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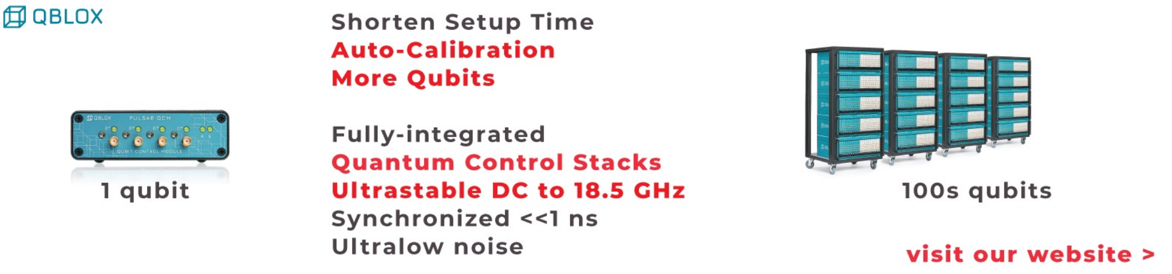

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Oxidation of Si(001) with a hyperthermal O-atom beam at room temperature: Suboxide distribution and residual order structure

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Synchrotron radiation photoelectron spectroscopy (SR-PES) and crystal truncation rod (CTR) scattering profiles were used to investigate an ultrathin SiO_2 overlayer on a Si(001) surface formed by a 5 eV O-atom beam at room temperature. The SR-PES spectra indicated that the suboxides in the O-atom-beam oxidized film were concentrated on the SiO_2 surface rather than at the Si/SiO_2 interface. The CTR scattering data of the O-atom-beam oxidation film had a lower intensity near (1 1 L) ($0.3 < L < 0.8$), suggesting a lower content of the SiO_2 ordered structure in the oxide film. An inverse diffusion of the interstitial Si atoms in the oxidation kinetics can explain the data. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2190467]

A laser detonation O-atom-beam source, which delivers an energetic (with a translational energy between 1 and 10 eV) and high-intensity ($10^{13}-10^{15}$ at. cm^{-2} s^{-1}) pulsed O-atom beam, has been developed for space environmental simulation studies. Recently, this laser detonation O-atom-beam source has been used to fabricate an ultrathin SiO_2 film at room temperature. The O atoms involved in the beam were in the ground state $[O(^3p)]$ and had an estimated ion content of less than the ppm level. This atom-beam source provides the O atoms with a translational energy up to few eV. This translational energy can promote the oxidation reaction with Si. Our previous studies verified that a hyperthermal O-atom beam can oxidize a Si surface at room temperature.[1,2] Also synchrotron radiation photoelectron spectroscopy (SR-PES) determined that the SiO_2 layer formed by a hyperthermal O-atom beam contains fewer suboxides compared to that formed by high-temperature oxidation in an O_2 atmosphere.[3] Quantitative analysis of the SR-PES spectra indicated that the thickness of the structural transformation layer is less than a monolayer thick regardless of film thickness. Moreover, the translational energy dependence of the SR-PES spectra suggests that the oxidation reaction may occur in the topmost SiO_2 layer. These findings imply that both the O atom and the interstitial Si atom act as an oxidant in the hyperthermal O-atom-beam oxidation at room temperature. If the above-mentioned interstitial Si atoms are predominant in the oxidation kinetics, then the interstitial Si atoms would influence the structure of SiO_2. The present study examines the structures of the oxide film formed by a hyperthermal O-atom beam and by rapid thermal oxidation (RTO) using SR-PES and crystal truncation rod (CTR) scattering.

The native oxide on Si(001) was removed by standard RCA cleaning and prior to the experiment, H-terminated Si(001) surfaces were prepared by a HF treatment. The H-terminated Si(001) surfaces were immediately installed in the O-atom-beam apparatus. Details of the O-atom-beam apparatus are described elsewhere.[4,5] This study used O-atom exposure without a heat treatment. The Si sample was irradiated with an O-atom beam with a translational energy of 5.4 eV and a flux of 1.8×10^{15} at. cm^{-2} s^{-1}. A 2.4 nm thick oxide film was formed by an O-atom fluence of 3.6×10^{18} at. cm^{-2}. The RTO film, which measured 2.5 nm thick, was formed on the Si (001) wafer obtained from the same Si single crystal at 950 °C in an O_2 atmosphere. The SR-PES measurements were conducted using a surface chemistry end-station installed in the high-resolution soft x-ray beam line, BL23SU, at the SPring-8 facility.[6] In contrast, the CTR measurements were conducted in BL-4C at the Photon Factory.

Figure 1 compares the SR-PES spectra of a RTO film (a) to an O-atom-beam oxidation film (b). Monochromated synchrotron radiation sources with photon energies of 825 and 891 eV were used for Si 2p high-resolution photoelectron spectroscopy. The takeoff angle of the photoelectron settled at 0° (bulk sensitive, black lines) or 70° (surface sensitive, gray lines) with respect to the surface normal. All spectra shown in Fig. 1 are normalized by the Si^{0+} peak intensity. The Si^{4+} peak intensities in the bulk sensitive spectra indicate that the oxide thicknesses of the RTO and O-atom-beam oxidized samples are nearly identical. Since the spectra shown in Fig. 1 are normalized by the Si^{0+} intensity, the background between the Si^{0+} and Si^{4+} peaks, which originates from the Si^{0+} photoelectrons that are inelastically scattered in the SiO_2 film, are at the same level in both panels. (This is the philosophy for the background calculation in Shirley's method.) As shown in the panels of Fig. 1, the signal intensities between the Si^{0+} and Si^{4+} peaks, i.e., suboxides, are close to each other.

To clearly demonstrate the difference in the SR-PES spectra, Fig. 2 compares the same SR-PES spectra, but the spectra are normalized by the Si^{4+} peak intensity. Figure 2(a) shows the SR-PES spectra for the RTO oxide. The SR-PES

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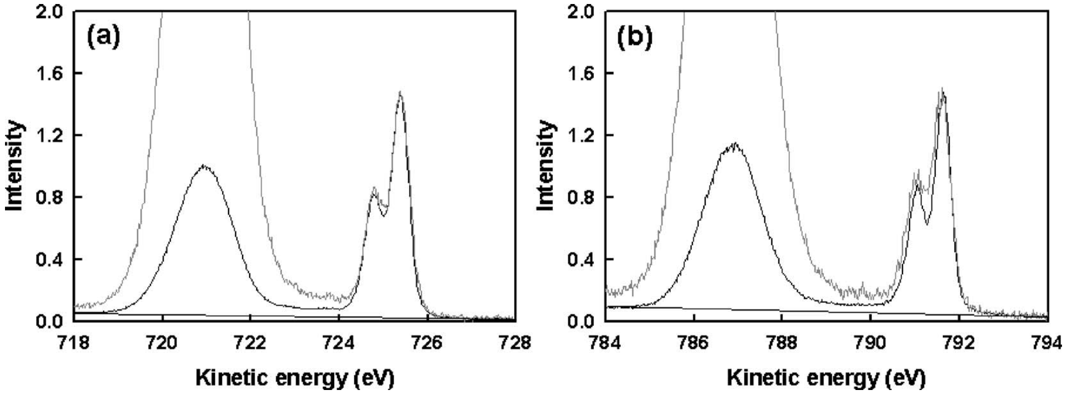

FIG. 1. Si 2p SR-PES spectra of RTO (a) and O-atom-beam oxidation films (b). Black and gray lines indicate SR-PES spectra with a photoelectron takeoff angle of 0° and 70° with respect to the surface normal direction, respectively. The spectra in each panel are normalized by the Si^{0+} peak intensity.

spectrum of the RTO oxide with a takeoff angle of 70° does not have an obvious suboxide peak, whereas the spectrum with a takeoff angle of 0° has two humps (indicated by the triangles). The peak energies are assigned to the Si^{2+} and Si^{3+} peaks since the humps are shifted 1.7 and 2.4 eV from the Si $2p_{3/2}$ peak.[8] The fact that the suboxide peaks are obvious only in the bulk sensitive spectrum indicates that the suboxides are concentrated in a deep region, i.e., at the Si/SiO_2 interface. In contrast, the surface sensitive spectrum for the O-atom-beam oxide film has very small humps [Fig. 2(b)]. These small humps are assigned to the Si^{2+} and Si^{3+} peaks since the peak positions of the humps are 1.8 and 2.6 eV from the Si $2p_{3/2}$ peak. [The difference in the peak position in the RTO and O-atom-beam oxide films is probably due to the charge up or stress in the SiO_2 film since the peak position of the Si^{4+} peak is also shifted 4.4 eV in Fig. 2(a), but is shifted 4.7 eV in Fig. 2(b).] No hump is obvious in the bulk sensitive spectrum of the O-atom-beam oxide film. Hence, it is concluded that the suboxides in the O-atom-beam oxidized film are distributed at the SiO_2 surface rather than the Si/SiO_2 interface.

Figure 3 compares the intensity profiles of [1 1 L] ($0.3 < L < 1.5$) CTR scattering of the O-atom-beam oxidation and RTO films. The main spectral difference in these two CTR scattering profiles is that the scattering intensity near [1 1 L] ($0.3 < L < 0.8$) is weak for the O-atom-beam oxidation film. The hump (or extra peak) near [1 1 0.45] in the CTR scattering profile of the thermally grown oxide has been investigated.[7–9] Tatsumura *et al.* have reported that the hump intensity monotonically increases as the oxidation temperature is lowered.[10] They also found that thermal annealing decreases the hump intensity. From these experimental findings, it has been concluded that the origin of the hump is not from the recrystallization of SiO_2. A molecular dynamics calculation has also suggested that the hump is due to the remaining higher degree of residual order from the parent Si crystal with intrinsic stress.[10] Thus, the hump near [1 1 L] ($0.3 < L < 0.8$), which is observed in the RTO film, is due to the residual ordered structure in SiO_2 film. In contrast, a hump is not observed for the O-atom-beam oxide film (Fig. 3). These results clearly indicate that the O-atom-beam oxide film does not involve a residual ordered structure in SiO_2.

The SR-PES and CTR results suggest that the oxidation kinetics of the O-atom-beam oxidation are different from that of RTO. Recent theoretical investigations have proposed a diffusion process for atomic oxygen.[11–13] According to these studies, the O atom inside SiO_2 tends to react with the SiO_2 network and forms a peroxy linkage. An exchange of the diffusing O atom and the network O atom is a diffusion mechanism (reconstruction of Si–O network). On the other hand, diffusion of O_2 molecules is generally believed to proceed without modifying the SiO_2 network. Tatsumura *et al.* have recently found that the peak at [1 1 0.45] in the CTR profile for thermally grown SiO_2 decreases following plasma oxidation, which includes the O atom as an oxidant.[14] They found that the O atom transforms the crystal phase SiO_2 into amorphous phase. From these theoretical and experimental investigations, this study hypothesized that the O-atom-beam

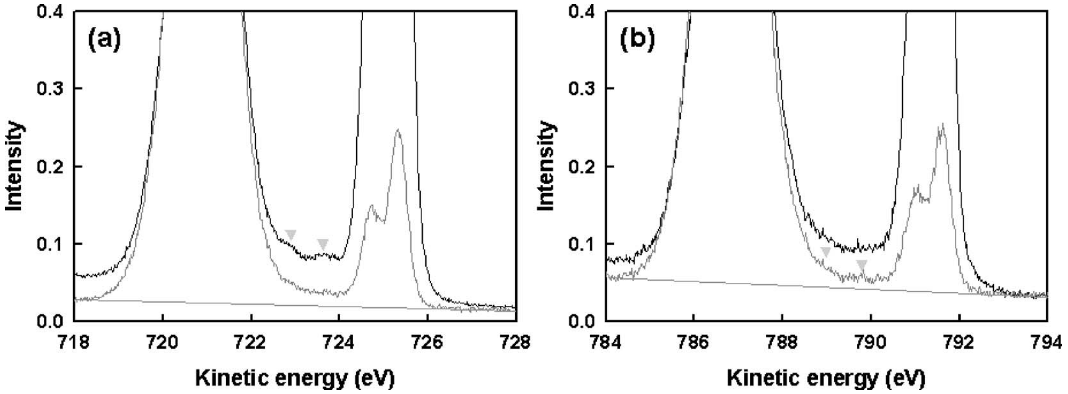

FIG. 2. Si 2p SR-PES spectra of RTO (a) and O-atom-beam oxidation films (b). Black and gray lines indicate SR-PES spectra with a photoelectron takeoff angle of 0° and 70° with respect to surface normal direction, respectively. Linear base lines are indicated in both spectra. The spectra in each panel are normalized by the Si^{4+} peak intensity.

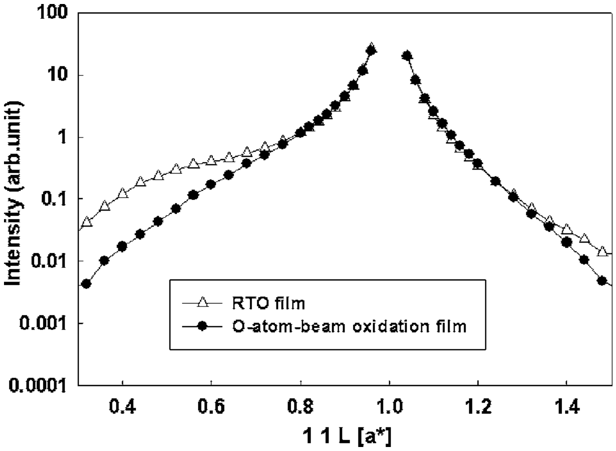

FIG. 3. Intensity profile of the CTR scattering near the [111] Bragg point. RTO film (△) and O-atom-beam oxidation film (●).

oxidation will form amorphous SiO_2. The CTR results support this hypothesis (Fig. 3). However, Kisa *et al.* have reported the cross-sectional transmission electron microscopy (TEM) results on SiO_x formed by 5.1 eV O-atom beam and concluded that O-atom exposure at 493 K produces an ordered silica structure.[15] The CTR results obtained in this study disagree with the conclusions of Kisa *et al.* since the CTR results suggest that SiO_2 does not involve an ordered structure based on the parent Si crystal. The ordered SiO_2 structure reported by Kisa *et al.* was not due to a direct insertion of the O atom into the Si diamond structure, but was due to the recrystallization of amorphous SiO_2 driven by the higher temperature and energy transfer from impinging O atoms.

The experimental results shown in Fig. 2 indicate that the suboxides in the O-atom-beam oxide film concentrate on the SiO_2 surface rather than at the Si/SiO_2 interface. This experimental result suggests that the O atom and Si atom react on the SiO_2 surface. The oxidation kinetics for O-atom-beam oxidation requires an inverse diffusion of the Si atom towards the SiO_2 surface. This oxidation mechanism also explains the incident energy effect on the direct reaction of Si and O previously reported.[3] However, according to the conventional diffusion mechanism as noted by Tatsumura *et al.*, the O-atom may recreate suboxides in SiO_2 by the scission of Si–O–Si network at the SiO_2 surface. Nevertheless, this scission effect does not explain the incident energy effect in oxidation. Therefore, inverse diffusion of the Si atom is, at least, partially responsible for the oxidation by the O-atom beam at room temperature.

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