Reactions and diffusion of atomic and molecular oxygen in the SiO_2 network

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To address the reactions and diffusion of atomic and molecular oxygen in SiO_2, the modification of the SiO_2 network on exposure to an atomic or molecular oxygen atmosphere is investigated by measuring the x-ray-diffraction profile of the residual order peak emanating from the oxide. Analyses of the peak intensity and its fringe pattern provide experimental evidence for the recent theoretical predictions, indicating that atomic oxygen is incorporated into the SiO_2 network near the surface and diffuses toward the interface along with modifying it even at a low temperature of 400 °C, whereas molecular oxygen diffuses without reacting with the bulk SiO_2 even at a temperature of 850 °C that is sufficiently high for oxidation reaction at the interface.

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I. INTRODUCTION

Silicon dioxide (SiO_2) films grown on crystal silicon (Si) constitute the principal gate dielectrics in metal-oxide-semiconductor devices. With the continual shrinkage of device size, the atomistic understanding of all processes involved in silicon oxidation becomes increasingly important.[1] In particular, the understanding of the diffusion of atomic and molecular oxygen in SiO_2 is an outstanding problem, since oxidation kinetics is governed largely by the oxygen diffusion process. Although thermal oxidation of Si in a dry O_2 atmosphere is one of the best methods of growing high-quality SiO_2, the growth rate is insufficiently low at low temperatures. In contrast with O_2 molecules, atomic oxygen is expected to be more reactive.[2] In fact, recent experiments using ultraviolet (UV) radiation[3] or Kr electronic excitation[4–6] demonstrated the possibility of the rapid low-temperature oxidation of Si.

Growth kinetics of silicon oxidation using O_2 molecules are reasonably well described by the Deal-Grove model,[7] which postulates that molecular oxygen diffuses through the growing SiO_2 layer and reacts at the Si–SiO_2 interface. ^{18}O-tagged oxygen diffusion experiments show that there is no oxygen exchange in bulk SiO_2 between oxygen molecules and network oxygen atoms.[8,9] This result means that O_2 diffuses in molecular form without reacting with a SiO_2 network. This picture is also supported by the detection of interstitial oxygen molecules,[10] by the linear dependence of the diffusion on the partial pressure of the gaseous O_2 both in thermal oxides[7] and silica membranes,[8,11] and by the similar diffusion properties of argon (an atom of approximately the same size as O_2).[12] Furthermore, there is a consensus among recent theoretical investigations that molecular O_2 in the spin-triplet state is energetically the most stable state in SiO_2.[13–15]

A diffusion process for atomic oxygen has been proposed by recent theoretical investigations.[16–18] The diffusion process proposed is as follows: An oxygen atom inside a SiO_2 tends to react with a SiO_2 network and to form a stable Si–O–O–Si structure (peroxy linkage). Diffusion of the introduced O atom consists of two steps: (i) a jump of the diffusing O atom around an adjacent Si and an incorporation of the atom into a neighboring Si–O bond, via a transition state with a fivefold coordinated Si atom and a onefold coordinated O atom, and (ii) an exchange of the diffusing O atom and the network O atom via a transition state with onefold and threefold coordinated O atoms. Hence, it is considered that there are significant differences between the diffusion mechanisms of atomic and molecular oxygen. However, experimental evidence on the atomic oxygen diffusion has been lacking.

The purpose of this paper is to provide experimental evidence for the difference in reactions and diffusion of atomic and molecular oxygen in SiO_2. Since overcoordinated and undercoordinated atoms are considered to promote switching of bond connections,[19] the diffusion process of atomic oxygen, as well as their incorporation into the SiO_2 network, may induce modifications of the SiO_2 network. On the other hand, diffusion of O_2 molecules is generally believed to proceed with no modification of the SiO_2 network. In this work, we investigate whether modification of the SiO_2 network occurs upon exposure to an atomic or molecular oxygen atmosphere by measuring the intensity profile of an x-ray-diffraction peak[20–22] that reflects the average structure of an oxide film. The origin of the diffraction peak on which we focus has very recently been clarified to be the residual order of Si atoms within SiO_2.[23,24] A silicon lattice is expanded during oxidation without completely disordering it. The intensity profile of the residual order peak can be used as a sensitive indicator for monitoring the structural changes of the thermal oxide. In fact, it was demonstrated that the peak intensity is decreased and ultimately removed by thermal annealing, indicating the decrease of residual ordering and complete conversion to amorphous SiO_2.[25]

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II. EXPERIMENT

We compare x-ray-diffraction profiles for three samples that were reoxidized in an atomic or molecular atmosphere after formation of base SiO_2 layers in a 100% dry O_2 atmosphere. The substrates were boron-doped Cz-Si(001) wafers with resistivity of 10–15 Ωcm and an off-angle of 0.4° toward the [010] direction. The base SiO_2 layers of 24.7-nm thickness (by ellipsometry with a refractive index of 1.46) were obtained by dry O_2 oxidation at 850 °C for 260 min. The atomic oxygen-exposed sample, hereafter referred to as the O-400 °C sample, was obtained by reoxidizing the base SiO_2 layer in an atomic radical O flow generated from high-density low-electron-temperature Ar/O_2 (=2000/10 sccm, 6.7 Pa) plasma at a substrate temperature of 400 °C for 125 min. The reoxidization process increased the oxide thickness by 1.5 nm. The applied microwave power and frequency were 2500 W and 2.45 GHz, respectively. The plasma apparatus employed (Tokyo Electron, Trias SPA) was designed to enable damage-free processes.[5,6,26,27] Two kinds of molecular oxygen-exposed samples were prepared as follows. One, hereafter the O_2-400 °C sample, was prepared under the same conditions as those of the O-400 °C sample except for a microwave power of 0 W; that is, the sample was exposed to a molecular O_2 flow. The treatment did not increase the oxide thickness ($<$ +0.1 nm). The other, hereafter the O_2-850 °C sample, was reoxidized in a 100% dry O_2 atmosphere at 850 °C until the thickness increase of 2.0 nm was achieved (25 min). X-ray-diffraction measurements using synchrotron radiation were performed on BL4C of the Photon Factory (KEK) by employing a four-circle diffractometer with a Si(111) crystal analyzer. The wavelength was chosen to be 0.154 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the diffraction intensity profiles for the O-400, O_2-400, and O_2-850 °C samples. In Fig. 1, the data for the sample with the base SiO_2 layer not subjected to reoxidization, hereafter the base SiO_2 sample, is shown. The intensity profiles are scanned along the crystal truncation rod (CTR) scattering extending from the 111 bulk Bragg peak. The CTR scattering is caused by the termination of Si lattice at the Si–SiO_2 interface and extends in the surface-normal direction, in this case, the direction rotated by 0.4° with respect to [001] toward [010]. In Fig. 1, the 111 bulk peak is located at $l=1.0$ and the CTR scattering is observed as the intensity decreasing with distance (d) from 111 according to $\sim 1/d^2$.

For the base SiO_2 sample, the residual order peak is clearly observed on CTR at $l=0.45$, corresponding to the position of $h,k,l=1.00$, 1.00, 0.45, in accordance with the previous reports.[20–22] One of the characteristic features of the peak is that its profile exhibits a Laue-function-like oscillation-fringe pattern. As shown in Fig. 2, the enlargement of Fig. 1, the peak profile consists of a main peak and several subpeaks, and the width of the main peak is twice as much as those of the subpeaks. Furthermore, the oscillation period (λ) is related to the inverse of the film thickness (t) by $\lambda = a_{Si}/t$, where a_{Si} is the silicon unit-cell dimension. In this case, λ is 0.023, agreeing well with the value estimated from the thickness of the base SiO_2 layer (0.543/24.7=0.022).

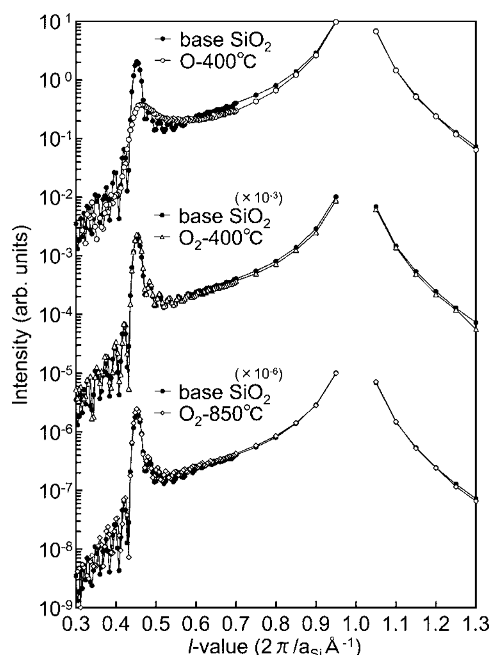

FIG. 1. X-ray-diffraction intensity profiles for the O-400 °C (circles), O_2-400 °C (triangles), and O_2-850 °C (squares) samples, coupled with the data for the base SiO_2 sample (filled circles). The intensity profiles are scanned along the CTR scattering extending from the 111 bulk Bragg peak and are plotted as a function of the l value in a silicon reciprocal lattice unit. The solid lines are guides for the eyes.

Exposure of the base SiO_2 layer to an atomic oxygen flow induces significant changes in its x-ray-diffraction property. The residual order peak is observed also for the O-400 °C sample, but its intensity is approximately one order of magnitude smaller than that for the base SiO_2 sample. In addition, the oscillation-fringe pattern around the peak completely disappears (Fig. 2). Note that the remarkable

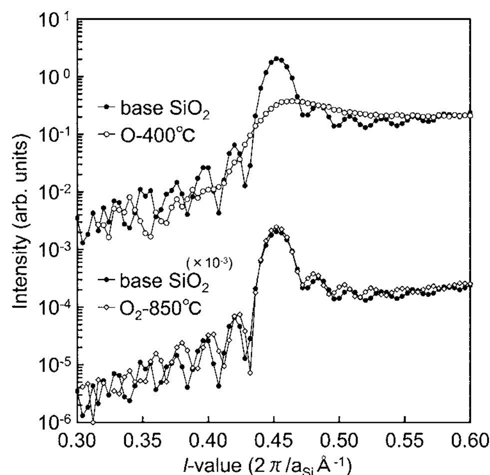

FIG. 2. Enlargement of the data in Fig. 1 for the O-400 °C (circles) and O_2-850 °C (squares) samples.

coincidence of the data at the higher angle side of 111 ($l > 1.0$) in Fig. 1 allows us to compare the data between the samples at the lower angle side. In contrast to the case of the O-400 °C sample, the intensity profile for the O_2-400 °C sample does not differ from that of the base SiO_2 sample (Fig. 1). Similarly, the intensity profile for the O_2-850 °C sample is almost the same as that for the base SiO_2 sample, but the peak intensity becomes slightly larger and the period of oscillation slightly decreases, becoming 0.021 (Fig. 2). This change of the period precisely reflects the thickness increase of 2.0 nm (i.e., $0.543/26.7=0.020$). This change of the period together with the slight increase of the peak intensity indicates that the reoxidization process produced the oxide with the same structure as the base SiO_2 at the $Si-SiO_2$ interface.

The decrease in the peak intensity at $l=0.45$ means an increase in the static disorder of Si atoms within bulk SiO_2.[25] Hence, the result for the O-400 °C sample is solid evidence that atomic oxygen reacts with the bulk SiO_2 and modifies its network structure even at a low temperature of 400 °C. In contrast, the result for the O_2-400 °C sample indicates no structural change occurs during the exposure to the molecular oxygen flow at 400 °C. For the O_2-850 °C sample, the thickness increase of 2.0 nm confirms that oxidant species needed to oxidize 6 or 7 Si layers have reached the $Si-SiO_2$ interface. Despite the passage of such a considerable amount of oxidant species, the peak intensity does not decrease. This clearly shows that molecular oxygen diffuses without reacting with the bulk SiO_2 even at a sufficiently high temperature of 850 °C for oxidation reaction at the interface.

The shape of the peak profile provides further information about the residual order distribution. A clear oscillation-fringe pattern around a diffraction peak is observed only for homogeneously ordered thin films having finite thickness and two distinct boundaries. If the structure is gradually disordered and converted to be amorphous near one of the boundaries, it is impossible to observe the oscillation pattern whose period is related to the film thickness.

To elucidate the structural change of the O-400 °C sample, we made two types of model structures and calculated the x-ray-diffraction profiles from them. Figure 3 schematically shows the positions of Si atoms in thermally grown[23,24] SiO_2 and explains the concept of the residual order. In Fig. 3, it is supposed that the Si atoms are moved from their crystal positions in the surface-normal direction and disordered during oxidation, but the Si atoms still remain sufficiently ordered to produce a detectable diffraction peak. Recent molecular dynamics simulation demonstrated the possible existence of a SiO_2 structure consisting of corner-sharing SiO_4 tetrahedrons with the bond length and angle of amorphous SiO_2 and showing an average arrangement of Si atoms corresponding to the expanded Si lattice.[23] Model A in Fig. 3(a) is a homogeneous structure in the sense that the static disorder for the Si atoms from the ordered positions is constant throughout the film. On the other hand, model B in Fig. 3(b) is a gradually disordered structure with a gradually increasing static disorder from the interface to the surface.

Figure 4 shows the x-ray-diffraction profiles calculated for models A and B. The structures used for the calculation in Fig. 4 are shown in Fig. 5. The preparation procedure of the model structures is as follows. The (001)-terminated Si model (19 800 atoms) is formed, which is 11.93 nm thick along [001] (88 atomic layers) and 5.76 nm long along $[1\bar{1}0]$ and [110] (15×15 atoms per atomic layer). The Si lattice, except for the substrate region (8 atomic layers), is expanded toward [001] with expansion ratio of 2.21, resulting in the expanded Si lattice of the thickness of 24 nm. Each Si atom is displaced from its ordered position. Each component of the displacement vector, $\mathbf{d}(x,y,z)$, is generated according to the normal distribution function with a standard deviation $(\sigma), f(x)=(1/\sqrt{2\pi}\sigma)\exp(-x^2/2\sigma^2)$. Model A has a constant σ of 0.8 Å. Model B has a linearly increasing $\sigma(z)$ with $\sigma=0.8$ Å at the interface and $\sigma=2.2$ Å at the surface.

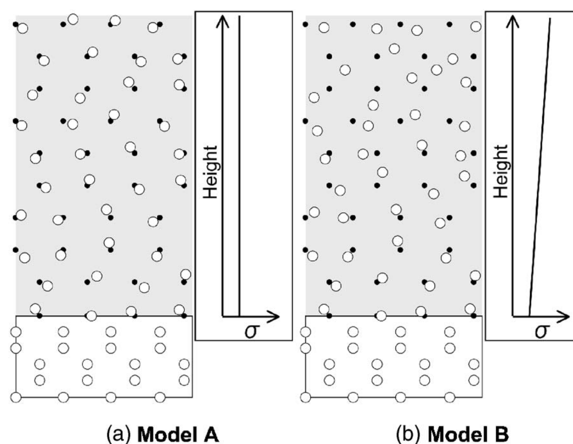

FIG. 3. Schematic illustration of the positions of Si atoms in thermally grown SiO_2. The open circles represent Si atoms. The inside of the box is the substrate region. The small black dots show the positions of the expanded Si lattice in the absence of static disorder: (a) Model A: a homogeneous structure and (b) Model B: a gradually disordered structure.

Despite their simplicity, models A and B, respectively, are able to reproduce the characteristic features of the residual order peaks for the base SiO_2 and O-400 °C samples. The gradually disordered structure for the O-400 °C sample provides further evidence that atomic oxygen is incorporated into the Si–O network near the surface and diffuses toward the interface along with modifying it. Note that the original structure of the thermal oxide is not completely homogeneous but shows an inclined distribution of the residual order

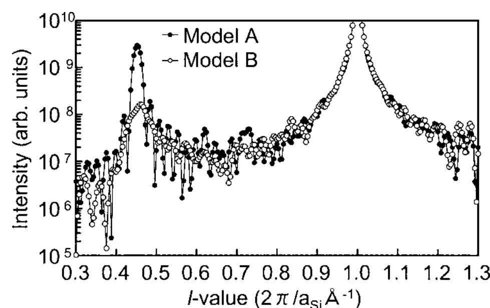

FIG. 4. X-ray-diffraction intensity profiles calculated for Model A and Model B in Fig. 5 on the basis of kinematical diffraction theory.

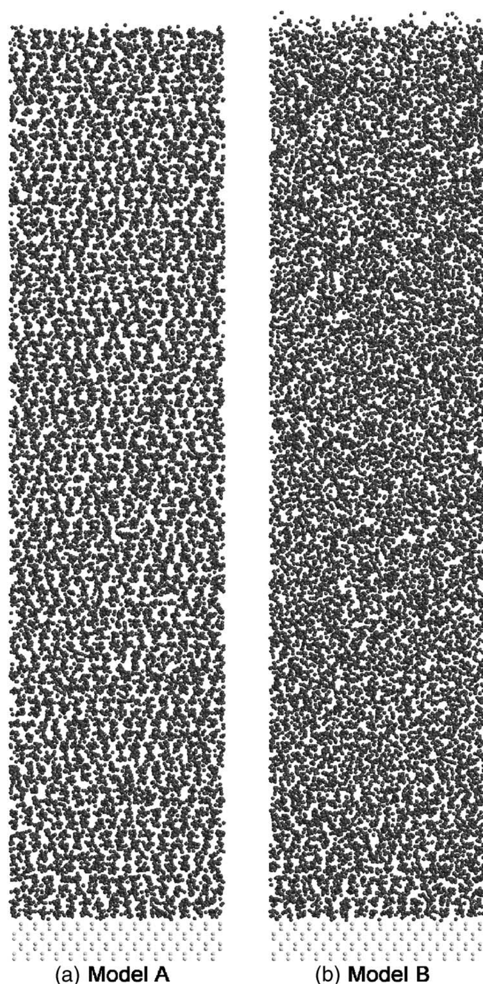

FIG. 5. Side views of the model structures used for the calculation in Fig. 4, in [110] projection. Dark gray spheres represent Si atoms in the oxide region and light gray spheres represent Si atoms in the substrate region: (a) Model A: a homogeneous structure and (b) Model B: a gradually disordered structure.

to some extent, depending on its formation process.[20,24] The result obtained indicates that diffusion of atomic oxygen additionally increases the slope of the residual order distribution. In the O-400 °C sample, the residual order persists near the interface but is lost near the surface.

The plasma process for atomic O generation is also accompanied by generation of UV wavelength photons. Kazor and Boyd performed UV irradiation experiments and suggested an UV-assisted diffusion model involving ionic oxygen formation and space-charge creation due to photoinjection of electrons from Si.[3] In that model, drift movement of ionized oxidants due to an electric field caused by the space charge plays an important role. Although the influence of UV irradiation is difficult to assess in the present experiment, it is clear from the present data that atomic O passing through the SiO_2 reacts with the SiO_2 network and modifies it.

IV. SUMMARY

In summary, we present experimental evidence for the recent theoretical predictions on reactions and diffusion of atomic and molecular oxygen in SiO_2. Even at a low temperature of 400 °C, atomic oxygen reacts with the SiO_2 network near the surface and diffuses toward the interface with changing bond connections. In contrast, molecular oxygen does not react with the SiO_2 network at a sufficiently high temperature of 850 °C for oxidation reaction at the interface. The network modification effect of atomic oxygen found in this work would be useful for relieving the intense stress near the Si–SiO_2 interface or for amorphizing unfavorable polycrystalline region in amorphous oxide films.

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