Layer-by-Layer Oxidation of Si(001) Surfaces

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1. Introduction

As individual devices are scaled down, the gate-oxide thickness of MOS devices will reach the nanometer level. Thus, atomic-scale roughness at the SiO_2/Si interfaces will need to be controlled, and an understanding of initial oxidation kinetics will be indispensable. Although there have been previous reports on oxygen adsorption kinetics [1], the oxidation kinetics of the initial several layers have not been studied in detail due to the difficulty of experimentally investigating the oxidation processes of specific sub-surface layers. In this study, we used scanning reflection electron microscopy (SREM) to investigate the initial oxidation of Si(001) surfaces. By combining the SREM technique with Auger electron and x-ray photoelectron spectroscopy (AES and XPS), we could analyze the oxidation kinetics layer-by-layer.

2. Experimental

Our experiments were carried out using an ultrahighvacuum (UHV) surface analysis system that performs SEM, SREM, AES, and XPS. Details of this system are described elsewhere [2]. A 30-keV electron beam with a 2-nm diameter was used for the SREM. The images were obtained by using a specular reflection spot. The AES and XPS measurements were performed using an electron gun for microscopy and Mg K α excitation, respectively. Oxidation of Si(001)-2x1 surfaces prepared by flash heating was carried out by introducing molecular oxygen into the chamber.

3. Results and Discussion

Figures 1(a) to (d) show SREM images of Si(001) surfaces before and after oxidation under various conditions. For the initial Si(001)-2x1 surface (Fig. 1(a)), the bright and dark areas correspond, respectively, to alternating 1x2 and 2x1 terraces. Note that the step structure was preserved after oxidation (Figs. 1(b) to (d)), and that the SREM contrast at these terraces reversed at each oxidation step. As we previously reported concerning the oxidation of Si(111) surfaces [3], since an amorphous SiO₂ layer does not contribute to electron diffraction spots, the SREM images reveal the SiO2/Si interfaces. Also, our calculation showed that the specular spot intensity from bulk-terminated SiO2/Si(001) interfaces differed between these alternating terraces. These results clearly imply layer-by-layer oxidation of the Si(001) surface. Moreover, since the interfacial structure was preserved during the oxidation, step-flow oxidation can be ruled out. Here, we discuss the layer-by-layer oxidation mechanism in terms of the random nucleation of nanometer-scale oxide islands.



Fig. 1. SREM images of Si(001) surfaces before and after oxidation. (a) Initial Si(001)-2x1 surface. (b) Results of oxidation under 2×10^{-6} Torr oxygen gas pressure at room temperature for 3 min; (c) After 17 min of oxidation at 635°C following 15 min of oxidation at room temperature; (d) After 65 min of oxidation at 700°C at an increased 2×10^{-5} Torr gas pressure following the oxidation shown in (c).

We also performed an AES analysis on the same surface at each oxidation step. The normalized oxygen Auger peak intensity was plotted in Fig. 2 as a function of oxidation time. The oxidation conditions are shown at the top of the figure. We found that the staircase increase in the Auger peak intensity coincided with the phase of the SREM contrast, and that the oxidation at room temperature and 635 °C corresponded, respectively, to the first- and second-layer oxidation.

To investigate the oxidation kinetics in detail, we measured the time dependence of the oxygen Auger peak intensity during oxidation in a temperature range from room temperature to 635°C. Figures 3(a) - (d) show typical results,



Fig. 2. The change in oxygen Auger peak intensity during oxidation under various conditions. The oxide thickness was estimated from XPS measurement. Points (a) to (d) correspond to the conditions in Fig. 1.



Fig. 3. The normalized oxygen Auger peak intensity as a function of oxidation time. Figures (a) and (b) to (d) were taken, respectively, at 1×10^{-7} and 2×10^{-6} Torr oxygen gas pressures. The solid lines show the results of curve fitting by independent Langmuir-type reaction.

where Fig. 3(a) and Figs. 3(b) to (d), respectively, were obtained at 1×10^{-7} and 2×10^{-6} Torr oxygen gas pressure. For the first-layer oxidation (Fig. 3(a)), the Auger peak saturated around 0.2, and the reaction fits well with Langmuir-type behavior. At the higher oxygen pressure, the first-layer oxidation was completed within 2 min, and the

second-layer oxidation also fits well with the Langmuir-type reaction (Figs. 3(b) to (d)). The temperature dependence of the initial oxidation rate estimated from the curve fitting showed that the first-layer oxidation - that is, the oxygen atom chemisorption onto the uppermost layer and insertion into the first sub-surface layer - was a barrier-less reaction. Figure 4 is an Arthenius plot of the reaction rate of the second-layer oxidation (initial oxidation rate in the Langmuir-type reaction). The activation energy of the second layer was found to be 0.3 eV. These results will be discussed based on the latest first-principles calculations [4].



Fig. 4. Arrhenius plot of the initial reaction rate of the secondlayer oxidation.

4. Conclusion

We investigated the initial oxidation of Si(001) surfaces by SREM, AES, and XPS. The periodic reversal of the SREM contrast revealed layer-by-layer oxidation while the interfacial step structure was maintained. The oxidation kinetics of the first and second layers were investigated through the change in the oxygen Auger peak intensity at various temperatures. Oxygen adsorption onto the uppermost layer and oxygen atom insertion into the back-bond were found to be a barrier-less reaction. The activation energy of the second-layer oxidation was found to be 0.3 eV.

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