

## Stability-Instability Transition of Reaction Fronts in Thermal Silicon Oxidation

Thermal silicon oxidation is important not only for the formation of gate dielectric oxide films on a silicon surface but also for size control of silicon nanostructures. Therefore, the modeling of oxidation kinetics has been extensively explored on planar silicon surfaces and at the interface between growing silicon oxide film and planar or nanoscale silicon surfaces. Thanks to recent *in situ* experiments and theoretical calculations, our understanding the silicon oxidation kinetics at the interface between thermal silicon oxide and Si(001) has progressed considerably [1,2]. For surface oxidation, the thermal oxidation can be categorized into two domains – active oxidation (etching) and passive oxidation (oxide growth) – depending on the oxygen pressure and oxidation temperature. However, the morphological stability of the growing interface, i.e., the reaction fronts in the growth regime, which governs the roughening at the interface, has not been well clarified yet. In this work, to reveal whether the interface stress affects the stability of oxidation fronts, we systematically explore the details of the roughening at the interfaces in thermal silicon oxide films on Si(001) as a function of oxidation temperature by combining atomic force microscopy (AFM) (destructive method) and synchrotron X-ray reflectivity measurements (XRR) (nondestructive method).

The B-doped Si(100) wafers were subjected to various annealing conditions in an Ar atmosphere containing a small constant fraction of O<sub>2</sub> gas (0.20 ± 0.01%). Morphologies at the interface were observed in air by tapping-mode AFM immediately after the removal of the as-grown silicon oxide layers. XRR measurements of the samples thermally oxidized in the furnace were performed using the z-axis goniometer at beamline BL24XU [3]. The 0.124 nm X-ray wavelength was used at the incident angle by varying the angle from 0.1 to 4.0°.

Figure 1 shows the temperature dependence of roughness at the interface between thermal SiO<sub>2</sub> grown in 0.2% O<sub>2</sub>-Ar mixture for 2.5 h and the silicon substrates with miscut angles below 4°, obtained by AFM. The interface becomes rough owing to the formation of interfacial multiple step structures at oxidation temperature (T<sub>ox</sub>) > 1150°C and has the maximum roughness at T<sub>ox</sub> = 1250°C. The temperature-dependent roughening can therefore be categorized into three regions with respect to growth temperature: (I) T<sub>ox</sub> < 1150°C, where roughness is constant; (II) 1150 < T<sub>ox</sub> < 1250°C, where roughness sharply increases as oxidation temperature increases and is maximum at 1250°C independent of miscut angles

below 4°; and (III) 1250 < T<sub>ox</sub> < 1380°C, where interface roughness gradually decreases; that is, the roughened interface becomes smooth during the oxidation as the oxidation temperature increases. There is maximum roughness at around 1250°C, indicating that there are competing mechanisms causing the roughening and smoothing as discussed below.

To understand the mechanism of the temperature dependence underlying the interface roughening and smoothing, we performed XRR measurements on the samples with  $\theta = 0.1^\circ$  and analyzed the density and thickness of the oxide film and interface transition layers on the basis of a two-layer model. We plot the fitting parameters of the samples oxidized at different temperatures in Figs. 2(a) - 2(c). As seen in Fig. 2(a),  $\sigma_{i-s}$  is constant in region (I), but it becomes extremely rough from T<sub>ox</sub> = 1150°C with the roughness reaching a maximum at T<sub>ox</sub> = 1250°C in region (II). It then gradually becomes smaller in region (III). In contrast to  $\sigma_{i-s}$ , the surface roughness of the silicon oxide bulk film ( $\sigma_f$ ), which has the largest roughness in the interfaces of the films at T<sub>ox</sub> < 1250°C, becomes smaller in regions (I) and (II) with some modulations and behaves as  $\sigma_{i-s}$  in region (III). The  $\sigma_{f-i}$ , on the other hand, is almost constant in regions (I) and (II), but the interface becomes slightly rough above 1250°C, and the roughness finally becomes the largest at 1380°C.

The density ratio between the interfacial transition layers and silicon oxide bulk film ( $d_i/d_f$ ), which is larger than unity, decreases from 1.12 to 1.05 between 1000 and 1380°C (Fig. 2(b)), while  $t_i$  gradually decreases as T<sub>ox</sub> increases (Fig. 2(c)). This indicates that the planar density of the transition layers  $d_s$ , which is defined as

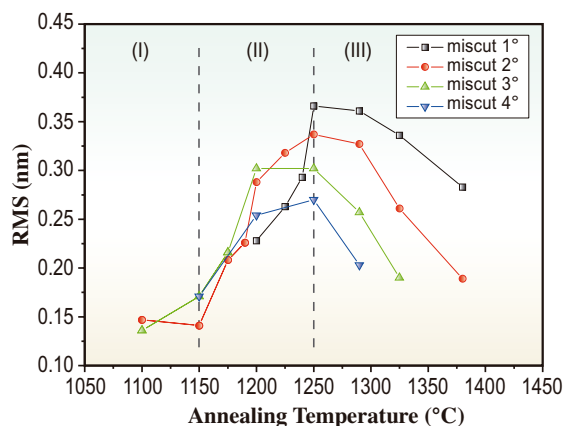


Fig. 1. Rms vs oxidation temperature. Samples miscut at several angles were thermally oxidized in the 0.2% oxygen-Ar mixture for 2.5 h. Three characteristic regions are labeled (I), (II), and (III) with respect to the oxidation temperature.

$d_i t_i$ , becomes smaller with  $T_{ox}$ .

On the basis of the AFM and XRR results, the remarkable temperature dependence of oxidation kinetics at the  $\text{SiO}_2/\text{Si}(001)$  interface can be explained as follows: the decreasing in the density and thickness of the interfacial transition layers with increasing  $T_{ox}$  indicate that the stress generated by the high-temperature oxidation ( $>1100^\circ\text{C}$ ) is mainly relieved in the interfacial transition layers. The oxidation-induced stress at the interface therefore becomes smaller as  $T_{ox}$  increases. In region (I), where the lateral diffusion of silicon species at the interface is negligibly small [2], the oxidation-induced stress between the silicon oxide bulk films and interfacial transition layers is

balanced via the relaxation of stress in the transition layers, because  $\sigma_{f-i}$  is almost constant in this region (Fig. 2(a)). The high degree of  $\sigma_f$  is indicative of the small degree of viscosity of the oxide film compared with that of the interfacial transition layers, although it becomes smaller with increasing  $T_{ox}$ . In region (II), the lateral diffusion of silicon species becomes prominent at the  $\text{SiO}_x(i)\text{-Si}$  interface [2]. As a result, the strain induced by the oxidation is relieved through the dense and high-viscosity interfacial transition layers not only perpendicular to but also parallel to the  $\text{SiO}_x(i)\text{-Si}$  interface. In region (III), the relaxation of the oxidation-induced stress in the silicon oxide bulk film possibly plays an important role in the decrease in  $\sigma_{i-s}$ . The  $\sigma_f$  and  $\sigma_{i-s}$  become almost the same at  $T_{ox} = 1250^\circ\text{C}$  and then coincidentally become smaller with increasing  $T_{ox}$ , whereas  $\sigma_{f-i}$  gradually increases in region (III) (Figs. 2(a) - 2(c)). The results indicate that the oxide film and interface transition layers act together at  $T_{ox} > 1250^\circ\text{C}$  and imply that the oxidation-induced strain is homogeneously relaxed not only in the interfacial transition layers but also in the entire region of the silicon oxide bulk films by relaxation via viscosity flow in the silicon oxide bulk film with high-temperature annealing. This feature is consistent with the presence of the transition in the density of the interfacial transition layers at  $1200^\circ\text{C}$  (Fig. 2(b)). The homogeneous strain distribution in the silicon oxide bulk film via viscous flow causes the uniform reaction rate at the interface. This explains the onset of the smoothing of the  $\text{SiO}_x(i)\text{-Si}$  interface and the smoothing of the surface of silicon oxide bulk films.

In summary, we discovered a temperature-dependent morphological instability-stability transition at the  $\text{SiO}_2/\text{Si}(001)$  interface during thermal silicon oxidation above  $1100^\circ\text{C}$  in dilute oxygen atmosphere in a furnace. The transition implies a strain effect on the oxidation kinetics at the interface between the dense and thin interfacial transition layers and the substrate at  $T_{ox} > 1250^\circ\text{C}$ .

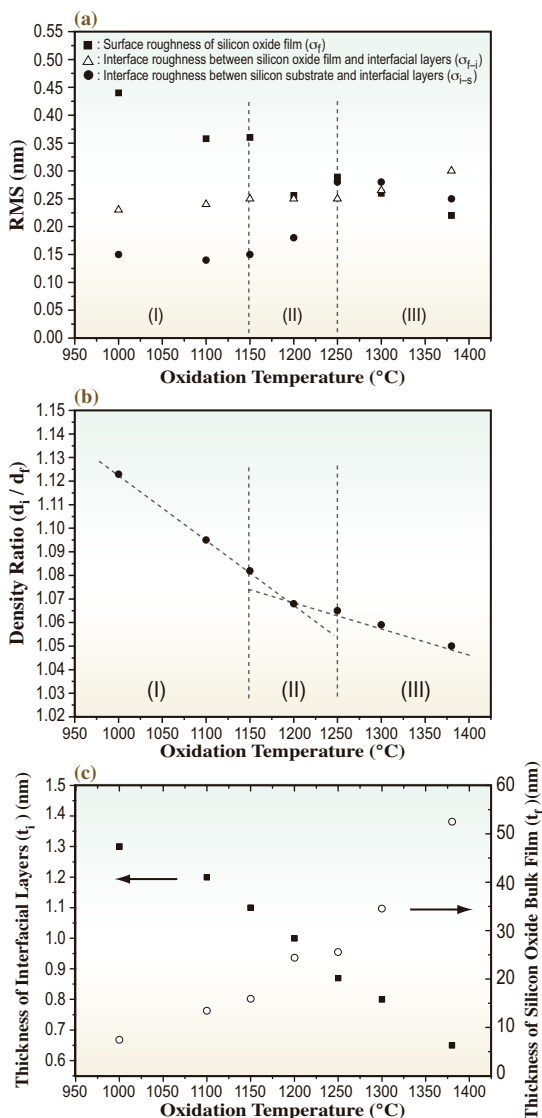


Fig. 2. Plots of best-fit parameters for XRR measurements on samples grown at oxidation temperatures between 1000 and  $1380^\circ\text{C}$  in the 0.2%  $\text{O}_2/\text{Ar}$  mixture. (a) Roughness at the surface ( $\sigma_f$ ) and interfaces between silicon oxide bulk film and interfacial transition layers ( $\sigma_{f-i}$ ) and between interfacial transition layers and silicon substrate ( $\sigma_{i-s}$ ). (b) Density ratio between interfacial transition layers ( $d_i$ ) and silicon oxide film ( $d_s$ ). Dotted lines are two types of linear fittings. (c) Thicknesses of interfacial transition layers ( $t_i$ ) and silicon oxide bulk films ( $t_o$ ).

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