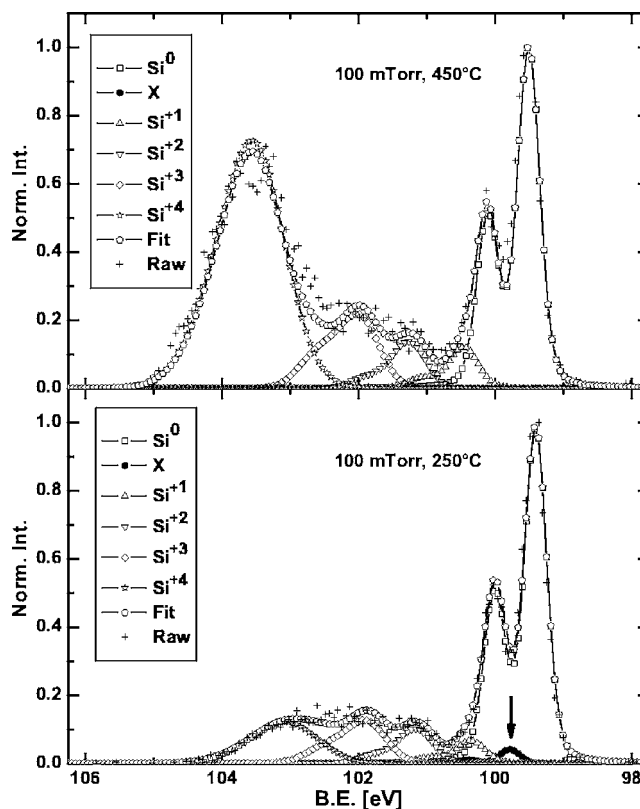


FIG. 2. High-resolution XPS scans at 450 °C (top) and 250 °C (bottom), after a 30 min oxidation at 100 mTorr. Spectra were fit using six doublets corresponding to Si⁰, four oxidation states, and the Si-H component at 100 eV visible only at lower temperatures.

spectra have been plotted as a function of temperature with normalization to the intensity of the Si^0 component, I_{Si^0} . Figure 1 clearly shows that the intensity of the oxide component, $I_{\text{Si}^{4+}}$, starts to increase rapidly as the substrate reaches temperatures near 400 °C. Not only is a dramatic enhancement in the Si^{4+} component intensity evident above 425 °C, but a careful analysis also reveals that the position of this peak shifts toward higher binding energies by about 0.5 eV as the oxide thickness grows. This energy shift can be attributed to a lack of core-hole screening from electrons in the bulk Si bulk substrate, probably due to valence band mismatch as the oxide thickness is increased,^{6,11} but also perhaps to the onset of slight charging at the surface of the oxide.

Previous studies have shown that the adsorption of water on silicon is mainly dissociative, with the formation of -H and -OH species passivating the surface at lower temperatures.¹² The enhanced growth rates we observe at temperatures above 425 °C thus suggest an abrupt modification of the Si-H and Si-OH bonding states. One possible explanation for the faster oxidation at 425 °C is that it is the result of the initiation of the thermal desorption of hydrogen molecules. The intensity of the Si-H peak X has been included in our fits to the real-time spectra of Fig. 1, but it is difficult to accurately estimate its contribution due to its strong overlap with Si^0 and the combined effects of moderate resolution and statistical accuracy in the raw data. However, with the high-resolution XPS spectra in Fig. 2 collected after the real-time measurements, it is possible to gauge the presence of this peak at the end of each oxidation run. Figure 2 thus shows two high-resolution XPS spectra at 250 and 450 °C together with their fitted components. While a Si-H peak is indicated at 250 °C, the spectrum at 450 °C does not show any sign of Si-H, suggesting that the oxidation growth rate is directly related to the presence of Si-H bonding on the surface. These results are qualitatively consistent with prior work by Enta *et al.*,⁷ who report that the Si-H component remains above 500 °C but moves to higher binding energies with a significant reduction of its intensity. In the case of Fig. 2 the lack of a Si-H signal at 450 °C is most likely due to a lower surface sensitivity with respect to this prior experiment, where the kinetic energy of the detected photoelectrons was only 40 eV while in our case it is 255 eV.

In order to gain more quantitative information on wet oxidation kinetics, we plot in Fig. 3 the time evolution of the oxide thickness growth rate, as measured via the ratio of $I_{\text{Si}^{4+}}$ and I_{Si^0} intensities, for seven different temperatures.^{13,14} This plot provides a clear indication of the different dynamics of silicon wet oxidation at this higher pressure of 100 mTorr as a function of temperature. It is clear that the samples below 350 °C show very similar, and significantly lower, growth rates. In these cases the coverage of the oxide thickness barely reaches one monolayer of oxide, suggesting that hydroxyl groups hinder the oxidation process. On the other hand, in agreement with Fig. 1, starting at 400 °C and more obviously above 425 °C, the system enters an active regime wherein the oxidation proceeds much faster. In particular, in the early stages of oxidation, at 450 and 500 °C, the curves exhibit a steep slope immediately after the insertion of the water vapor. For those curves at temperatures of

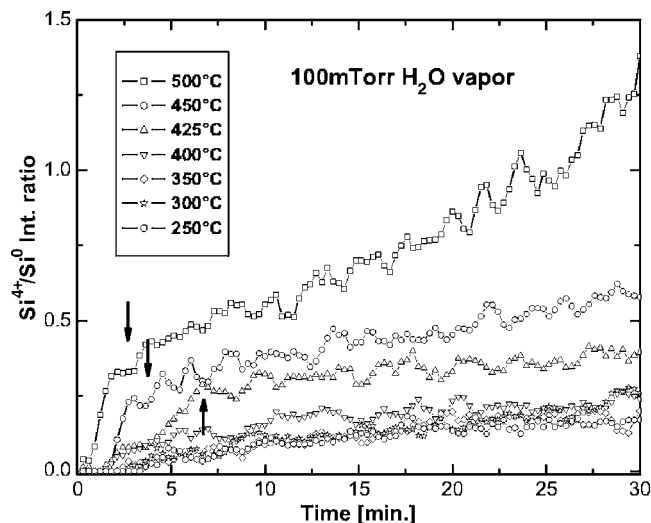


FIG. 3. Growth rate evolution at seven different temperatures. This plot again illustrates the strong oxide formation enhancement above 400 °C.

425 °C and higher, two distinct regimes can be clearly seen: a rapid regime in the early stages followed by a quasisaturated regime of much slower growth. In addition, as the temperature increases, the slopes of the rapid regimes are steeper, indicating a faster growth of the oxide at a higher substrate temperature. At the same time, the quasisaturation point occurs at shorter times for higher temperatures. Finally, once the quasisaturation point is reached, the growth rate slows down, yet oxidation continues, as shown in Fig. 3. Growth rates from linear fits to the quasisaturated regimes are shown in Table I, together with corresponding substrate temperatures. It is interesting to note that the growth rates of this quasisaturated regime in wet oxidation are much higher than the linear regime of the DG model, which is only 8×10^{-4} Å/h at 1 Torr and 500 °C.¹ Clearly, these two distinct regimes in wet oxidation show very different behaviors from the DG model.

As a final comment, it is not only interesting but also very important to compare these wet oxidation APXPS results to similar APXPS results for the dry oxidation case to get a complete overall picture, with the result of the latter type to be published shortly.¹⁵ However, in order to have an adequate comparison between these two processes, a more detailed approach needs to be taken, since there are several factors that differentiate them: the higher density of dry oxide, the presence of hydrogen desorption in wet oxidation, and different delays in the diffusion of the oxidant due to strain effects at the interfaces. Of course, pressure dependence of the wet oxide growth rate also needs to be considered. We plan to expand these studies accordingly.

TABLE I. Growth rates calculated from least-square fits to the quasisaturation regimes of Fig. 3, which begin at the temperatures indicated by the arrows in the figure.

Temperature (°C)	400	425	450	500
Slope	2.12 Å/h	2.88 Å/h	6.12 Å/h	12.6 Å/h

IV. CONCLUSIONS

In this work, the early stages of an *in situ* wet thermal oxidation process on Si(100)–(2 × 1) are studied via APXPS and growth rates are monitored *in situ* for the first time. Above the temperature of 400 °C, a rapid initial increase of the oxide growth rate is found, followed by a quasisaturated regime. Below 350 °C, oxide growth rates are significantly slower without any rapid initial growth or saturation limit. The presence of these two regimes and its strong temperature dependence above 400 °C cannot be explained within the conventional DG model. The lack of Si-H bonding states in high-resolution XPS spectra at temperatures above 425 °C is consistent with previous works reporting hydrogen desorption on Si surface. Finally, the further application of APXPS to problems of interest in semiconductor technology is most promising. For example, future studies with a higher luminosity spectrometer and better multichannel detection which we are planning should make it possible to resolve all oxidation states as a function of time.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. C.S.F. was supported by the Humboldt Foundation, the Helmholtz Association, the Jülich Research Center, the University of Hamburg, and BESSY, Berlin. Y.E. was supported by Overseas Advanced Education and Research Program from the Ministry of Education, Science, Sports, and Culture of Japan. K.S.L and S.K.K were supported by Creative Research Initiatives (ReC-SDSW) of MOST/KOSEF.

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