Scaling and Universality of Roughening in Thermal Oxidation of Si(001)

Hiroo Omi,[*] Hiroyuki Kageshima, and Masashi Uematsu
NTT Basic Research Laboratories, NTT Corporation, 3-1 Wakamiya, Morinosato, Atsugi, Kanagawa 243-0198, Japan

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By analyzing atomic force microscopy images, we derive a continuum equation that quantitatively explains the roughening at the Si(001)-SiO_2 interface during thermal oxidation at the temperature at 1200 °C in an Ar atmosphere containing a small fraction of O_2. We also show that there is a phase transition in the universality class from a disordered to step-terrace structure at the interface at oxidation temperatures between 1150 and 1380 °C with the miscut angle of the substrate as the scaling parameter.

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The existence of universality is prominent in roughening phenomena on surfaces and at interfaces [1]. The essential features of the roughness evolution depend only on certain symmetries and on the dimensionality of the system, not on the detailed interactions. Much research has focused on classifying the universality of roughness evolution during growth and etching processes, such as molecular beam epitaxy [2] and chemical and plasma etching [3]. However, most of these studies are concerned with only the surfaces [1,2,4]; few have examined interface roughness.

The roughening at the $SiO_2/Si(001)$ interface during thermal silicon oxidation has been of particular interest in the few studies on the interface [5,6], because understanding the mechanism of the interface roughening is technologically very important at present [7,8]. Chen and Gibson pioneeringly attempted to show the universality class of this interface by stochastic differential equations for the time evolution of interface height [9]. Their interpretation was that the interface oxidation kinetics should be written as the Langevin equation

$$\frac{\partial h(r,t)}{\partial t} = \mu \nabla^2 h(r,t) + \eta(r,t), \tag{1}$$

where μ is a constant, and $\eta(r,t)$ is a noise term describing the oxidation of silicon, which is considered to happen randomly at silicon atom sites. The oxidation model indicates that oxygen atoms randomly form SiO_2 islands on the terrace shown in the second term on the right side, but that the resulting roughness is smoothened by the first term.

However, we have shown that self-aligned step-terrace structures are formed at an interface grown above 1325 °C in dilute oxygen-Ar gas mixtures [10]. This clearly implies that lateral diffusion of silicon species occurs at the interface, leading to the formation of the step-terrace structure, and suggests the possibility of the existence of another universality class. In this Letter, we present quantitative descriptions of roughening at the interface at high temperature and reveal, for the first time, another universality class. We further show a phase transition in the universality class from the disordered to the step-terrace structure with the miscut angle of the substrate as the scaling parameter.

We used B-doped Si(100) wafers (resistivity = 1–10 Ω cm) with miscut angle θ of 0.5°, 1.0°, 2.0°, 3.0°, or 4.0° toward the [110] direction. The wafers were thermally oxidized in a furnace made of silicon carbide at temperatures between 1150 and 1380 °C in an Ar atmosphere containing a small constant fraction of O_2 gas ($0.20 \pm 0.01\%$ and $2.00 \pm 0.01\%$). In the experiments, the Ar flow rate was constant throughout at 2.0 l/min. The rate of heating and cooling from the base furnace temperature of 600 °C was 5 °C/min or less. Under these conditions, we obtained silicon oxide layers >20 nm thick. Before introducing the wafers into the furnace, we etched them in 1% HF and 99% doubly deionized (DDI) H_2O by volume in order to remove native silicon oxide layers. Following the annealing treatment, the samples were etched in 0.5% HF: 99.5% DDI H_2O, by volume, for 2–20 min, to remove the silicon oxide layers. Morphologies at the interface were observed in air by tapping mode atomic force microscopy (AFM) immediately after the removal of the silicon oxide layers. The radii of the silicon cantilevers used in the AFM measurements were less than 2 nm. Note here that we could not find any evidence that the etching affects the AFM results at least for the stated resolution and measured area [11], as was carefully checked in Ref. [10].

Figure 1 shows AFM images of the interfaces between thermal silicon oxide layers grown at 1200 °C in a 0.20% O_2-Ar mixture and the Si(001) substrate with miscut angle

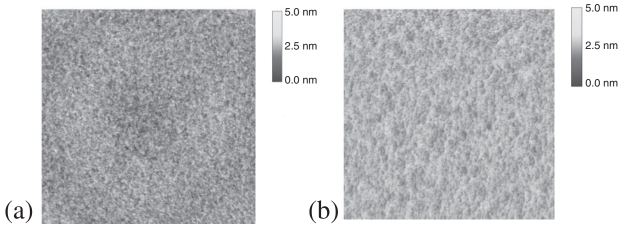

FIG. 1. AFM images of the Si(001) surface after annealing for (a) 1.0 and (b) 6 h at 1200 °C followed by chemical etching. The image size is 2 μm by 2 μm. The full topographic scale, 5.0 nm, is shown.

of 1.0°. As can be seen in Fig. 1(a) and 1(b), the interface morphology evolves with oxidation time t in the 0.20% mixture. For $t = 1$ h, the interface has no characteristic feature and is rough [root mean square roughness (rms = 0.179 nm = $1.32z_{\mathrm{SL}}$) [Fig. 1(a)], but for $t = 6$ h, it becomes rougher (rms = 0.237 nm = $1.74z_{\mathrm{SL}}$) and exhibits atomic steps with randomly fluctuating edges. Here, z_{SL} is the Si(001) spacing, which is approximately 0.136 nm. The presence of interfacial steps was also checked by cross-sectional transmission electron microscopy at the $\mathrm{SiO_2/Si(001)}$ interface, which suggest that the steps are not created by the removal of $\mathrm{SiO_2}$.

To quantitatively understand the dynamical behaviors at the Si(001)-$\mathrm{SiO_2}$ interface, we carried out scaling analyses on the AFM images in Figs. 1(a) and 1(b). In Fig. 2, we plot interface width $W(L, t)$, defined by the rms, as a function of scaling length L for $t = 1$ and 6 h. The scaling hypothesis requires that $W(L, t) \propto L^{\alpha}$ for $L \ll \xi$ [1]. Here, ξ is the correlation length, within which the surface heights of any two points are correlated, and α is the roughness exponent. We found that the roughness exponent α is 1.0 ± 0.3 for each oxidation time and that the ξs are 60 nm for $t = 1$ h and 40 nm for $t = 6$ h. In order to get a more accurate value of α, we also plot power spectral densities (PSD) of the AFM images for $t = 1$ and 6 h [in Figs. 2(c) and 2(d)], 10, 15, and 20 h. For a rough two-dimensional surface, in general, the PSD behaves as $\mathrm{PSD}(1/q) \propto (1/q^{2(\alpha+1)})$ [12]. From PSD analyses on these AFM images, α was found to be 1.00 ± 0.036, which is in good agreement with the α value obtained from our scaling analyses by $W(L, t)$. The analyses of the samples with the other miscut angles also showed that the roughness exponent is close to unity regardless of either oxidation time above 2.5 h or substrate miscut angles, implying that the scaling law is universal for oxidation in 0.20% $\mathrm{O_2}$-Ar atmosphere at 1200 °C.

For a further analysis of the time evolution of the interface morphology in Fig. 1, we plot the interface width $W(L, t)$ as a function of t in Fig. 3. Oxidation time for each sample was derived from silicon oxide layer thickness X using Deal-Grove's linear-parabolic equation $t + \tau = (1/B)X^2 + (A/B)X$, where A and B are constants and term τ is the correction for the presence of an initial oxide layer

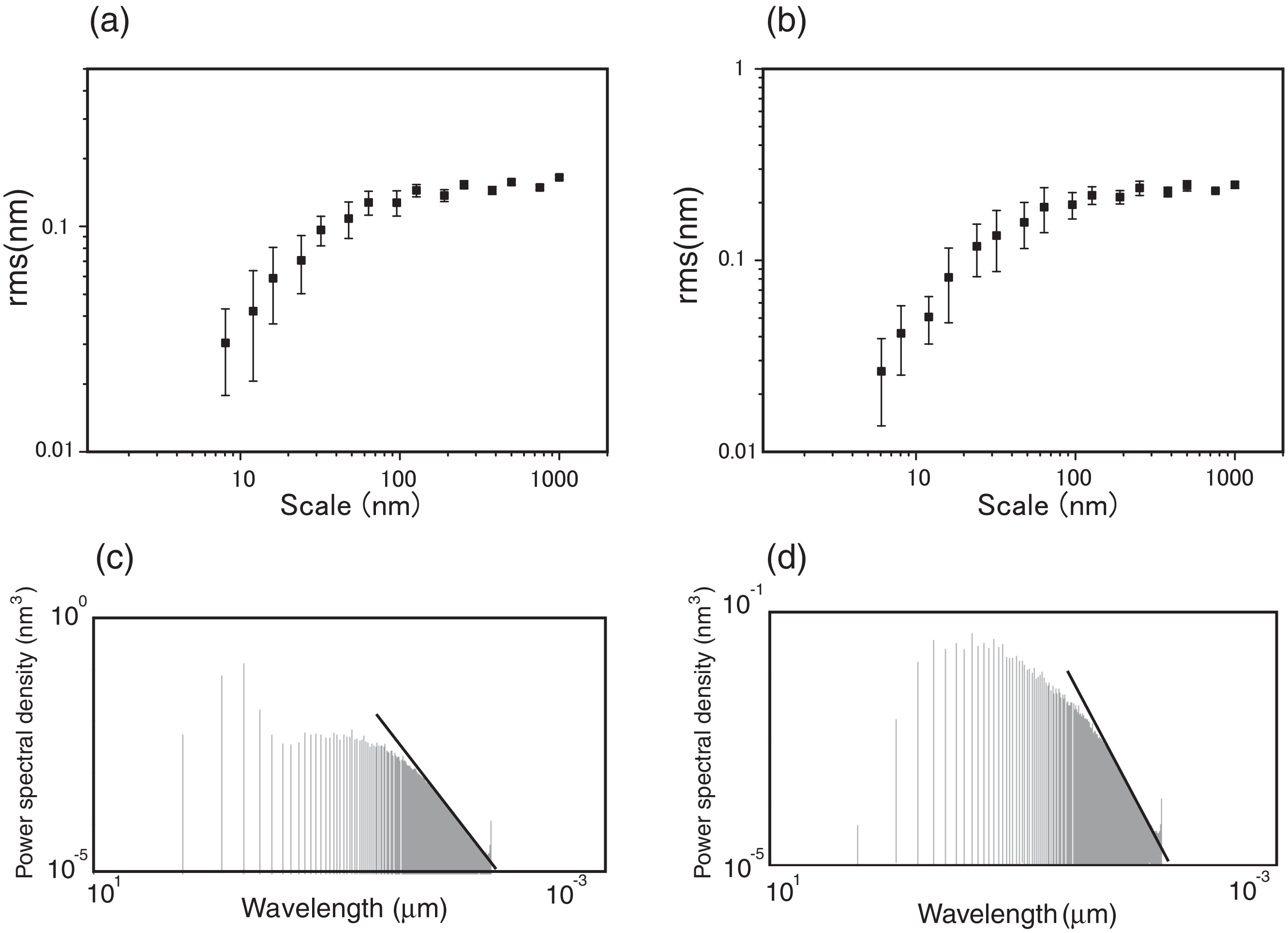

FIG. 2. Root mean square roughness, $W(L, t)$, vs length scale; (a) and (b) were determined from the AFM images in Figs. 1(a) and 1(b), respectively. (c) and (d) PSD curves were obtained from AFM images in Figs. 1(a) and 1(b), respectively.

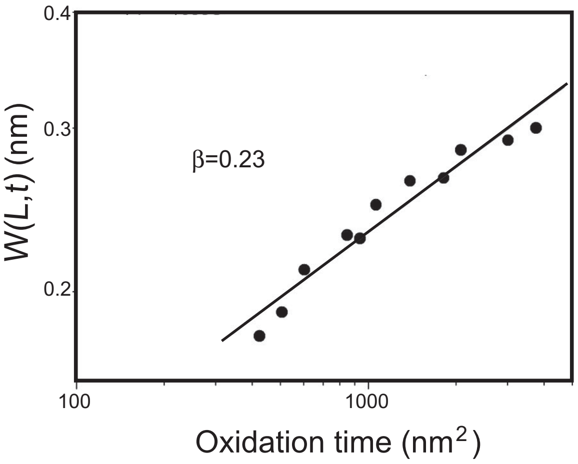

FIG. 3. Log-log plots of $W(L, t)$ vs oxidation time. The slope of the solid line is $\beta = 0.23 \pm 0.02$. Thermal silicon oxidations were performed in 0.20% O_2–99.80% Ar atmosphere at 1200 °C.

[13,14]. The scaling law requires $W(L, t) \propto t^{\beta}$, where β and is the growth exponent. As seen in Fig. 3, the Si(001)-SiO_2 interface becomes rougher linearly with oxidation time when the slope β is 0.23 ± 0.2 for 21 nm $< X <$ 100 nm.

The exponents α and β obtained from the AFM images are in a good agreement with a linear Langevin equation, the so-called Mullins-Herring (MH) equation for crystal growth on a surface [1], which leads to the scaling law $\alpha = 1.0$ and $\beta = 0.25$ for the two-dimensional space. When we apply the MH equation to the high-temperature silicon thermal oxidation at the interface as in Eq. (1), the oxidation kinetics can be written as

$$\frac{\partial h(r, t)}{\partial t} = -D\nabla^4 h(r, t) + \eta(r, t). \qquad (2)$$

The first term of the right side of Eq. (2) addresses the kinetic rearrangement due to diffusion at the interface. D is the diffusion constant, which was experimentally determined as described later. According to Ref. [1], the MH equation is a good expression for pure diffusion-controlled growth on a surface, such as in molecular beam epitaxy, where the Si self-diffusion mainly dominates the interface morphological relaxation. Hence, in the case of high-temperature thermal oxidation, our interpretation is that roughness evolution is governed by competition between the generation of the noise term related to the thermal oxidation and the smoothening effect by diffusion of atoms at the growing interface. This would mean that the interface diffusion plays an important role in roughening at the oxidation temperature of 1200 °C and O_2 concentration of 0.20%. The emergence of the step-terrace morphology at the interface therefore indicates that something like the ordering in Fig. 1(b) is occurring via a step-flow mass transport process such as a steady state anneal.

In contrast to the exponents for the 0.20% mixture, we obtained the results of exponents $\alpha = 0.11 \pm 0.14$ and $\beta = -0.01 \pm 0.14$ for the 2.00% mixture at 1200 °C. The exponents are nearly equal to $\alpha = \beta = 0$, which confirms the validity of Eq. (1). The changes in the exponents elucidate that the first term of the right side of Eq. (2) changes from $\nabla^4 h$ to $\nabla^2 h$ with increasing oxygen concentration. This clearly indicates that the mechanism of the oxidation depends on the concentration of oxygen gas. These findings mean that the continuum equation should be described as

$$\frac{\partial h(r, t)}{\partial t} = \mu\nabla^2 h(r, t) - D\nabla^4 h(r, t) + \eta(r, t), \qquad (3)$$

which suggests that there is competition between the linear terms $\nabla^2 h$ and $\nabla^4 h$ generating the characteristic horizontal length $L_1 = (D/\mu)^{1/2}$ [1] between the oxidation at 0.20% and that at 2.00% oxygen. That is, there is a transition in the mechanism of the roughening and it should be characterized by the parameter of the length L_1, which means that if we could change the L_1 by mean terrace width l of the substrate ($l = z_{SL}/\tan\theta$), we would be able to observe the transition at the different temperatures.

We controlled the length by changing the miscut angle θ of the substrate and examined the interface morphology for $t = 2.5$ h as a function of oxidation temperature in the 0.2% O_2-Ar mixture. Figure 4 plots the interface morphological evolution versus $1/T$ and l. As can be clearly seen, as expected, we found that there is a boundary between disordered and step-terrace interface morphology, such as a

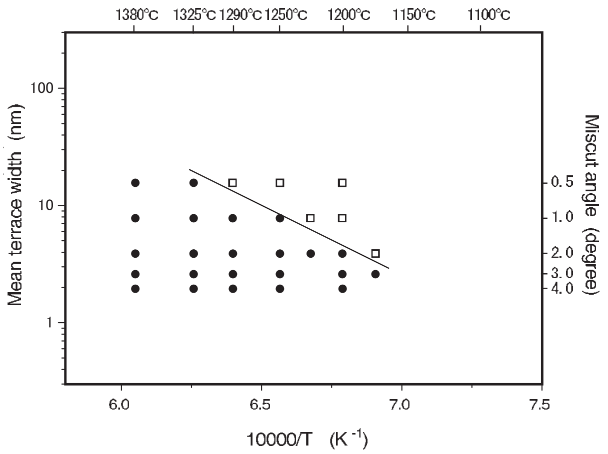

FIG. 4. Plots of interface structure as a function of mean terrace width with various miscut angles and thermal silicon oxidation temperatures. Solid circles and open squares represent step-terrace and disordered structures at the interface, respectively. Some plots for the 0.5° miscut Si (001) are derived from Ref. [10].

kind of phase transition, which depends on the oxidation temperature and the mean terrace width of Si substrate. We indeed succeeded in controlling the phase transition by changing l. In addition, the boundary exhibits an Arrehnius relationship as a function of l and transition temperature, indicating that the step-terrace structure formation at the interface is actually limited by diffusion-related behavior. From the slope in Fig. 4, using the relationship $D_{\mathrm{ST}} = l^2 t$ under the assumption that steps will emerge when the diffusion length of some species becomes the mean terrace width, we derived the Arrhenius equation $D_{\mathrm{ST}} = 0.7 \exp(-4.9 \pm 0.7\ \mathrm{eV/kT})\ \mathrm{cm}^2/\mathrm{s}$, where k is Boltzman's constant. The diffusion coefficient obtained by the boundary, D_{ST}, should correspond to D in Eqs. (2) and (3). We found that the diffusion coefficient agrees with those of the self-diffusivity of silicon via SiO molecules $D_{\mathrm{SiO}}^{\mathrm{SD}}$ [15] within our experimental error, even though these values were obtained by different methods. At 1200 °C, for example, $D_{\mathrm{ST}} = 1 \times 10^{17}\ \mathrm{cm}^2/\mathrm{s}$, $D_{\mathrm{SiO}}^{\mathrm{SD}} = 2 \times 10^{17}\ \mathrm{cm}^2/\mathrm{s}$. In addition, D_{ST} is different from those of oxygen in silicon oxides [16], silicon in silicon [17], and interstitial Si and vacancies in Si [10]. These results support the lateral diffusion of Si species, most likely SiO [15], at the interface. The transition we observed at 1200 °C from 0.2 to 2.0% can be explained as follows: the diffusing Si species, i.e., SiO, become oxidized in the oxide when they meet oxygen atoms traveling through it, which greatly reduces the number of Si species returning to the interface. Then, the second term in Eq. (3) contributes less to the roughening and the first term become dominant.

In conclusion, on the basis of scaling analyses, we quantitatively determined the universal classes of the oxidation kinetics that governs roughening at the Si(001)-SiO_2 interface during thermal silicon oxidation above 1150 °C in dilute oxygen atmosphere in a furnace. The linear Langevin equation [Eq. (2)] is favored under the oxidation condition (i.e., high temperatures and low oxygen concentration) that promotes the probability of the lateral diffusion of Si species at the growing interface.

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*Corresponding author.
Email address: homi@will.brl.ntt.co.jp

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