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Kinetics of oxidation on hydrogen-terminated Si(100) and (111) surfaces stored in air

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We have investigated the oxidation of hydrogen-terminated Si(111) and (100) surfaces stored in air, using synchrotron radiation photoemission spectroscopy and infrared absorption spectroscopy in the multiple internal reflection geometry. We demonstrate that water present in air is predominantly involved in the oxidation of surface Si–H bonds, and that native oxide starts to grow when the surface hydrogen coverage is decreased. In order to explain the latter phenomenon, we propose a kinetic model of oxidation which considers the manner in which native oxide formation preferentially occurs on those portions of the surface where the Si–H bonds are oxidized. We suggest that the oxidation of surface Si–H bonds, the rate of which is strongly dependent on the humidity of air, is a rate-limiting step in the native oxide formation on hydrogen-terminated Si surfaces. © 1996 American Institute of Physics. [S0021-8979(96)03507-4]

I. INTRODUCTION

It is well established that treatment in dilute hydrofluoric acid (HF) solution produces a hydrogen-terminated, clean Si surface.^{1–4} This treatment is widely used in the fabrication of semiconductor devices such as metal–oxide–semiconductor (MOS) devices. The hydrogen-terminated Si surface is chemically inert, but, when exposed to air for a long term, is oxidized by oxidants present in air to generate the so-called native oxide film. Since native oxide most probably degrades the quality of Si epitaxial film or thin gate oxide film which is grown on the HF-treated Si surface, the undesirable formation of native oxide film must be suppressed. In order to fabricate high-reliable ultra-large-scale integration (ULSI) devices, therefore, we need an understanding of the mechanism of oxidation of hydrogen-terminated Si surfaces in the atmospheric environment.

A number of studies have so far been carried out to investigate the chemical and structural natures of HF-treated, hydrogen-terminated Si surfaces.^{5,6} Interestingly, x-ray photoemission spectroscopy (XPS) studies^{7,8} revealed that oxidation proceeds layer by layer on HF-treated surfaces stored in water or exposed to room air; that is, the native oxide thickness increases step by step. An important point about this phenomenon is that the native oxide thickness exhibits a steep increase and then saturates. In our previous studies,^{9,10} we have investigated the early stages of oxidation of hydrogen-terminated Si(111) and (100) surfaces stored in air, using infrared absorption spectroscopy (IRAS) in the multiple internal reflection geometry. We demonstrated that the oxidation of the outermost Si atom proceeds through the successive conversion of both Si–H and Si–Si backbonds around the Si atom into the Si–O bond,⁹ and that moisture in air plays a crucial role in the oxidation of the topmost layer of hydrogen-terminated Si surfaces.¹⁰ However, the atomic

processes leading to the formation of native oxide have not yet been fully elucidated.

The main purpose of this study is to elucidate how the oxidation of surface Si–H bonds is correlated with the native oxide formation. Synchrotron radiation photoemission spectroscopy (SR-PES) is utilized to follow oxidation-induced chemical changes of hydrogen-terminated Si surfaces and to monitor the evolution in the native oxide thickness caused by exposure of the surface to room air. SR-PES, in which soft x rays with a variable photon energy are used as the exciting photon source, is quite surface sensitive, and therefore is beneficial to the investigation of initial stages of oxidation of Si surfaces. As in our previous works,^{9–12} we also use IRAS to follow oxidation-induced chemical changes in the surface Si hydride species. In order to interpret PES and IRAS data, we propose a kinetic model of oxidation in which the formation of native oxide is supposed to follow the oxidation of surface Si–H bonds. We are able to explain the evolution of both the surface hydrogen coverage and the native oxide thickness in terms of the proposed oxidation model.

II. EXPERIMENT

Samples used here were obtained from *n*-type P-doped Si(100) and (111) wafers. The samples were treated in dilute hydrofluoric acid (HF) following the RCA cleaning. After the surface treatment, the samples were stored in room air with different humidities and in a desiccator in which the relative humidity was set at 10%.

The oxidation of hydrogen-terminated Si surfaces caused by exposure to air was monitored by IRAS and SR-PES. IRAS measurements were performed using the multiple internal reflection (MIR) geometry.¹³ MIR-IRAS is quite surface sensitive and is a powerful tool for investigating chemical states of Si surfaces.¹⁴ The samples used for the measurements were $0.38 \times 10 \times 50 \text{ mm}^3$ with 45° bevels on each of the short edges. The infrared radiation exiting an interferometer (BOMEM MB-100) was focused at normal

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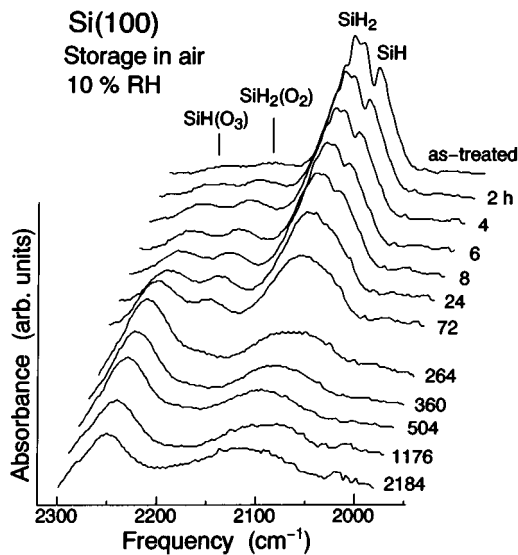


FIG. 1. Si-H stretching vibration spectra of the hydrogen-terminated Si(100) surface exposed to room air with 10% relative humidity for different exposure times. The figure attached to each spectrum indicates the exposure time (in hours).

incidence onto one of the two levels of the sample, and propagated through the wafer, internally reflecting about 100 times. The radiation that exited the sample through the other level, was focused onto a liquid-N₂-cooled HgCdTe detector. The reflection spectra measured for chemically oxidized Si surfaces were used as the background reference spectra. The chemical oxidation was performed by immersing the samples into a 1:1 boiled solution of H₂SO₄:H₂O₂ for 5 min.

SR-PES measurements were carried out on beam line BL-2 at the Synchrotron Radiation Laboratory (SRL), University of Tokyo. The synchrotron radiation emerging from a 400-MeV storage ring (INS-SOR) was monochromatized with a grazing incidence monochromator and then irradiated onto the sample in a ultrahigh vacuum (UHV) chamber, the base pressure of which was in the range of 10⁻¹¹ Torr. The photoelectrons were detected with a double-pass cylindrical mirror analyzer (DCMA). To monitor the formation of native oxide, the samples stored in room air for different durations were transferred into the UHV chamber, and valence band and Si 2*p* core-level photoemission spectra were measured for each sample with photon energies of 90 and 130 eV, respectively.

III. RESULTS AND DISCUSSION

A. Si(100)

Figure 1 depicts typical Si-H stretching vibration spectra of the HF-treated Si(100) surface exposed to room air with 10% relative humidity, collected for different exposure times. As is shown in the top spectrum of the figure, the surface immediately after HF treatment exhibits two peaks at 2080 and 2110 cm⁻¹ which are due to the monohydride Si (SiH) and dihydride Si (SiH₂), respectively.¹⁵ The Si-H stretching vibration spectrum for the HF-treated Si(100) surface is characterized by an intense SiH₂ peak. This is simply due to the fact that the ideal, bare Si(100) surface has two

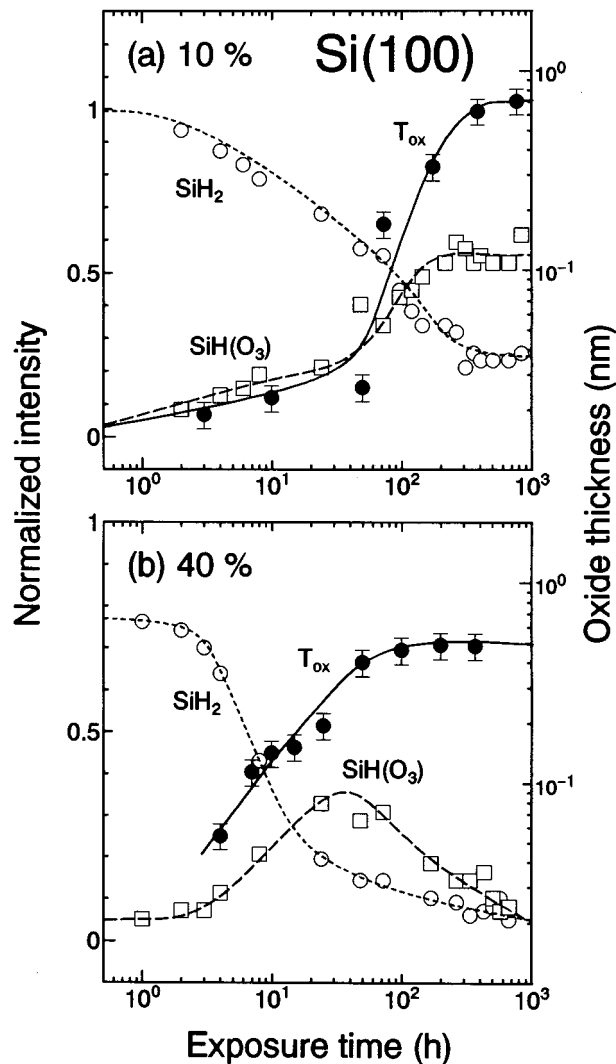


FIG. 2. SiH₂ intensity and oxide thickness as a function of exposure time, collected for (a) 10% and (b) 40% humidity.

dangling bonds per Si atom, and hydrogen termination of those dangling bonds produces the dihydride Si. When the surface was exposed to air for several hours, new peaks appeared at 2200 and 2250 cm⁻¹, which are attributed to intermediate oxidation states SiH₂(O₂) and SiH(O₃), respectively.^{3,9,12} SiH₂(O₂) and SiH(O₃) refer to atomic configurations in which, besides hydrogen atoms, two and three oxygen atoms are bound to the surface Si atom, respectively. As shown in Fig. 1, the hydride modes, SiH and SiH₂, decreased in intensity with exposure time. This clearly indicates that surface Si atoms previously having Si-H bonds were oxidized by exposing the surface to room air. On the other hand, the intensities of SiH₂(O₂) and SiH(O₃) initially increased and then dropped. We have previously interpreted the observed evolution in intensity of the hydrides and intermediate oxidation states as being due to the oxidation process in which four bonds around the surface Si atom, which initially were the Si-Si backbond and the Si-H bond, are converted to the Si-O bond in succession.⁹ Later, we demonstrated that the rate of the oxidation of surface Si atoms strongly depends on the humidity of air, rather than the sur-

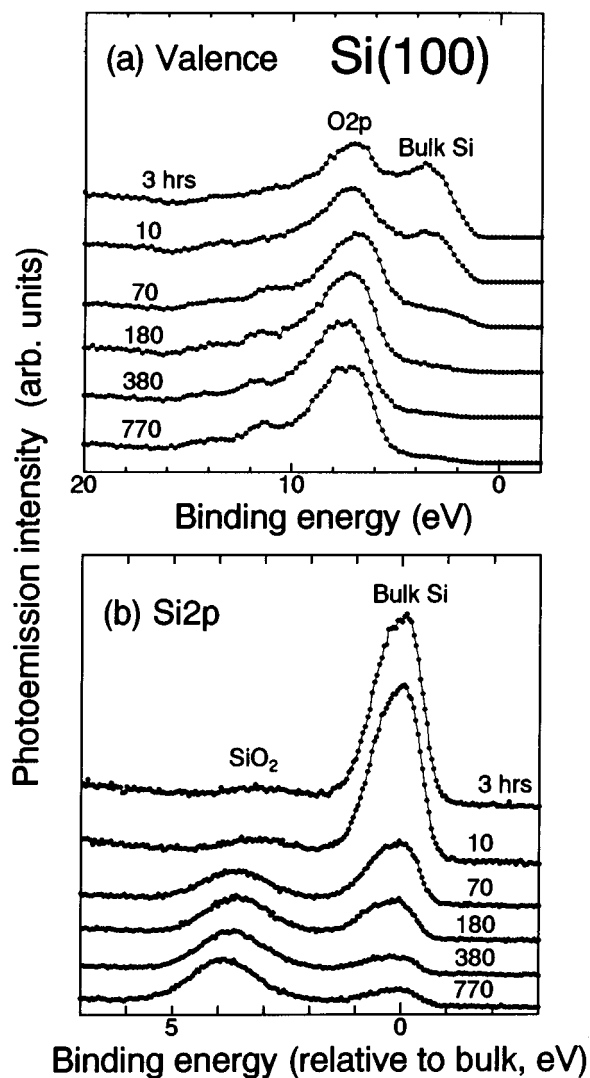


FIG. 3. (a) Valence band and (b) Si $2p$ core-level photoemission spectra of the hydrogen-terminated Si(100) surface exposed to room air with 10% relative humidity for different exposure times. The figure attached to each spectrum indicates the exposure time (in hours).

face roughness.¹⁰ In Fig. 2, we plot the SiH₂ intensity as a function of exposure time, taken for two different humidities: 10% and 40%. We have normalized the SiH₂ intensities to the initial intensity, i.e., the SiH₂ intensity measured for the surface immediately after HF treatment. We see the oxidation of surface Si atoms is significantly retarded for lower humidity. We therefore confirm that moisture in room air is crucial to the oxidation of the topmost layer of hydrogen-terminated Si(100) surfaces.

Figures 3(a) and 3(b) respectively show valence band and Si $2p$ core-level photoemission spectra of the hydrogen-terminated Si(100) surface exposed to room air with 10% relative humidity, collected for different exposure times. In the valence band photoemission spectra of Fig. 3(a), a broad peak at 3-eV binding energy is attributed to photoemission of the valence band electrons of the bulk Si crystal. A broad peak observed at 7 eV is due to the O $2p$ lone pair orbital of silicon oxide, SiO₂. As the exposure time increases, the bulk Si peak decreases in intensity whereas the oxide peak grows

up. This clearly shows that the hydrogen-terminated surface becomes increasingly oxidized by exposure to air. In the Si $2p$ core-level spectra shown in Fig. 3(b), a broad peak which is located at binding energies approximately 4 eV higher than the bulk Si peak is due to SiO₂. The oxide peak intensity increases with increase of exposure time, indicating the formation of native oxide on the surface exposed to air. We can determine the oxide thickness from the Si $2p$ photoemission intensity ratio between the bulk Si and SiO₂ peaks, according to the formula given by Himpsel *et al.*¹⁶ We plot in Fig. 2 the oxide thickness thus determined as a function of exposure time, together with the normalized intensities of SiH₂ and SiH(O₃). Figure 2 indicates three important points: First, the oxide formation is significantly retarded when the humidity of air is reduced. This gives further evidence to our conclusion that water plays a crucial role in the oxidation of the hydrogen-terminated Si(100) surface. Second, when the SiH₂ intensity drops, the oxide thickness starts to increase. This strongly suggests that when the topmost layer of the hydrogen-terminated Si(100) surface is oxidized, the surface becomes easily attacked by O₂ and H₂O, leading to a steep increase in the oxide thickness. Third, the oxide thickness saturates for a long-term exposure to air. The saturation thickness was approximately 0.6 nm. We have previously investigated the oxidation of hydrogen-terminated Si surfaces by ultraviolet (UV) ozone, and revealed that when the oxide thickness reaches about 0.5 nm, the oxidation rate begins to level off.¹¹ Note that this thickness is close to the saturation thickness mentioned above. We therefore consider the oxide thickness of about 0.6 nm as a critical thickness at which the structure of silicon oxide film changes and the oxidation mechanism varies correspondingly.

Another interesting point about Fig. 2 is that both the oxide thickness and the SiH(O₃) intensity begin to increase simultaneously. This implies that oxidation of Si-Si backbonds of the surface Si atom takes place as native oxide is formed. This is reasonable because the backbonds must be oxidized to form a silicon oxide film which is mainly composed of Si-O-Si bridging bonds. The SiH(O₃) intensity should decrease for a long-term exposure to air, because the remaining Si-H bonds are finally oxidized by water or O₂. This is the case for 40% humidity, as shown in Fig. 2(b). For 10% humidity, however, the SiH(O₃) intensity does not drop even for a 1000-h exposure to air. This suggests that surface Si-H bonds remain after such a prolonged exposure to air, and provides evidence that moisture is mainly involved in the oxidation of surface Si-H bonds.

B. Si(111)

Figure 4 shows typical Si-H stretching vibration spectra of the HF-treated Si(111) surface exposed to air with 40% relative humidity, recorded at different exposure times. As is shown in the top spectrum of Fig. 4, the surface immediately following HF treatment exhibits two peaks at 2080 and 2130 cm⁻¹ which are due to the monohydride Si and trihydride Si (SiH₃), respectively.¹⁵ The SiH peak is dominant since the ideal, bare Si(111) surface has a dangling bond per Si atom. However, other hydride modes, SiH₂ and SiH₃, showed up

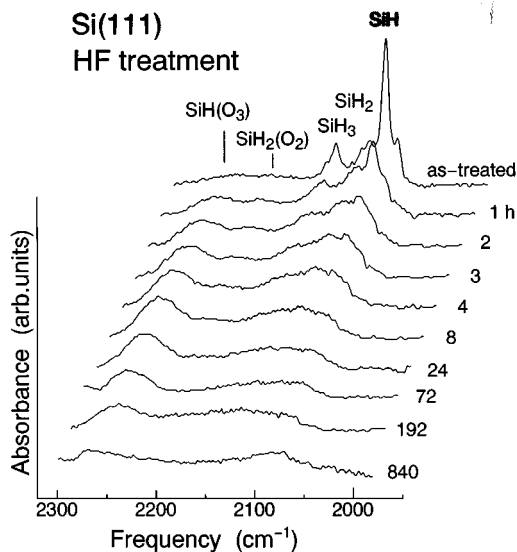


FIG. 4. Si-H stretching vibration spectra of a series of HF-treated Si(111) surfaces exposed to air with 10% humidity for different durations. The figure attached to each spectrum indicates the exposure time (in hours).

too. This implies that the HF-treated Si(111) surface is rough on the atomic scale, which is consistent with the IRAS results of Chabal *et al.*^{15,17} When the surface was exposed to air for a few hours, the SiH peak almost completely vanished, indicating the oxidation of Si-H bonds protruding from the surface. Figure 5 shows the evolution of the SiH and SiH(O₃) peak intensities collected for two different humidities: 10% and 40%. We can clearly see that the oxidation of surface Si atoms is remarkably delayed when the humidity is reduced, which is the same trend as observed for Si(100).

We plot in Fig. 6 representative valence band and Si 2*p* core-level photoemission spectra of the hydrogen-terminated Si(111) surface exposed to air with 10% relative humidity, measured at different exposure times. In Fig. 6, we see that with increasing exposure time, the bulk Si peak decreases whereas the oxide peak increases. This is the same trend as was observed on the Si(100) surface, and indicates that native oxide is generated on hydrogen-terminated Si(111) surfaces during storage in room air. However, there is a marked difference from the Si(100) case: At exposure times below 10 h the oxide-induced peak is quite weak, as is shown in the topmost spectrum of Fig. 6(a). Figure 6(b) shows that the SiO₂ peak cannot be identified at exposure times below 50 h. These observations suggest that oxidation of Si-Si backbonds of the surface Si atom is significantly suppressed on the hydrogen-terminated Si(111) surface at the earliest stage of oxidation. In contrast to Si(111), the formation of a thin native oxide was observed on the Si(100) surface even at exposure times below 10 h, as shown in Fig. 3. The oxide thickness at these exposure times was approximately 0.2 nm. The oxide thickness did not increase notably until the hydrogen coverage was reduced. We therefore speculate that a small amount of native oxide is formed on the hydrogen-terminated Si(100) surface immediately after HF treatment and it may have a stabilizing effect on the surface.

We plot in Fig. 5 the native oxide thickness collected for two different humidities, as a function of exposure time. The

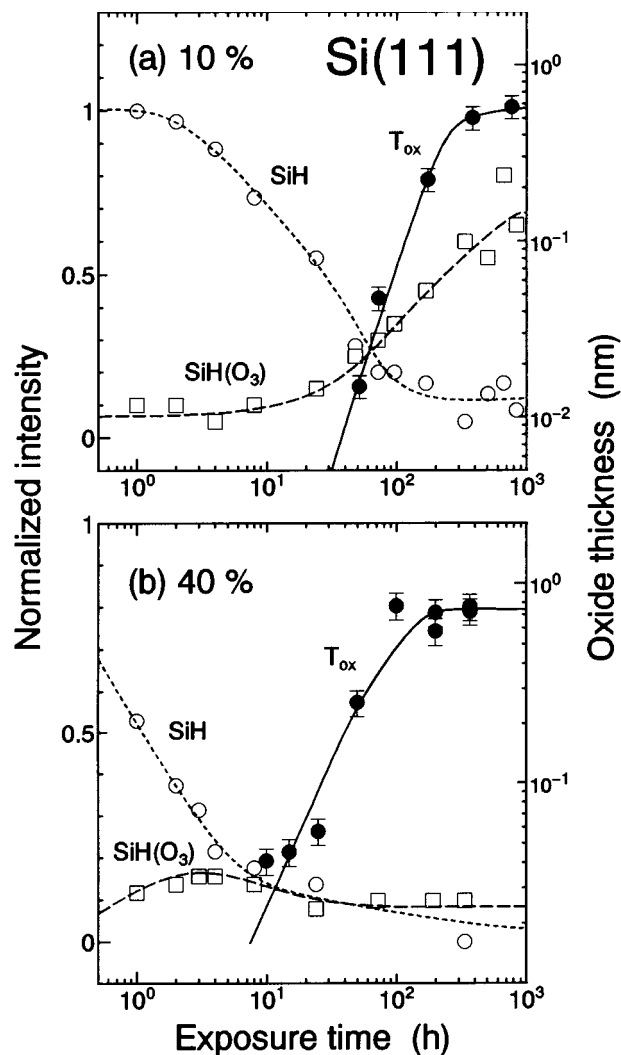


FIG. 5. SiH peak intensity and oxide thickness as a function of exposure time, measured for two different humidities: (a) 10% and (b) 40%.

native oxide formation was retarded when the humidity of air was low. Also, we see that when the SiH intensity decreases, the oxide thickness starts to increase steeply. These are the same trends as was observed for the Si(100) surface. It is interesting to note that for higher humidity, SiH(O₃) does not grow; on the other hand, for lower humidity the SiH(O₃) intensity and the oxide thickness increases simultaneously. This suggests that when the humidity is high, almost all the surface Si-H bonds are oxidized before the backbond oxidation occurs, and therefore confirms the idea that moisture is mainly involved in the oxidation of surface Si atoms having Si-H bonds protruding from the surface.

IV. KINETICS OF OXIDATION

The experimental results presented above suggest that water present in air is crucial to the oxidation of surface Si-H bonds. We understand that H₂O much more readily reacts with the surface Si-H bond than O₂. Oxidation in-

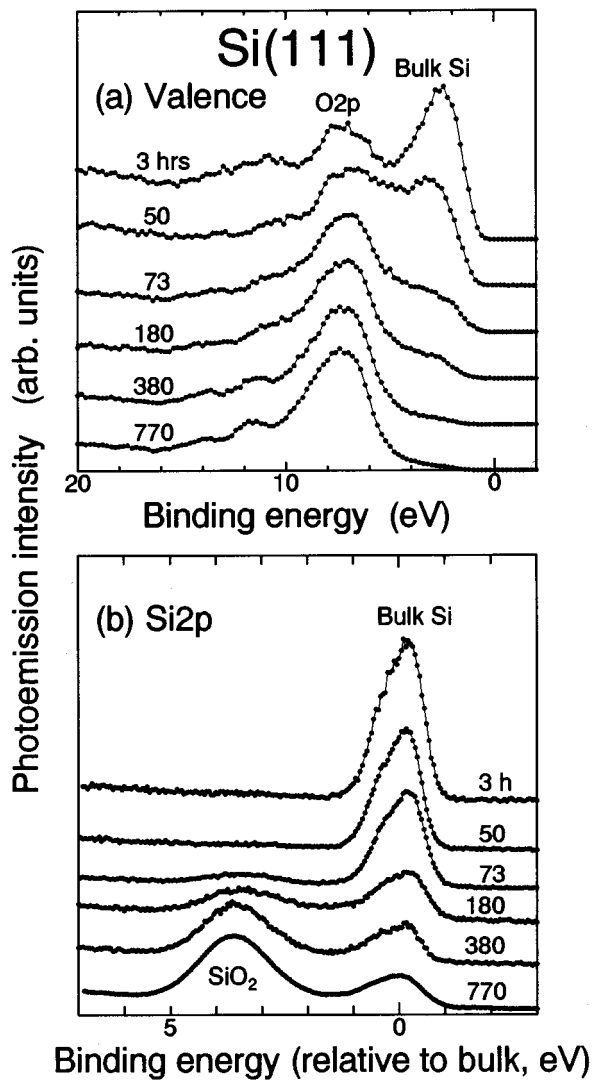
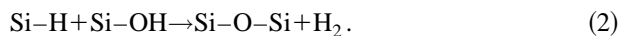
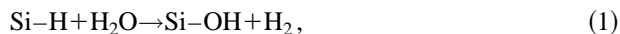


FIG. 6. (a) Valence band and (b) Si 2p core-level photoemission spectra of the hydrogen-terminated Si(111) surface exposed to air with 10% relative humidity for different exposure times. The figure attached to each spectrum indicates the exposure time (in hours).

duced by water most probably generates the Si-OH and the Si-O-Si bridge bonds on the surface through reactions as follows:



As a consequence of these reactions, the surface which initially was *hydrophobic*, becomes *hydrophilic*. When the surface turns hydrophilic, then it will more readily react with O_2 and H_2O compared to the hydrogen-terminated, hydrophobic surface. This would lead to an enhancement in the oxidation rate. Indeed, the present experimental results clearly show that when the surface hydride species diminish, native oxide starts to grow. Based on these arguments, we propose a kinetic model of oxidation which considers the manner in which native oxide formation preferentially occur on those portions of the surface where surface Si atoms are oxidized.

Oxidation of Hydrogen-Terminated Si Surface

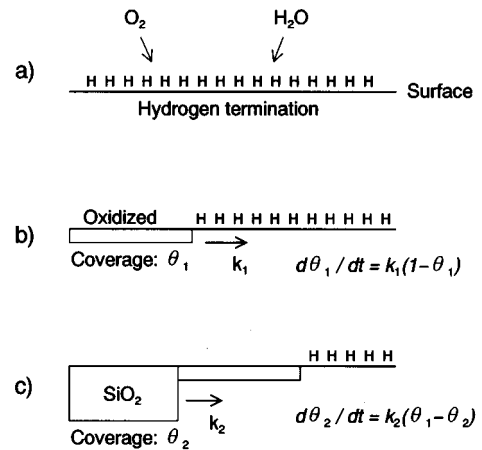


FIG. 7. Oxidation model proposed.

The oxidation model proposed is schematically illustrated in Fig. 7. We assume that the oxidation is a two-step, first-order process. At the first step of the oxidation, surface Si-H bonds are oxidized to produce an oxidized surface, as shown in Fig. 7(b). We here consider the *oxidized* surface as one on which surface Si-H bonds were converted to oxygen-related bonds, such as Si-OH and Si-O-Si bonds. This oxidation process most likely occurs on the entire surface, irrespective of whether steps and kinks are present or not,¹⁰ and could be strongly influenced by the concentration of water present in air, i.e., the humidity of air. The rate equation for this oxidation process can be simply given by

$$\frac{d\theta_1}{dt} = k_1(1 - \theta_1), \quad (3)$$

where θ_1 is the coverage of the oxidized surface, and k_1 is the oxidation rate. The SiH peak intensity on Si(111) or the SiH_2 peak intensity on Si(100) gives the measure of the hydrogen coverage and therefore should be proportional to the value $(1 - \theta_1)$. At the second step of the oxidation, native oxide formation favorably proceeds on the oxidized surface, as is depicted in Fig. 7(c). Based on the finding that the oxide thickness reached the saturation value of about 0.6 nm for a prolonged exposure to air, we assume the lateral growth of a native oxide layer with approximately 0.6 nm thick. Then the rate equation for this process can be given by

$$\frac{d\theta_2}{dt} = k_2(\theta_1 - \theta_2), \quad (4)$$

where θ_2 is the surface coverage of a 0.6-nm-thick native oxide layer and k_2 is the rate of native oxide formation. In this model, when the entire surface is covered with a 0.6-nm-thick native oxide layer, $\theta_2 = 1$. We can obtain the hydrogen coverage $(1 - \theta_1)$ and the oxide coverage θ_2 by integrating Eqs. (3) and (4) with the initial condition of $\theta_1 = \theta_2 = 0$. We plot in Fig. 8 the calculated values of $(1 - \theta_1)$ and θ_2 as a function of exposure time, for $k_1 = 0.5 \text{ h}^{-1}$ and $k_2 = 0.5, 0.05$,

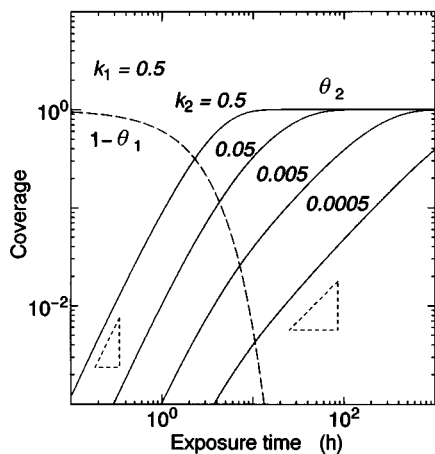


FIG. 8. Calculated values of $(1-\theta_1)$ and θ_2 as a function of time (in hours), with $k_1 = 0.5 \text{ h}^{-1}$, and $k_2 = 0.5, 0.05, 0.005$, and 0.0005 h^{-1} .

0.005, and 0.0005 h^{-1} . An important point about Fig. 8 is that when the hydrogen termination persists, the rate of increase of the oxide coverage; i.e., the slope of the curve is enhanced compared to the case where the hydrogen coverage is low, as depicted by two dashed triangles. A simple calculation predicts that when the surface is almost completely terminated with hydrogen, the oxide thickness increases in proportion to the square of the exposure time t ; that is, $\theta_2 \propto t^2$. On the other hand, if the hydrogen termination is broken, the oxide thickness varies linearly with the exposure time; that is, $\theta_2 \propto t$. This difference reflects the fact that native oxide growth is suppressed when the surface is covered with a hydrogen monolayer which acts as a passivation layer for oxidation.

Figure 9 shows comparison of the calculated values of $(1-\theta_1)$ and θ_2 with the normalized intensity of SiH_2 and the native oxide thickness collected for the hydrogen-terminated Si(100) surface exposed to air with three different humidities. The oxide thicknesses have been normalized to the saturation thickness. Agreement between the experiment and calculation (solid curves) is good for 10% and 20% humidity. In particular, the calculation reproduces the trend that the native oxide thickness exhibited a steep increase when the surface hydrogen coverage began to decrease. However, we notice that the calculation cannot explain the experiment at low exposure times. We attribute this discrepancy to the formation of a thin native oxide which, as described above, occurs immediately after HF treatment. Dashed curves in Fig. 9 represent the results of model calculation obtained on the assumption that the oxidation of surface Si-H bonds and the native oxide formation proceed independently of each other and simultaneously; that is, the native oxide formation is a single-step process. Under this assumption, the calculation cannot explain the observed steep increase in the oxide thickness. For 40% humidity, the evolution of the oxide thickness can be explained with a nonsimultaneous, single-step model. It seems that the oxidation process for higher humidity is different from lower humidity. The rate parameters k_1 and k_2 used in the calculations were approximately an order larger for 40% humidity than for 10% and 20%. This indicates that

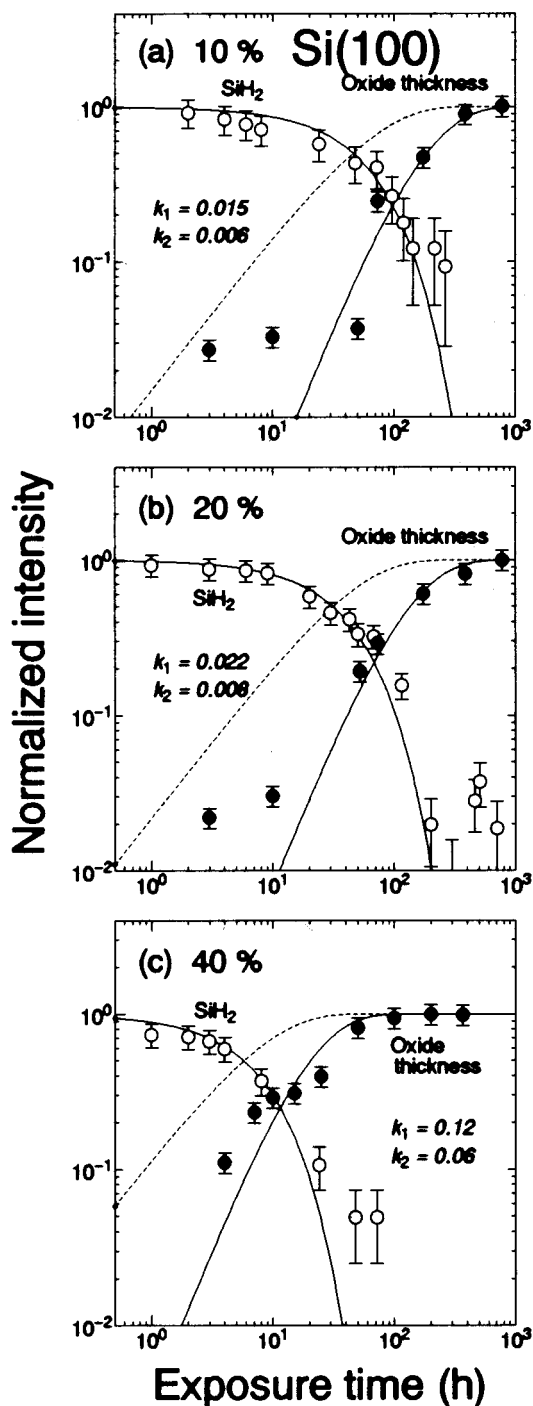


FIG. 9. Normalized SiH_2 intensity and oxide thickness for the Si(100) surfaces exposed to air with (a) 10%, (b) 20%, and (c) 40% humidity, compared with the calculated values of $(1-\theta_1)$ and θ_2 . The values of k_1 and k_2 are in the units of h^{-1} .

moisture in room air plays a crucial role in the oxidation of surface Si-H bonds and the formation of native oxide.

Figure 10 plots the results of model calculation compared with the normalized intensity of SiH and the normalized oxide thickness obtained for the Si(111) surface exposed to air with three different humidities. Agreement between the experiment and calculation (solid curves) is fairly good. Es-

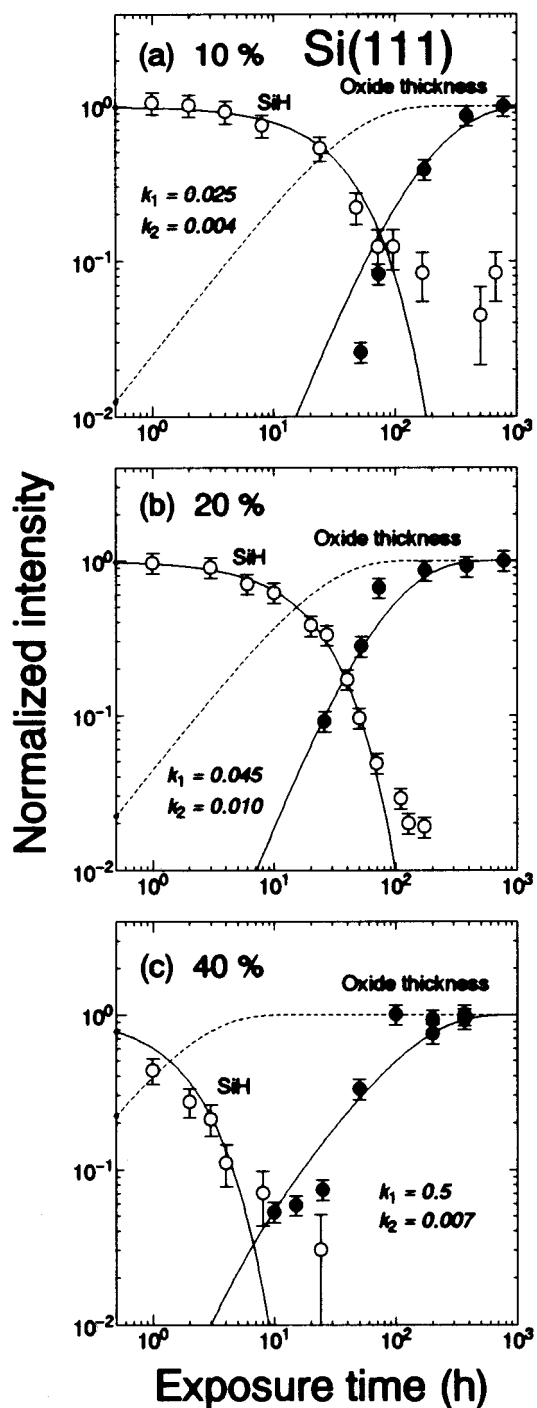


FIG. 10. Normalized SiH intensity and oxide thickness for the Si(111) surfaces exposed to air with (a) 10%, (b) 20%, and (c) 40% humidity, compared with the calculated values of $(1-\theta_1)$ and θ_2 . The values of k_1 and k_2 are in the units of h^{-1} .

pecially for 10% and 20% humidity, the calculation adequately reproduces the steep increase in the oxide thickness which took place when the hydrogen coverage started to decrease. On the other hand, a good fit to the experiment was not obtained with a single-step model (dashed curves). An interesting point about Fig. 10 is that k_1 is strongly dependent on the humidity, while k_2 stays in the same order as the humidity is varied. This suggests that the oxidation of sur-

face Si-H bonds is predominantly caused by moisture in air, while the formation of native oxide is mainly caused by the attack of the oxygen molecule, which is the dominant oxidant present in air.

V. SUMMARY

We have studied the kinetics of oxidation on the hydrogen-terminated Si(111) and (100) surfaces stored in air, using synchrotron radiation photoemission spectroscopy and infrared absorption spectroscopy in the multiple internal reflection geometry. We confirmed that water present in air is predominantly involved in the oxidation of surface Si atoms having Si-H bonds, and native oxide starts to grow when most of the surface Si atoms are oxidized. We interpreted the latter phenomenon in terms of a kinetic model of oxidation which considers the manner in which the native oxide formation preferentially takes place on those portions of the surface where the surface Si atoms are oxidized. It was suggested that the oxidation of surface Si-H bonds, the rate of which is strongly dependent on the humidity of air, is a rate-limiting step in the native oxide formation.

The reason is not clear why water more readily reacts with the surface Si-H bonds than the oxygen molecule. To elucidate this difference in reactivity between H_2O and O_2 , we need further investigation; for example, *ab initio* molecular orbital calculations are necessary.

ACKNOWLEDGMENTS

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