Strong Temperature Dependence of the Initial Oxide Growth on the Si(111)\(^7\times 7\) Surface

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Temperature dependence of oxide growth kinetics on the Si(111)\(^7\times 7\) surface has been investigated by ultraviolet photoelectron spectroscopy. The amount of adsorbed oxygen on the Si surface during oxidation can be obtained from the O 2p spectra, which showed that the amount of oxygen increased with temperature below 600°C. It was found that the results cannot be described by the dual-oxide-species model for Langmuir-type adsorption in which adsorbed oxygen hardly moves on the surface. Therefore, we propose a new reaction model in which the migration and agglomeration of metastable oxygen on the surface should be considered. By studying the results of work function, we concluded that more adsorbed oxygen on the surface may incorporate into the back bond and a larger amount of defects can be generated at the Si/SiO\(_2\) interface at higher temperature.

Keywords: Ultraviolet photoelectron spectroscopy; Thermal oxidation; Si oxides; Adsorption kinetics; Real-time photoelectron spectroscopy

I. INTRODUCTION

Silicon oxide is one of the key ingredients in the fabrication of semiconductor devices and it has been investigated for decades, nevertheless, it still remains a subject of debate. At present, the strain occurring in the structure of SiO\(_2\) films is known to affect the growth of SiO\(_2\) films and produce defects (Si atom emission + vacancy generation) at the Si/SiO\(_2\) interface during oxidation of the Si(001) surface [1]. Though the initial oxidation process of the Si(111)\(^7\times 7\) surface has been investigated by both photoemission experiments [2, 3] and first-principles density functional theory calculations [4], the defects at the Si/SiO\(_2\) interface during oxidation of the Si(111) surface are far from being understood. Furthermore, in order to clarify kinetics of the oxygen on Si(111), it is imperative to present an initial oxidation model that can interpret the generation of point defects during the Si(111) oxidation.

The generally adopted dual-oxide-species (DOS) model [5] describes that the kinetics of oxygen on Si(001)2\times1 surface will change from the oxide growth to the etching of SiO\(_2\) films with increasing temperature. The model shows that two adsorbed oxygen species exist on the surface, the metastable oxygen M1, which can migrate on the surface and the stably bonded oxygen M2. It is noted that M1 can hardly migrate on the surface and its lifetime is extremely short, whereas the stable oxygen M2 is the main species on the surface below 600°C. In this case, it is difficult for the oxygen molecules to adsorb on a site where oxygen has already adsorbed so the rate of oxide growth is proportional to the coverage of oxygen on the surface. This is a Langmuir-type adsorption. On the other hand, two-dimensional oxide island growth, in which the metastable oxygen M1 migrates and then agglomerates forming two-dimensional nucleation sites on the Si(001) surface, and etching through SiO desorption also occurs above 600°C simultaneously. With increasing temperature, the active oxidation occurs and residence time of M1 is extremely short, and SiO desorbs without the growth of a SiO\(_2\) film.

Nevertheless, the migration of adsorbed oxygen molecules on the Si(111)\(^7\times 7\) surface at low temperature, as well as the longer life time of the metastable oxygen M1, has been observed by photoelectron measurements [6, 7] and scanning tunneling microscopy (STM) [8–10], which cannot be described by the DOS model. This obvious conflict calls for a detailed and thorough reinvestigation of the kinetics of oxygen adsorption on the Si(111)\(^7\times 7\) surface during the initial oxidation. Molecular oxygen on the Si(111)\(^7\times 7\) surface was also claimed based on STM [8, 9] and X-ray photoemission spectroscopy (XPS) [11]. Moreover, a metastable vibrational feature was observed, which was tentatively ascribed to a molecular chemisorption state, by electron energy loss spectroscopy [12]. It is suggested by the valence-band spectra [13] that the first adsorption site of oxygen is the back-bond of an adatom. However, the kinetics and lifetime of metastable oxygen on the Si(111) surface depend on temperature have not been determined so far.

In the present paper, real-time ultraviolet photoelectron spectroscopy (UPS) was performed to understand the temperature dependence of the kinetics of oxygen adsorption on the surface and to clarify the Langmuir-type adsorption on the Si(111)\(^7\times 7\) surface at low temperature, below 600°C, during initial oxidation. We propose a modified Langmuir-type adsorption model, which is affected by the generation of point defects, to interpret the results of temperature dependence. Moreover, it is intriguing to find that a larger amount of defects generate at the interface at higher temperature by the observation of the work function at various temperatures.

II. EXPERIMENTAL

The real-time ultraviolet photoemission measurements were performed using the Ultraviolet Photoelectron Spectroscopy-Reflection High Energy Electron Diffraction-Auger Electron Spectroscopy (UPS-RHEED-AES) composite apparatus at Tohoku University [1, 14].
The sample was a high Boron-doped $p$-type Si(111)7×7 substrate. The sample was cleaned by the simple RCA method and then introduced into the apparatus. In UHV, the sample was degassed by annealing and flushed to 1000°C to remove the surface oxide layer. The sample was heated by a pulse current to avoid trajectory changes in the low-energy secondary electrons due to the magnetic field of the heating current and the shift of the spectra due to the sample voltage. The temperature was measured using an infrared thermometer calibrated by a thermocouple pair. The ultraviolet light was the He-I (21.22 eV) resonance line. The flow rate of He (11 sccm) and discharge current (40 mA) were constant to maintain the light intensity during measurements in all the experiments. The valence band and secondary electron cutoff were alternatively measured during oxygen exposure. From these spectra, the O 2p photoelectron spectra and the secondary electron cutoff spectra were obtained in 22 and 21 s, respectively.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the time evolution of the O 2p photoelectron spectra while exposing the Si(111)7×7 surface to an oxygen pressure of 1.6×10⁻⁵ Pa at 600°C. The O 2p peak of the spectra was observed as a function of oxidation time. In order to summarize temperature dependence of the adsorbed oxygen, the oxygen uptake curves shown in Fig. 2 were obtained. The peak intensity of the O 2p intensities increase steeply during oxidations at all temperatures, and saturation of O 2p intensity strongly depends on temperature. In order to evaluate the O 2p intensity quantitatively, we analyzed the O 2p uptake curves by using Eqs. (1) and (2), which are based on the DOS model.

\[
I_{O2p} = A_0 (1 - \exp(-t/\tau)),
\]  

(1)

\[
I_{O2p} = A_0 \theta_0 \frac{1 - \exp(-kt/\tau)}{\theta_0 + \exp(-kt/\tau)}.
\]  

(2)

We used Eq. (1) for the curves below 600°C and Eq. (2) for the curves above 600°C in the 2D island growth [15]. Within the DOS model, the saturation of the O 2p intensity is assumed constant and independent of temperature, whereas the saturation of the O 2p intensity during the Si(111) oxidation strongly depends on temperature.
$A_0$ is added to improve the fitting, $1/\tau$ is the adsorption coefficient, $\kappa = (\theta_0 + 1)/\theta_0$, and $\theta_0$ gives the oxide coverage, at which the two-dimensional island growth commences. Figure 3 shows the temperature dependence of the amount of adsorbed oxygen $A_0$ and the adsorption coefficient $1/\tau$ during oxidation of the Si(111)7×7 surface at an oxygen pressure of $3\times10^{-5}$ Pa. $A_0$ increases whereas $1/\tau$ decreases with temperature, which indicate that the amount of adsorbed oxygen and the rate of oxygen adsorption depend on temperature during Langmuir-type adsorption on the Si(111)7×7 surface. It is seen from the experimental results that the characteristics of the oxidation of the Si(111) surface cannot be interpreted by DOS model (Fig. 4(a)) because the model assumes that the amount of adsorbed oxygen does not increase with temperature. In order to discuss the strong temperature-dependent results, we modified the DOS model and showed the new model in Fig. 4(b). The new model considers that the oxygen molecules precursor on the Si(111)7×7 surface migrate for some time before adsorbed on the adatom site and then dissociate to incorporate into the back bond of the adatom during the initial oxidation. Moreover, more adsorbed oxygen could insert into the backbond and diffuse to a deeper layer to form a thicker film with the temperature increased. The suggestion is compatible with the previous studied by STM which reported that the adsorbed oxygen molecules can agglomerate on the Si(111)7×7 surface [16] and also confirms the NEXAFS result that the incoming oxygen molecules can be trapped at the site where the oxygen atom has been inserted into the back bond [7, 17]. Therefore, it was found that the thickness depends on temperature, which violated the DOS model, but it could be interpreted by the modified model.

In order to obtain more information on the adsorbed metastable oxygen kinetics, we investigated the secondary electron spectra to obtain the time evolution of the work function. The work function $\Phi$ is given by Eq. (3),

$$E_F = E_k(VL) + h\nu - \Phi, \quad (3)$$

where $E_F$ is the Fermi energy, $E_k(VL)$ is the vacuum level, and $h\nu$ is the energy of the ultraviolet light. According to the cutoff of the secondary electron spectra, the vacuum level can be obtained, and then the work function can be calculated. In order to get the cutoff position of the vacuum level, we considered the shape of the secondary electron spectra in fitting the curves. We assumed that the ideal vacuum level is defined by the step function $H(E)$, which is expressed by Eq. (4),

$$H(E) = \begin{cases} \int_0^E I_0 \, \exp \left(-\frac{(x - E_k(VL))^2}{\omega^2}\right) \, dx, & \text{if } E \geq E_k(VL) \\ 0, & \text{if } E < E_k(VL) \end{cases} \quad (4)$$

However, owing to the influence of the electron energy analyzer on the secondary electron spectra, the response function of the electron energy analyzer is given by the Gauss function, which is expressed by Eq. (5),

$$G(E) = \exp \left(-\frac{E^2}{\omega^2}\right), \quad (5)$$

where $\omega$ is the width of the Gauss function. Subsequently, we can precisely fit the secondary electron spectra with Eq. (6), which is obtained by the convolution between $H(G)$ and $G(E)$ shown in Fig. 5.

$$I(E) = (H \ast G)(E) = \int_{-\infty}^{\infty} H(E - x) \cdot G(x) \, dx$$

$$= I_0 \int_{-\infty}^{\infty} \exp \left(-\frac{(x - E_k(VL))^2}{\omega^2}\right) \, dx. \quad (6)$$

We obtained the vacuum level by using Eq. (6) and the work function was by Eq. (3).

Figure 6 shows temperature dependence of the time evolution of the work function during oxidation of the Si(111)7×7 surface. The work function increased sharply and decreased with oxidation time at room temperature, whereas it monotonously increased with increasing oxidation time above 300°C (Fig. 6). Basically, the time evolution of work function can be discussed by considering the changes in the work function due to the surface dipole layer ($\Delta\phi_{\text{dip}}$) and the effect of band bending due to the generation of defects at the Si/SiO2 interface ($\Delta BB$) [14]. Figure 7 schematically shows the change in the surface...
FIG. 6: Temperature dependence of the time evolution of the work function during oxidation of the Si(111) surface.

FIG. 7: Schematic illustration of the change in the surface dipole layer due to the oxygen adsorbed on the surface and inserted into the back bond.

dipole layer due to the oxygen adsorbed on the surface and the oxygen incorporated into the back bond. Since the electronegativity of oxygen is higher than that of silicon, the electron density moves toward the oxygen atoms when the oxygen and the silicon atoms bond. As a result, an electric dipole layer forms on the Si surface. This alludes that the work function increases due to the surface dipole layer where the surface is negatively charged and the subsurface is positively charged, which shows that the metastable oxygen is adsorbing on the Si(111) surface. On the other hand, because of the electron transfer, the electropositive surface due to the electron transfer to the subsurface produces a reduction in the work function, this suggests that the adsorbed oxygen has been incorporated into the back bond.

Band bending due to the generation of defects at the Si/SiO$_2$ interface also affects the work function. When the Si surface is oxidized, the Si atoms move from the interface to the surface [18] and into the oxide [1], and defects are generated at the interface. Simultaneously, the interface state density also increases, which causes band bending. Band bending of Si(001) can be investigated from the surface state due to the dangling bonds on the surface [14, 19], whereas it is difficult to obtain the band bending because the peak intensity of the surface state on the Si(111) surface is extremely low. In this study, to estimate the adsorbed oxygen sites, we estimate the oxygen states from the chemical shift of the O 2$p$ spectra.

FIG. 8: O 2$p$ photoelectron spectra during oxidation at room temperature and 600°C. There are mainly two peaks. One is the O$_i$ peak near the kinetic energy $E_k = 15$ eV, derived from the state of the stable oxygen that is incorporated into the back bond (Si–O–Si), and the other is the O$_m$ peak near $E_k = 19$ eV, derived from the state of the metastable oxygen that adsorbs on the surface (Si–O, Si–O–O) [20].

The intensity of the O$_i$ peak is nearly the same as that of the O$_m$ peak at 600°C during the whole oxidation. It is indicated that the oxygen adsorbed on the surface almost immediately incorporates into the back bond during oxidation, which confirms the suggestion from temperature dependent results of the O 2$p$ photoelectron spectra that more oxygen would insert into the back bond. Also the result suggested that the $\phi_{SDL}$ decreases during the whole oxidation. However it is insufficient to interpret the increase of work function during oxidation, we consider the effect of band bending should be taken into account. The oxidized Si is a $p$-type substrate; therefore, band bending will cause the increasing of work function [14]. Therefore, it is suggested that a large amount of defects are generated at the interface at 600°C.

On the other hand, the intensity of the O$_m$ peak is higher than that of the O$_i$ peak at room temperature during oxidation. This result indicates that the oxygen cannot insert into the back bond as soon as the metastable...
oxygen adsorbs on the surface, which leads to a conclusion that the longer lifetime of metastable oxygen at room temperature than that at high temperature, meets a consensus with the previous study [6]. We assume that $\phi_{SDL}$ will sharply increase due to the oxygen adsorbed on the surface and $\phi_{SDL}$ will decrease after the oxygen inserted into the back bond. This assumption can be confirmed from the time evolution of the work function. As shown in Fig. 6, at room temperature, the work function decreases after reaching a maximum. As described above, since band bending affects the increase of the work function, band bending does less effect to the decrease of the work function.

IV. CONCLUSIONS

In this paper, we presented a study of the temperature dependence of the initial oxidation stage of the Si(111)7×7 surface through the time evolution of the O 2p peak intensity from valence band photoemission measured by real-time UPS. It is found that the amount of the adsorbed oxygen on the surface increased with temperature which is in contradiction to the former studied on the oxidation on Si(001). we consider that the metastable oxygen molecular could migrate on the Si(111) surface during Langmuir-type adsorption below 600°C. Through the change in the work function and the peaks in the O 2p spectra, the formations of metastable and stable oxygen on the Si(111) surface could be observed. In high-temperature oxidation, a larger amount of adsorbed oxygen will incorporate into the back bond of the adatom than that in low-temperature oxidation, so that the lifetime of the metastable oxygen on the surface at low temperature is longer than that at high temperature. The results reconciled the former results and also provided a detailed understanding of the generation of defects at the interface that more defects generated at the interface at higher temperature.

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