

Oxidation Processes on H-Terminated Si(100) Surfaces Studied by High-Resolution Electron Energy Loss Spectroscopy

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The initial oxidation processes of H-terminated Si(100) surfaces have been investigated by using high-resolution electron energy loss spectroscopy (HREELS) at room temperature and 300°C. It has been found that an oxygen atom adsorbs on one of the two back bonds of a surface Si atom until the oxygen coverage is 0.4 and in the sequential oxidation the other back bond site starts to be occupied by a second oxygen atom. The structural relaxation of Si-O-Si bonds is observed at oxygen coverages above 0.4.

1. INTRODUCTION

The interaction of oxygen with Si(100) has been of great technological and scientific importance. Especially, with a reduction in the design rule of ultra-large scale integrated circuits (ULSIs), device characteristics are seriously ruled by the roughness and chemical structures at the SiO₂/Si interface. The understanding of oxidation mechanisms on Si surfaces is essential in realizing the well-controlled SiO₂/Si interface on an atomic scale. Recently, H-termination of Si surfaces has been noticed in ULSI technologies because of controlling the surface reactivity. However, the oxidation process of H-terminated Si(100) surfaces and the role of H atoms on the surface reaction are not clear yet.

We have studied the oxidation of H-terminated Si(100) surface^{1, 2)} and reported that there exist two oxidation steps in the initial oxidation of H-terminated surfaces at room temperature.³⁾ In the present paper, we examine the structural relaxation of Si-O-Si bonds in the initial oxidation process by using high-resolution electron energy loss spectroscopy (HREELS).

2. EXPERIMENTAL

Experiments in the present study were carried out in an ultra-high vacuum (UHV) chamber, equipped with apparatuses of HREELS, low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The base pressure of the UHV chamber was less than 3×10^{-10} Torr. Reaction gases were introduced into the UHV chamber through a variable leak valve. Atomic hydrogen and oxygen were produced by using a tungsten filament heated at 1500°C. After the substrates were thermally cleaned at 1200°C in UHV chamber, the H-saturated surfaces were

prepared by atomic H exposure. The amount of molecular oxygen exposure was used as that of atomic oxygen exposure since the fraction of oxygen atoms dissociated by this method was not known. The oxygen coverage is defined as the ratio of the number of oxygen atoms to that of back bonds of surface Si atoms, determined by AES measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows HREELS spectra of H-terminated Si(100) surfaces with and without exposure to atomic oxygen at 300°C. Energy loss peaks for Si-2H species are observed in the spectrum of as-terminated Si(100) surfaces at energies of 61, 78, 112, and 258 meV, which correspond to a twisting (ν_{H1}), wagging (ν_{H2}), scissors (ν_{H3}) and stretching (ν_{H4}) mode, respectively. The LEED observation confirms that this surface has a 1x1 structure. Thus it can be concluded that a dihydride structure is formed on H-terminated Si(100) surfaces. The atomic O exposure leads to the appearance of two loss peaks at about 50 and 130 meV, corresponding to a symmetric bending (ν_{O1}) and asymmetric stretching (ν_{O2}) mode of Si-O-Si bonds, respectively. It should be noted that the loss peaks of Si-O-Si bonds shift to higher energies and the ν_{H4} peak of Si-2H splits into two peaks with increasing the amount of atomic O exposure. The vibrational energy shift reflects a change in local bonding structures, and the vibrational energy of the Si-2H stretching mode is changed by the number of O atoms bonded with the adjacent Si atom.⁴⁾ Therefore, these energy shifts give us important information on the atomistic oxidation process and the local bonding structure.

Figure 2 shows the loss peak intensities of the Si-2H stretching mode for the Si atom with zero or one

adjacent O atom ($n \leq 1$) and with two or three adjacent O atoms ($n \geq 2$) at 300°C as a function of atomic O exposure. Because of the resolution of HREELS measurements, the peaks of Si-2H and O-Si-2H and of 2O-Si-2H and 3O-Si-H

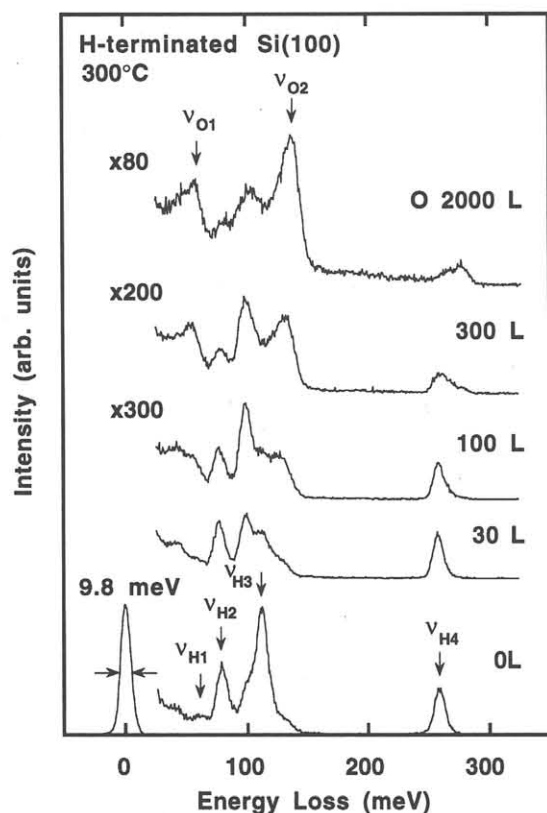


Fig. 1 HREELS spectra of H-terminated Si(100) surfaces without and with atomic oxygen exposure of 30, 100, 300 and 2000 L at 300°C. The exposure amount of atomic oxygen is indicated by using that of molecular oxygen.

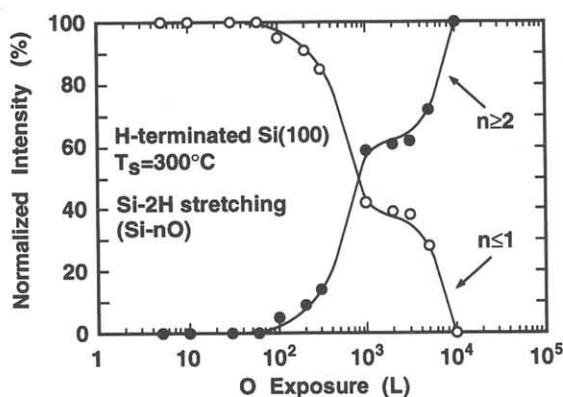


Fig. 2 Loss-peak intensities of a Si-2H stretching mode for the Si atom bonding with zero or one adjacent oxygen atom ($n \leq 1$) and with two or three adjacent oxygen atoms ($n \geq 2$) at 300 °C as a function of atomic oxygen exposure. The peak intensities are normalized to the intensity for the total Si-2H bonds.

could not be separated. In this figure, the peak intensities are normalized to the peak intensity for the total Si-2H bonds. It is noticed that the intensity of the Si-2H stretching mode with two O atoms increases above the 100-L-atomic-O exposure. At this exposure, the O coverage is estimated by AES measurements to be about 0.4. These results suggest that an O atom adsorbs on one of a pair of the back bonds until the O coverage of 0.4 and then the other site starts to be occupied by a second O atom, which leads to the conclusion that the oxidation of H-terminated Si(100) proceeds uniformly at the initial stage.

Figure 3 shows changes in the energy of a Si-O-Si asymmetric-stretching mode with increasing the O coverage. The experimental results for the oxidation of H-terminated Si(100) surfaces at room temperature and for the thermal oxidation at 850°C are also shown. A two-step process is clearly observed. Its turning point is also observed at an O coverage of about 0.4. The results of Figs. 2 and 3 indicate that the change in Si-O-Si geometric structures takes place when the second O atom adsorbs on the back-bond sites. Schaefer et al.⁵⁾ reported that the energy of a Si-O-Si asymmetric-stretching mode increases linearly with increasing oxide thickness in the oxidation on Si(100) clean surfaces. Therefore, the presence of Si-H bonds on the surface has an effect on structural relaxation of Si-O-Si bonds.

More detailed structural change in Si-O-Si bonds can be evaluated from a central-force-network model.^{6,7)} In this model, the frequencies of a symmetric bending, ν_{O1} , and of an asymmetric stretching mode, ν_{O2} , are described as

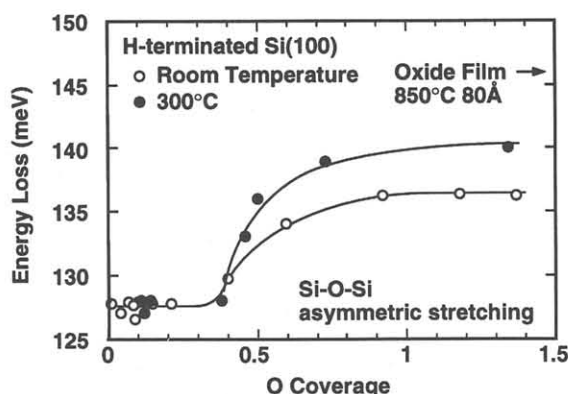


Fig. 3 Changes in the energy loss of a Si-O-Si asymmetric-stretching mode as a function of oxygen coverage for the oxidation on H-terminated Si(100) surfaces at room temperature and 300°C and for the thermal oxidation at 850°C.

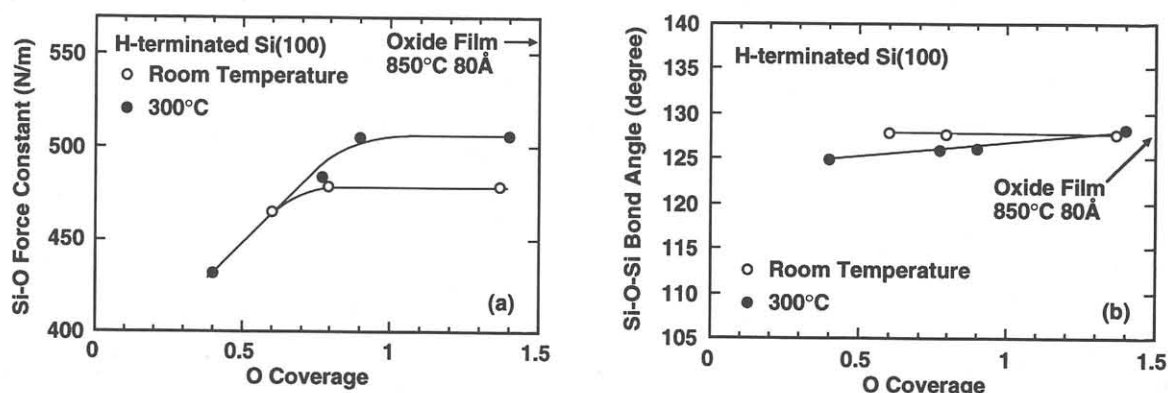


Fig.4 Changes in (a) the force constant and (b) the bond angle evaluated by using a central-force-network model as a function of oxygen coverage for the oxidation on H-terminated Si(100) surfaces at room temperature and 300°C and for the thermal oxidation at 850°C.

$$\nu_{O1}^2 = \frac{\alpha}{4\pi^2 m_O} (1 + \cos \theta), \quad (1)$$

$$\nu_{O2}^2 = \frac{\alpha}{4\pi^2 m_O} (1 - \cos \theta) + \frac{\alpha}{3\pi^2 m_{Si}}, \quad (2)$$

where α is the force constant of Si-O bonds, θ the bond angle of Si-O-Si, m_O and m_{Si} the mass of O and Si atoms, respectively. The force constants and the bond angles calculated by using Eqs. (1) and (2) are shown in Fig. 4(a) and 4(b) as a function of O coverage, respectively. It is found in Fig. 4(b) that in the second step the bond angle of Si-O-Si is nearly constant with O coverage and is independent of the substrate temperature. On the other hand, the dependences of the force constant of Si-O bonds on O coverage and on substrate temperature are similar to those of the vibrational energy for the Si-O-Si asymmetric stretching mode shown in Fig. 3. These results indicate that the structural change of Si-O-Si bonds in the second step is mainly caused by the change in the force constant rather than in the bond angle.

4. CONCLUSIONS

The initial oxidation processes of H-terminated Si(100) surfaces have been investigated by using high-resolution electron energy loss spectroscopy (HREELS). There are two steps in the initial oxidation of H-terminated Si(100) surfaces at 300°C. It is found that the adsorption of O atoms without changes in the vibrational energy of Si-O-Si species is occurred at O coverages below 0.4. On the other hand, the adsorption of O atoms at O coverages above

0.4 leads to the vibrational-energy change, which suggests the structural relaxation due to changing in force constants and bond angles. Moreover, an O atom adsorbs on one of the two back bonds of a surface Si atom until O coverage is 0.4 and in the sequential oxidation the other back bond site starts to be occupied by a second O atom. These results indicate that the oxidation of H-terminated Si(100) proceeds uniformly at the initial stage and that the change in Si-O-Si geometric structures takes place when the two back-bond sites of a surface Si atom are occupied by O atoms. This structural change is considered to originate from the change in the force constant.

References

- 1) H. Ikeda, K. Hotta, T. Yamada, S. Zaima, H. Iwano and Y. Yasuda, *J. Appl. Phys.* **77** (1995) 5125.
- 2) H. Ikeda, K. Hotta, T. Yamada, S. Zaima and Y. Yasuda, *Jpn. J. Appl. Phys.* **34** (1995) 2191.
- 3) H. Ikeda et al., *Ext. Abst. of Fifth Int. Conf. on the Formation of Semiconductor Interfaces*, Princeton, June 26-30, 1995.
- 4) J. A. Schaefer, D. Frankel, F. Stucki, W. Göpel and G. J. Lapeyre, *Surf. Sci.* **139** (1984) L209.
- 5) J. A. Schaefer and W. Göpel, *Surf. Sci.* **155** (1985) 535.
- 6) P. N. Sen and M. F. Thorpe, *Phys. Rev.* **B15** (1977) 4030.
- 7) F. L. Galeener, *Phys. Rev.* **B19** (1979) 4292.