Silicon thermal oxidation and its thermal desorption investigated by Si 2p core-level photoemission

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Abstract. Initial thermal oxidation of silicon and thermal desorption of silicon oxide have been investigated by Si 2p core-level photoemission with synchrotron radiation. The surface reaction processes are discussed from the difference in the chemically-shifted components, especially suboxides. On the thermal oxidation, time evolutions of suboxide intensities show a distinct temperature dependence, which is explained by two growth modes for the oxidation: first-order Langmuir-type adsorption mode and two-dimensional island growth mode at oxidation temperatures below and above 650 ºC, respectively. On the thermal desorption, the spectrum for the thermal oxide followed by annealing at 1000 ºC for 30 s in vacuum, whose thickness is nominally estimated at 3.7 Å, are compared with the 3.3 Å-thickness thermal oxide without the process of the annealing. The intensities of the suboxide components are considerably different between them, which can be explained by the formation and lateral growth of the voids in the annealed oxide layer.

1. Introduction
Since the silicon gate oxide in highly integrated metal-oxide-semiconductor field-effect-transistor (MOS-FET) devices is now required to reduce the thickness to a few tens of angstroms, understanding on the oxidation kinetics at the initial stage has become one of the most important issues in the semiconductor industry. In this respect, photoelectron spectroscopy for Si 2p core level provides useful information on the surface reaction, because with synchrotron radiation at optimized energy, it has high surface sensitivity of a few angstroms. Since the silicon-dioxide (SiO₂) component has large chemical shift about 4 eV in the Si 2p core-level spectrum and thus can be apparently distinguished from silicon-substrate component, it is easy to measure the oxidation rate at the initial stage. In addition, analysis of intermediated oxidation states, so-called suboxides [1,2], gives valuable information on atomic structures at SiO₂/Si interface.

In the previous studies, we measured the time evolutions of the SiO₂ component in the Si 2p core-level spectrum during the initial thermal oxidation of Si(100). We concluded that, at temperatures below 650 ºC, the oxidation proceeds randomly without formation of two-dimensional (2D) islands by the observation that the growth rate follows a first-order Langmuirian behavior, while at temperatures above 650 ºC, the oxidation was indicated to proceed via 2D nucleation because the growth exhibits some incubation time [3,4]. As mentioned above, the suboxide components in the spectrum, which exist at SiO₂/Si interface, are also very informative. In this study, therefore, we focus on the temperature dependence of the suboxide components to investigate the surface reaction at the initial stage and verify the above oxidation behaviors.
The thermal-desorption process of the SiO₂ layer on Si is also crucial in MOS-FET technology. Tromp et al. reported that 100 Å-thickness SiO₂ layer is thermally removed from the Si surface by the formation and lateral growth of voids in the oxide, exposing regions of atomically clean Si, while the surrounding oxide retains its initial thickness [5]. The same desorption behaviors were also observed for thinner oxide layer [6-8]. We here demonstrate the formation of the same kind of void by a comparison of the suboxide Si-2p components for thermal oxide layers with and without the process of the thermal desorption.

2. Experimental

Experiments were carried out at the beam line BL-3B at the Photon Factory, the High Energy Accelerator Research Organization. The photon energy was set at 135 eV, where the photoelectron inelastic attenuation length from the Si 2p core level in silicon is minimized. A mirror-polished, B-doped Si(100) wafer cut to a size of 20×5×0.5 mm³ was used as a silicon substrate. The wafer was chemically treated to passivate the surface and then annealed by resistive heating at 1000 °C in ultrahigh vacuum. The cleanliness of the surface was checked by the surface state in valence-band and Si 2p core-level spectra, which showed no contamination. For thermal oxidation, the 99.99 % oxygen gas was introduced into a reaction chamber through a variable leak valve. The overall instrumental energy resolution was estimated at about 0.2 eV. The Si 2p core-level spectra are deconvoluted by a least-square fitting procedure using the spin-orbit split Voigt functions.

3. Results and Discussion

3.1. Thermal oxidation

Figure 1 shows typical Si 2p core-level spectra of oxides on Si(100) grown at an oxygen pressure of 10⁻⁶ Torr and oxidation temperatures of (a) 700 °C and (b) 500 °C. All spectra consist of seven components: substrate silicon (Si⁰), three suboxides (Si¹⁺, Si²⁺, Si³⁺), stoichiometric oxide, that is, SiO₂ (Si⁴⁺), and two associated with surface strain layer [9] and/or bare Si surface [10] (S¹ and S²). The hatched peaks show the components at the oxidation time of 1 min, whose intensities are normalized by the intensity of Si⁰ in figure 2(a). We can see a distinct difference in the intensities of the suboxide components, Si¹⁺ and Si²⁺, as well as S¹ component between the spectra at 700 °C and 500 °C, although the intensity of Si⁴⁺ is almost same. Namely, the intensities of Si¹⁺ and Si³⁺ at 700 °C are much smaller than those at 500 °C, while the intensity of S¹ shows opposite behavior. Figures 2 (b) and 2 (c) show oxidation-time dependences of the suboxide intensities for 700 °C and 500 °C, respectively, normalized by Si⁴⁺. At the temperature of 700 °C, both Si¹⁺ and Si³⁺ intensities are almost kept constant, which means they increase in proportion to Si⁴⁺. On the other hand, at the temperature of 500 °C, as the oxidation proceeds, they both decrease monotonically.

Figure 1. Si 2p core-level spectra (dots) from SiO₂ layers on Si(100) grown at (a) 700 °C and (b) 500 °C. Solid lines denote the curve fittings using the spin-orbit split Voigt functions.
Figure 2. Comparisons of intensity ratios of chemical-shift components for Si 2p core-level spectra from SiO₂ layer grown (a) for 1 min, (b) at 700 °C, and (c) at 500 °C.

We interpret these results as the temperature dependence of the oxidation kinetics. As mentioned in the introduction, in the high temperature regime, the oxidation proceeds via 2D nucleation, which is probably due to SiO₂ formation, because the oxygen atom adsorbed on the surface is not stable and thus quickly desorbs from the surface as a volatile SiO molecule [11,12]. Once SiO₂ nucleus is formed, it laterally expands on the surface. Therefore, the suboxides exist only at the SiO₂/Si interface as shown in figure 3 (a). On the other hand, in the low temperature regime, the suboxides gradually change to SiO₂ as shown in figure 3 (b) because no SiO desorption occurs at the low temperature, showing Langmuirian behavior. Since the suboxides exist not only at the SiO₂/Si interface but also on the substrate Si surface, it should be observed that the suboxide intensities at 500 °C are higher than those at 700 °C as shown in Fig. 2 (a). With proceeding of the oxidation, it is obvious that the intensity ratio of suboxide to Si⁴⁺ decrease monotonically in case of figure 3 (b). In case of figure 3 (a), on the other hand, it is kept constant because SiO₂ island laterally grows without change of its thickness. This inference is consistent with the results in figure 2 (b) and (c). Thus, the oxidation kinetics mentioned above is reconfirmed by the observation of the change in the suboxide intensity in the Si 2p core-level spectra.

Figure 3. Schematic models for oxidation processes grown at (a) 700 °C and (b) 500 °C.

3.2. Thermal desorption
To investigate the thermal desorption of the SiO₂ layer, we first formed a thicker oxide layer. Figure 4(a) shows Si 2p core-level spectrum of the surface oxidized for 10 min at an oxygen pressure of 1 Torr and oxidation temperature of 800 °C. The thickness of the SiO₂ layer (D) can be calculated from
Figure 4. Si 2p core-level spectra (dots) from (a) SiO₂ layer grown at 800 °C and 1 Torr for 10 min, (b) partially-desorbed SiO₂ layer by heating the sample at 1000 °C for 30 s subsequently, and (c) SiO₂ layer grown at 750 °C and 10⁻⁴ Torr for 30 s.

the formula [13,14]:

\[
D = \lambda_{\text{SiO}_2} \sin \theta_e \ln \left( \frac{I_{\text{Si}^{4+} \text{SiO}_2}}{I_{\text{Si}^{0} \text{SiO}_2}} + 1 \right)
\]

where \( I_{\text{Si}^{4+}} \) is the measured Si⁴⁺ intensity, \( I_{\text{Si}^{0}} \) is the measured Si⁰ intensity, \( \theta_e \) is the electron emission angle with respect to the surface, \( \lambda_{\text{Si}} \) is the electron inelastic attenuation length in species \( Z \) (\( Z=\text{Si} \) or \( \text{SiO}_2 \)), \( n_z \) is density of Si atoms in species \( Z \), and \( \sigma_{\text{Si}} \) is the relevant differential atomic photo-ionization cross section of the Si 2p core level in \( Z \). At a photon energy of 135 eV, \( \lambda_{\text{SiO}_2} \) and the ratio \( I_{\text{Si}^{4+}} / I_{\text{Si}^{0}} \) are estimated from previous analyses of experimental data [13,14] at 0.68 nm and 0.5, respectively. Using these values, the SiO₂ thickness in figure 4 (a) is estimated at 15.0 Å. After the oxidation, the sample was heated at the temperature of 1000 °C for 30 s to desorb a part of the SiO₂ layer, which is shown in Fig. 4(b). The SiO₂ thickness for this sample is estimated at 3.7 Å, if we simply use the intensity ratio of Si⁴⁺ to Si⁰ for equation (1). However, the spectrum in figure 4 (b) is quite different from that for the thermal oxide layer without the process of the thermal desorption shown in figure 4 (c). The SiO₂ layer in figure 4 (c) is thermally grown at the temperature of 750 °C and at the pressure of 10⁻⁴ Torr for 30 s, whose thickness is estimated at 3.3 Å. In spite of the same intensity ratio of Si⁴⁺ to Si⁰, it is obviously seen that the suboxide intensities in figure 4 (b) are much less than those in figure 4 (c). The SiO₂ layer in figure 4 (c) is expected to be homogeneously grown as shown in figure 5 (c). In order to explain the suboxide intensities in figure 4 (b), therefore, we have
to consider the SiO$_2$ layer spatially inhomogeneous as shown in figure 5 (b). Namely, the SiO$_2$ layer is desorbed from the Si surface by the formation of voids in the SiO$_2$ layer, where a bare Si surface is exposed. In such a surface morphology, the intensity ratio of Si$^{4+}$ to Si$^{0}$ becomes small owing to the contribution to the Si$^{0}$ component from the bare Si surface even if the SiO$_2$ thickness is unchanged. The formation of the voids is also confirmed by the appearance of S1 and S2 components due to the bare Si surface in figure 4 (b), where the contribution by the surface strain layer in the oxide regime can be neglected owing to the thick oxide overlayer.

\[
I_{S_i^{0}} = \frac{n_i \sigma_i Z}{n_{SiO_2} \sigma_{SiO_2} \lambda_{SiO_2} \exp(D/\lambda_{SiO_2}) - 1} \quad (2)
\]

where $A$ is the suboxide thickness and $Z$ stands for the Si$^{X+}$ suboxide. From this equation, the SiO$_2$ thickness in figure 4 (b) is estimated at 13.4 Å, which is only a 10 percent reduction, if the thickness of the suboxide layer at the interface is unchanged by the sample heating. In the case in figure 4 (b), the intensity ratio of Si$^{4+}$ to Si$^{0}$ is given by

\[
I_{S_i^{0}} = \frac{C(1 - \exp(-S/\lambda_{Si}))}{(1 - C)\exp(-S/\lambda_{Si}) + C \exp(-D/\lambda_{Si})} \quad (3)
\]

where $C$ is the surface coverage of the SiO$_2$ layer, and $S$ is the thickness of the surface layer of bare Si corresponding to the S1 and S2 components, which involve the second layer and the surface defect [10] in our spectra. Therefore, we obtain

\[
C = \frac{1}{1 - \exp\left(S/\lambda_{Si} - D/\lambda_{SiO_2}\right) + I_{S_i^{0}}/I_{S_i^{4+}} \cdot I_{S_i^{0}}/I_{S_i^{4+}} \left\{\exp(S/\lambda_{Si}) - \exp(S/\lambda_{Si} - D/\lambda_{SiO_2})\right\}} \quad (4)
\]
Using the value of 13.4 Å calculated by equation (2) as $D$, $C$ is estimated at 0.38, when $S$ is assumed to be 3 Å, which corresponds to a few atomic layers of Si(100). Although further studies are indispensable to justify these estimations, the analysis of Si 2p core-level spectra gives valuable information on the desorption process of the SiO$_2$ layer.

4. Conclusion

Initial thermal oxidation of silicon and thermal desorption of silicon oxide have been investigated by Si 2p core-level spectra, especially suboxide components. The behaviors of the suboxide intensities clearly show temperature dependence, which is explained by two growth modes for the oxidation: a Langmuir-type adsorption mode and 2D island growth mode at temperatures of 500 °C and 700 °C, respectively. The SiO$_2$ layer partially desorbed by heating the sample at 1000°C indicates the inhomogeneous surface morphology, which is consistent with the void-formation model. In addition, the oxide thickness and the oxide coverage are estimated by the chemical-shift-component intensities of the SiO$_2$ layer.

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