Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

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

Permalink
https://escholarship.org/uc/item/9mv9q66c

Author
Rossi, Massimiliano

Publication Date
2008-09-05

Peer reviewed

eScholarship.org Powered by the California Digital Library
University of California

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

Massimiliano Rossi[1], Bongjin S. Mun[1,2*], Yoshiharu Enta[3*], Charles S. Fadley[1,4,8],

Ki-Suk Lee[5], Sang-Koog Kim[5], Hyun-Joon Shin[6], Zahid Hussain[1], Philip N. Ross Jr.[7]

[1]Advanced Light Source, Lawrence Berkeley National Laboratory,

Berkeley, California 94720, USA

[2] Department of Applied Physics, Hanyang University, Ansan, Kyeonggi 426-791, Korea,

[3]Faculty of Science and Technology, Hirosaki University,

3 Bunkyo-cho, Hirosaki 036-8561, Japan

[4]Department of Physics, University of California-Davis, Davis, California 95616, USA

[5]Research Center for Spin Dynamics & Spin-Wave Devices, and Nanospintronics

Laboratory, Department of Materials Science and Engineering, College of Engineering,

Seoul National University, Seoul 151-744, South Korea

[6] Pohang Accelerator Laboratory, POSTECH,

Hyoja Dong, Namgu, Pohang, Kyungbuk, 790-784, Korea

[7]Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley,

California 94720, USA

[8]Institute for Solid State Research, Juelich Research Center, DE-52425 Juelich, Germany

* Corresponding authors: BSMun@lbl.gov, enta@cc.hirosaki-u.ac.jp

Abstract

The initial stages of wet thermal oxidation of Si(100)-(2x1) have been investigated by in-situ ambient pressure x-ray photoemission spectroscopy (APXPS),

including chemical-state resolution via Si 2p 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 XPS. Substrate temperatures have been varied between 250 and 500°C. Above a temperature of ~400°C, two distinct regimes, a rapid and a quasi-saturated one, are identified and growth rates show a strong temperature dependence which cannot be explained by the conventional Deal-Grove model.

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 SiO_2 have 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 Grove[1] 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 20nm. However, in the case of thinner layers, it has been shown that the DG model needs to be modified and 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 non-destructive, 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 ultra-high 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 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 atomic scale.

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)-(2x1) 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 2p core level spectra have been recorded while the chamber pressure was held at 100 mTorr of water vapor pressure or ~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 H_2SO_4/H_2O_2 for 10 minutes, rinsed in deionized water, and dipped in a 50% HF solution for 30 seconds. A thin oxide layer passivating the surface is then grown by immersing the sample in $HCl:H_2O_2:H_2O=1:1:4$ at 80°C for 10 minutes. 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 2p 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 100mTorr throughout the experiment. Continuous acquisition of the Si 2p core-level range monitor in real time the formation of chemically shifted oxidation states on the initially-clean silicon surface. The incoming photon energy was set to 350eV. 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 oxidation state. The scanning time of a single spectrum for such real-time measurements was 18 seconds, 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 feed-back 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 2p (Si^0), three intermediate oxidation states (Si^{1+}, Si^{2+}, Si^{3+}), stoichiometric Si oxide (Si^{4+}) and an additional component located next to the Si^0 state that has been attributed to Si-H (X)[6]. Each doublet was considered as a Voigt function with free Gaussian width, a fixed Lorentzian width of 85meV, a spin-orbit splitting of 600meV 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].

III. Results and discussion

Fig. 1 shows a collection of spectra acquired after exposing the clean silicon surface to water vapor for 30 minutes at temperatures between 250 and 500°C, and Fig. 2 high-resolution spectra after oxidation at the two different temperatures. To permit easier visualization in Fig. 1, the fitted spectra have been plotted as a function of temperature with normalization to the intensity of the Si^0 component, I_{Si^0}. Fig. 1 clearly shows that the intensity of the oxide component, $I_{Si^{4+}}$, starts to increase rapidly as the substrate reaches temperatures near 400°C. Not only a dramatic enhancement in the Si^{4+} component intensity is evident above 425°C but a careful analysis also reveals that the position of this peak shifts towards 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 it 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. Fig. 2 thus shows two high-resolution XPS spectra at 250°C 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 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 is 255 eV.

In order to get 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 $I_{Si^{4+}}$ 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 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°C and 500°C, the curves exhibit a steep slope immediately after the insertion of the water vapor. For those curves at temperatures of 425°C and higher, two distinct regimes can be clearly seen, a rapid regime in the early stages followed by a quasi-saturated regime of much slower growth. In addition, as the temperature increases, the slopes of the rapid regimes are steeper, indicating faster growth of oxide at higher substrate temperature. At the same time, the quasi-saturation point occurs at shorter times for higher temperatures. Finally, once the quasi-saturation point is reached, the growth rate slows down, yet oxidation continues, as shown in Fig. 3. Growth rates from linear fits to the quasi-saturated regimes are shown in Table 1, together with corresponding substrate temperatures. It is interesting to note that the growth rates of this quasi-saturated regime in wet oxidation are much higher than the linear regime of the DG model, which is only 8×10^{-4} Å/hr at 1Torr 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 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.

IV. Conclusions

In this work, the early stages of in-situ wet thermal oxidation process on Si(100)(2xl) are studied via APXPS and growth rates are monitored in-situ for the first time. Above the temperature of 400oC,a rapid initial increase of oxide growth rate is found, followed by a quasi-saturated regime.
Below 350oC, 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 multi-channel detection which we are planning should make it possible to resolve all oxidations states as a function of time.

Acknowledgements: This work was supported by the U.S. Department of Energy under contract no. DE-AC03-76SF00098 and DE- AC02-05CH11231.
C.S.F. was supported by the Humboldt Foundation, the Helmholtz Association, the Jiilich 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, Culture, Sports, Science and Technology of Japan. K.S.L and S.K.K were supported by Creative Research Initiatives

(ReC-SDSW) of MOST/KOSEF.

References:

---

1 B.E. Deal and A.S. Grove, J. Appl. Phys. 36, 3770 (1965)

2 Y.J. van der Meulen, J. Electrochem. Soc. 119, 531 (1972)

3 Y. Kamigaki and Y. Itoh, J. Appl. Phys. **48**, 2891 (1977).

4 H. Z. Massoud, J. D. Plummer, and E. A. Irene, J. Electrochem. Soc. **132**, 2685 (1985).; R. M. C. de Almeida S. Gonçalves, I. J. Baumvol, and F. C. Stedile, Phys. Rev. B **61**, 12992 (2000).;C. Krzeminski, G. Larrieu, J. Penaud, E. Lampin, and E. Dubois, J. Appl. Phys. **101**, 064908 (2007).;

5 F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, G. Hollinger, Phys. Rev. B. 38 (1988) 6084

6 S. Dreiner, M. Schurmann, C. Westphal and H. Zacharias, Phys. Rev. Lett. 86 (2001) 4068

7 Y. Enta, Y. Miyanishi, H. Irimachi, M. Niwano, M. Suemitsu, N. Miyamoto, E. Shigemasa, H. Kato, J. Vac. Sci. Technol. A 16(3) (1988) 1716

8 Y. Enta, Y. Miyanishi, H. Irimachi, M. Niwano, M. Suemitsu, N. Miyamoto, E. Shigemasa, and H. Kato, J. Vac. Sci. Technol. A **16**, 1716 (1998); Y. Enta, Y. Miyanishi, H. Irimachi, M. Niwano, M. Suemitsu, N. Miyamoto, E. Shigemasa, and H. Kato, Phys. Rev. B **57**, 6294 (1998).

9 Y. Enta, D. Shoji, M. Shinohara, M. Suemitsu, M. Niwano, N. Miyamoto, Y. Azuma, H. Kato, Jpn. J. Appl. Phys. Vol.38(1999) 253 M.K. Weldon, B.B. Stefanov, K. Raghavachari, and Y.J. Chabal Phys. Rev. Lett. 79, (1997) 1513;

10 D. F. Ogletree, H. Bluhm, G. Lebedev, C. S. Fadley, Z. Hussain, and M. Salmeron, Rev. Sci. Instrum. **73**, 3872 (2002).

11 A. Pasquarello, M.S. Hybertsen, R. Car, Phys. Rev. B. 53 (1996) 10942

12 M.K. Weldon, B.B. Stefanov, K. Raghavachari, and Y.J. Chabal Phys. Rev. Lett. 79, (1997) 1513;

13 M. P. Seah and S. J. Spencer, Surf. Interface Anal. 33, 640 (2002).

14 The thickness of oxide is based on the following formula from references 5, 6 and 12:

$$d = \Lambda_{e,Si^{4+}} \sin\theta_e \ln\left[\frac{I_{Si^{4+}}}{I_{Si^0}} \cdot \frac{I_{Si^0,0}}{I_{Si^{4+},\infty}} + 1\right]$$

$$I_{Si^0,\infty} = n_{Si^0}\sigma_{Si^0}\Lambda_{e,Si^0}$$

$$I_{Si^{4+},\infty} = n_{Si^{4+}}\sigma_{Si^{4+}}\Lambda_{e,Si^{4+}}$$

where $I_{Si^{4+}}$ is the measured Si^{4+} intensity, I_{Si^0} is the measured Si^0 intensity, θ_e is the electron

emission angle with respect to the surface, $\Lambda_{e,Y}$ is the electron inelastic attenuation length in species Y (Y=Si or SiO_2), n_Y is density of Si atoms in species Y, and σ_Y is the relevant differential atomic photo-ionization cross section of the Si 2p core level in Y. At a photon energy of 350 eV, Λ_{e,SiO_2} and $\frac{I_{Si,Y}}{I_{SiO_2,Y}}$ for pure Si and pure SiO_2 are estimated from previous analysis of experimental data to be 9.8Å and 1.47, respectively.

[15] Y. Enta, B. S. Mun, M. Rossi, C. S. Fadley, K.-S. Lee, S.-K. Kim, Z. Hussain, P. N. Ross Jr. *In preparation.*

Figure Captions

Figure 1 – Comparison of Si 2p spectra after a 30-minute oxidation at 100 mTorr, normalized to the Si^0 peak intensity. Both a strong oxidation enhancement and a slight Si^{4+} peak shift to higher binding energy can be observed above 400°C.

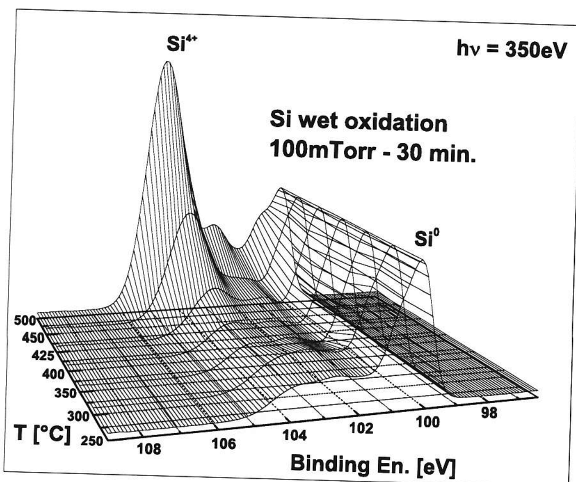
Figure 2 – High Resolution XPS scans at 450°C (top) and 250°C (bottom), after a 30 minute oxidation at 100 mTorr. Spectra were fit using 6 doublets corresponding to Si^0, 4 oxidation states and the Si-H component at 100eV visible only at lower temperatures

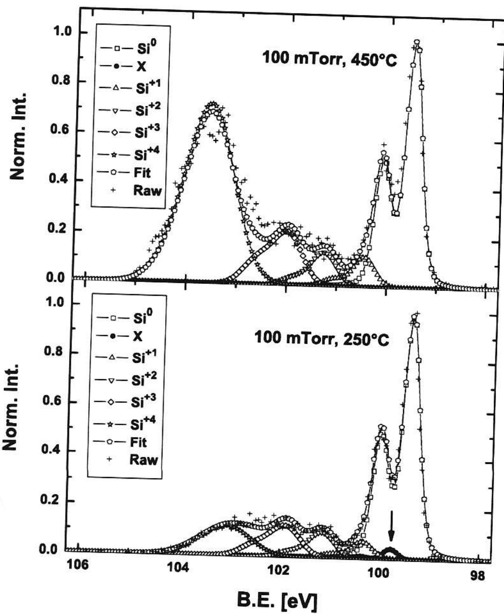
Figure 3 –Growth rate evolution at seven different temperatures. This plot again illustrates the strong oxide formation enhancement above 400°C.

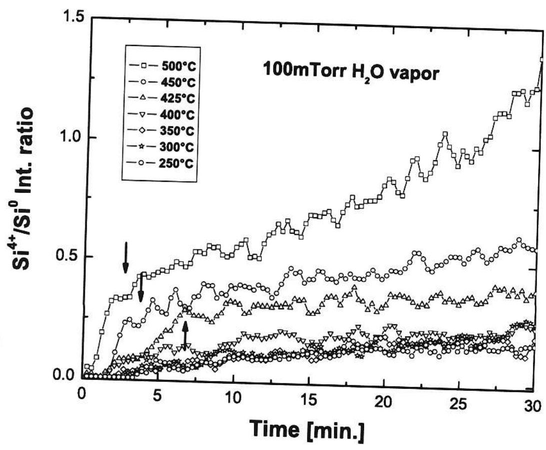
Tables

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

Table 1 - Growth rates calculated from least-square fits to the quasi-saturation regimes of Fig. 3, which begin at the temperatures indicated by the arrows in the figure.


Si4+
hν = 350eV
Si wet oxidation
100mTorr - 30 min.
Si0
500
450
425
400
350
300
T [°C]
250
108
106
104
102
100
98
Binding En. [eV]


100 mTorr, 450°C
100 mTorr, 250°C
Si0
X
Si+1
Si+2
Si+3
Si+4
Fit
Raw
Norm. Int.
B.E. [eV]


100mTorr H_2O vapor
500°C
450°C
425°C
400°C
350°C
300°C
250°C
Si^{4+}/Si^{0} Int. ratio
Time [min.]
0.0
0.5
1.0
1.5
0
5
10
15
20
25
30