

## Study on Oxidation of Si(100)-2x1 Surfaces by Scanning Tunneling Microscopy/Scanning Tunneling Spectroscopy

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The oxide formation on Si(100)-2x1 surfaces at room temperature has been studied by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). The formation of dark area and bright protrusions due to oxygen exposure is observed by STM. It can be found at bright protrusion sites that the density-of states of back bond states and  $\pi$  interaction states of dangling bonds are reduced with increasing oxygen adsorption. At an average SiO<sub>2</sub> thickness of 0.4 nm, the STS spectra indicates the formation of the valence band and the conduction band of SiO<sub>2</sub>.

### 1. INTRODUCTION

With a reduction of device dimensions in ultra-large scale integrated circuits (ULSI's), understanding and precise control of oxidation on Si surfaces becomes strikingly important in ULSI technologies. A number of studies on oxidation of Si surfaces have been reported by using various experimental techniques such as x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). However, the initial oxidation processes are not fully understood yet because of the lack of spatial resolution of these techniques. The combination of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) is a very powerful tool to get information on atomic arrangements and local electronic states of surfaces on an atomic scale.

In this paper, we present an *in-situ* study of oxidation processes of Si(100)-2x1 surfaces on an atomic scale by using STM/STS. The changes in electronic states of Si(100) surfaces by oxygen adsorption and the formation of potential barriers at the SiO<sub>2</sub>/Si(100) interface have been examined.

### 2. EXPERIMENTAL

An ultra-high vacuum (UHV) STM/STS system equipped with a cylindrical mirror analyzer for Auger electron spectroscopy (AES) and a reflection high-energy electron diffraction (RHEED) apparatus was used in this experiment. The base pressure in the UHV chamber was less than  $2 \times 10^{-11}$  Torr. N-type Si(100) substrates with a resistivity of 1000-2000  $\Omega$ cm were cleaned by direct current heating at 1100°C for 2 min at a pressure less than  $4 \times 10^{-10}$  Torr. After thermal cleaning, a 2x1 surface structure was observed by STM and the AES spectra did not show any trace of impurities such as carbon and

oxygen.

The initial oxidation of Si(100)-2x1 reconstructed was performed by exposing the clean surface to molecular oxygen in the pressure range of  $1 \times 10^{-8}$  to  $4 \times 10^{-7}$  Torr at room temperature. Atomic oxygen, produced by decomposition of oxygen molecules on a tungsten filament heated at 1500°C, was also used to grow thick oxide at a pressure of  $9 \times 10^{-6}$  Torr. STM imaging was performed in a constant current mode. In STS measurements, current-voltage curves were recorded by keeping a constant tip-sample separation and the spectra were obtained by averaging current-voltage curves measured at different positions in a scan area.

### 3. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the STM images of the clean Si(100) surface and the Si(100) surface exposed to molecular oxygen of 1 L (1 L =  $1 \times 10^{-6}$  Torr s), in which the same area is scanned at a negative sample bias of -1.3 V (occupied state images), respectively. Thermally cleaned surfaces have the 2x1 dimer-row reconstruction with defects, as shown in Fig. 1. After exposing the Si(100)-2x1 surface to 1-L-O<sub>2</sub>, the dark features are observed to spread around the defects existed on the surface prior to the O<sub>2</sub> exposure and are created also on dimer rows. In addition, a small number of bright protrusions can be also observed (not shown in this image). These features of room temperature oxidation agree well with previous reports<sup>1, 2)</sup> and both of the dark sites and bright protrusions are considered to be oxidized states. However, etching reaction cannot be ruled out on the formation of dark areas in the present experiment. Figures 2(a) and 2(b) show the STM images of the Si(100) surface exposed to 4.5-L- and 15 -L-O<sub>2</sub> observed at -1.4 and +3.0 eV, respectively. In Fig. 2(a), the bright protrusions are

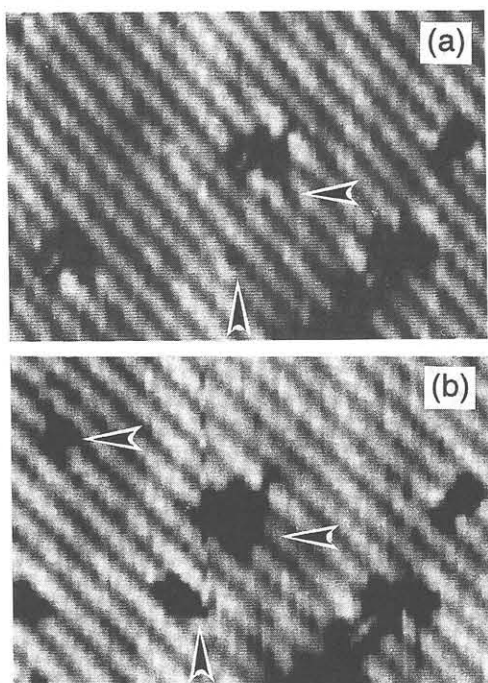


Fig. 1 STM images of the (a) Si(100)-2x1 surface and (b) 1-L-O<sub>2</sub>-exposed surface at room temperature for a sample bias of -1.3 V. The same area of about 9.4x13 nm<sup>2</sup> was scanned.

randomly nucleated and the density of dark areas is increased. The Si(100)-2x1 dimer structure is still observed in the remaining part of surfaces. In Fig. 2(b), on the other hand, the surface is completely covered with the bright protrusions and the Si(100)-2x1 area is not observed.

The changes in averaged STS spectra at sample bias from -2 to 2 V are shown in Fig. 3 for various conditions of oxygen exposure. These spectra are rescaled by the quantity of  $(V/I)(dI/dV)$ , which is approximately proportional to the surface density-of-states (DOS).<sup>3)</sup> The spectra in Figs. 3(a) and 3(d) are averaged in the whole scan area and those in Figs. 3(b) and 3(c) are in the bright protrusion site as seen in Fig. 2. In the clean surface spectrum of Fig. 3(a), the peaks at -0.7 and +0.3 eV, labeled by S<sub>1</sub> and S<sub>2</sub>, can be assigned to a  $\pi_b$  bond state and a  $\pi_a^*$  antibonding state of a  $\pi$  interaction between the dangling bonds on each of the Si dimer atoms for the symmetric dimer model, respectively.<sup>4, 5)</sup> The peak S<sub>3</sub> of about +1.3 eV is attributed to a back bond state,<sup>6, 7)</sup> which is located in the dark region between dimer rows. The STS spectrum of Fig. 3(b) measured at the bright protrusion site shows that the peak intensities of  $\pi_b$  and  $\pi_a^*$  states are reduced and the peak S<sub>3</sub> of back bond states disappears. This fact suggests that oxygen atoms adsorb on the Si back bond sites of the Si(100)-2x1 surface in the

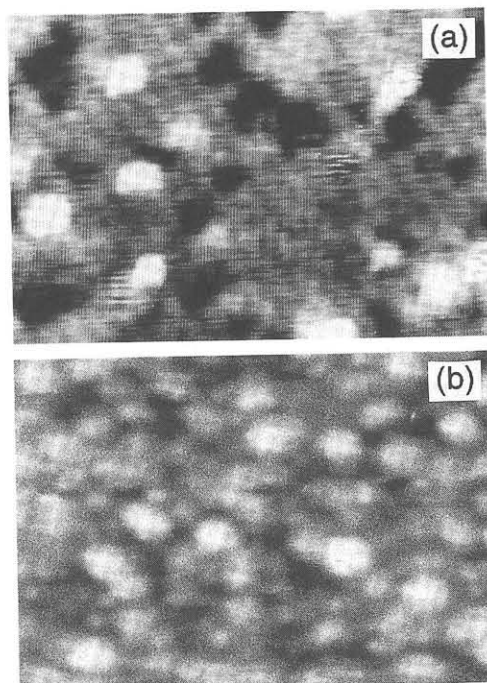


Fig. 2 STM images of the Si(100) surface with oxygen exposure of (a) 4.5 L and (b) 15 L at room temperature for a sample bias of -1.4 and +3.0 V. The scan area was about 10x15 nm<sup>2</sup>.

initial stage of oxidation, which is consistent with the conclusion obtained by HREELS measurements.<sup>8, 9)</sup> After exposing the surface to 15-L-O<sub>2</sub>, the peaks of  $\pi_b$  and  $\pi_a^*$  states are completely vanished and a gap near the Fermi level is broadened. In this stage, the spectra are independent of the probing sites although the oxidized surface has inhomogeneity as seen in Fig. 2(b). Finally, the width of the gap is expanded to about 1.1 eV at a 10<sup>4</sup>-L exposure of atomic oxygen, which is very close to a band gap of Si.

The averaged STS spectra from -6 V to 6 V are shown in Fig.4 for the (a) clean Si(100)-2x1 surface and the surfaces with (b) 15-L-O<sub>2</sub> and (c) 10<sup>4</sup>-L-O exposure. The tip-sample separation is wider than that in Fig. 3. For comparison, the top of the valence band and the bottom of the conduction band of bulk SiO<sub>2</sub> are also indicated by arrows of E<sub>v</sub> and E<sub>c</sub> in Fig.4, respectively. It can be seen that a dip in DOS around +3.5 eV and an increase in DOS intensity below -5.5 eV become noticeable with increasing the amount of exposure. The band edges of SiO<sub>2</sub> indicated by arrows are in agreement with the measured DOS curve. From AES measurements, the average thicknesses of SiO<sub>2</sub> at exposures of 15-L-O<sub>2</sub> and 10<sup>4</sup>-L-O was determined to be about 0.2 and 0.4 nm, respectively. Thus it is considered that the observed states in the energy range of -5.3 to 3.8 eV include the information of the DOS at the

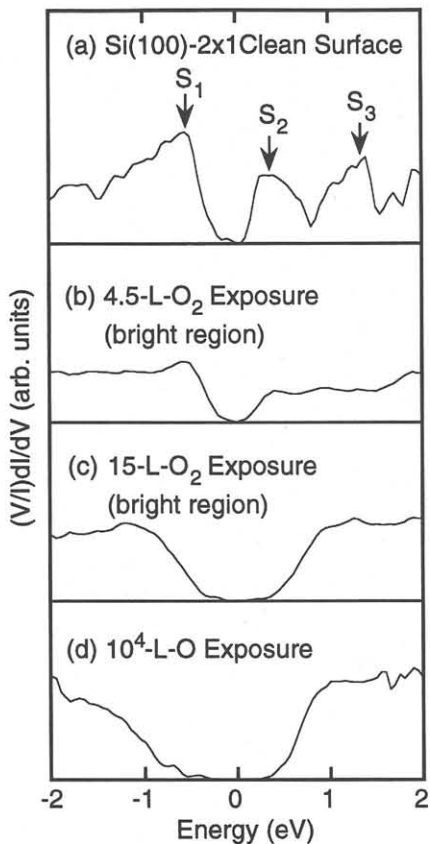


Fig. 3 STS spectra of the (a) Si(100)-2x1 surface and (b) 4.5-L-O<sub>2</sub>, (c) 15-L-O<sub>2</sub> and (d) 10<sup>4</sup>-L-O exposed surfaces. The spectra of (a) and (d) were averaged in the whole scan area and those of (b) and (c) in the bright protrusion region as seen in Fig. 2. The constant separation conditions of sample bias and current were +2 V and 0.3-0.4 nA, respectively.

SiO<sub>2</sub>/Si interface because electrons flow through the potential barriers of SiO<sub>2</sub> by tunneling. The broad peak marked by S<sub>4</sub> observed at about +5 eV in Fig.4 (c) is considered to originate from the unoccupied states of SiO<sub>2</sub> since no peak is observed in the Si(100)-2x1 spectrum.

#### 4. CONCLUSIONS

The oxidation of Si(100)-2x1 surfaces at room temperature has been studied by STM and STS. In the STS spectrum of clean Si(100)-2x1 surfaces, the surface states due to the  $\pi$  interaction between dangling bonds on Si dimer atoms and the back bond states can be observed. In STM images, the formation of dark regions and bright protrusions due to oxidation is observed. At a exposure to 4.5-L-O<sub>2</sub>, it is found that the back bond states are vanished and the dangling bond states became small in the STS spectra at the bright protrusion sites, which suggests that oxygen atoms adsorb on the Si back bond sites in the

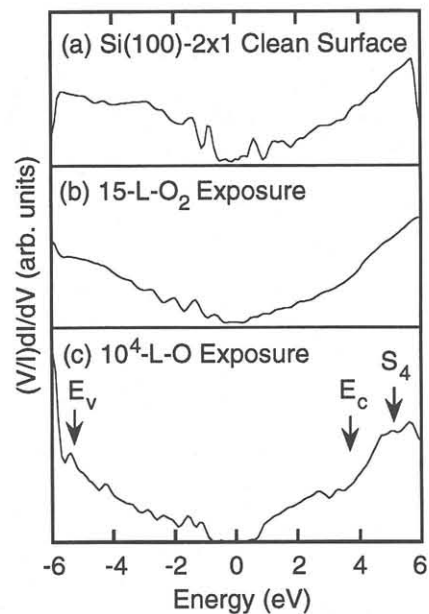


Fig. 4 STS spectra of the (a) Si(100)-2x1 surface, (b) 15-L-O<sub>2</sub> and (c) 10<sup>4</sup>-L-O exposed surfaces at room temperature. The spectra were averaged in the whole scan area. The constant separation conditions of sample bias and current were +6 V and 0.8-0.4 nA, respectively.

initial oxidation stage. After exposing the surface to 10<sup>4</sup>-L-O, at which thin SiO<sub>2</sub> films with an average thickness of 0.4 nm are grown on Si surfaces, the width of a gap near the Fermi level is broadened to about 1.1 eV and, furthermore, the increases in DOS intensity below -5.3 eV and above 3.7 eV can be observed, which suggests the formation of the valence and conduction bands of SiO<sub>2</sub>.

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