Structural transition layer at SiO_2/Si interfaces

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The valence-band and the O 2s core-level spectra of ultrathin (about 1 nm) SiO_2 layers [which are formed at the initial stages of oxidation of hydrogen-terminated Si(100) substrates] were measured by high-resolution x-ray photoelectron spectroscopy. The energy difference between the valence band and the core level was found to be greater than that for the bulk SiO_2. A first-principle molecular-orbital calculation was performed on $Si_2O_7H_6$ clusters in order to obtain the energy difference (which depends on the structure of SiO_2 layers). A comparison of the experimental data and the molecular-orbital calculations indicates that the intertetrahedral bond angle, $\theta_{\text{Si-O-Si}}$, is 135° to 140° in the SiO_2 structural transition layers at the SiO_2/Si interfaces. [S0163-1829(99)03708-X]

I. INTRODUCTION

The thermally-grown SiO_2/Si interface has been extensively studied because of its significant role in metal-oxide semiconductor field-effect transistors (MOSFET's).[1,2] Since current device technology demands a dramatic shrinkage of MOSFET size, the structure in the vicinity of the SiO_2/Si interface has recently become a fundamental issue to be clarified. This shrinkage leads to a reduction of gate-oxide film thickness to as small as 5 nm; namely, 14 layers of the SiO_2 molecule. There are two kinds of distinct regions near the interface: compositional transition layers and structural transition layers. Compositional transition from Si to SiO_2 occurs abruptly[3] through one Si atomic layer, which consists of intermediate oxidation states such as Si^{1+}, Si^{2+}, and Si^{3+}. Contrary to this, structural transition from the bulk Si to the bulk SiO_2 takes place to a much greater extent. On the Si side of the interface, the transition layers have been revealed to consist of two Si atomic layers that have an atomic arrangement different from that for bulk Si.[4] On the other hand, on the SiO_2 side of the interface, the structure of the transition layer is considered to be as much as 1-nm thick. The existence of the latter structural transition layers has been confirmed by a change in the etching rate of SiO_2 near the interface[5] and by a change in the stretching vibration energy of Si-O bonds near the interface.[6,7] Moreover, it has recently also been confirmed by x-ray reflectivity measurement suggesting that the density of SiO_2 changes near SiO_2/Si interfaces.[8] Nevertheless, little is known about the structure itself in the SiO_2 transition layers. So far, in a comparison with the bulk SiO_2 structure, two kinds of characteristic structures have been proposed. First, the structure of the transition layer in the SiO_2 was studied by Grunthaner *et al.*[9] This study was based on a unique spectral reconstruction procedure for x-ray photoelectron spectroscopy (XPS) core-level spectra of 2.3-nm thick SiO_2 on a Si substrate. They suggested that the structure of the transition layers has the corner sharing SiO_4 tetrahedron network as the bulk SiO_2 does but has the intertetrahedral Si-O-Si bond angle smaller than the bulk SiO_2. However, by using ultraviolet photoelectron spectroscopy, Hollinger *et al.*[10] found an anomalous valence-band spectrum for the transition layer of 1.1-nm thick SiO_2 on a Si substrate. They considered this spectrum is due to a change in coordination from 4:2 for the corner sharing tetrahedron network instead of a reduction in the intertetrahedral Si-O-Si bond angle.

Such a controversial result may come partly from the difficulty in uniformly preparing ultrathin oxide layers. We have recently succeeded in extremely uniform oxidation of Si substrates.[11–13] Using this oxidation method, oxidation proceeds in layer-by-layer mode at the interface.[11] It was found that the lateral size of the atomically flat oxidized region (formed during the layer-by-layer oxidation) is as much as 3–6 nm even at an average SiO_2 layer thickness of 0.7 nm.[13] These observations show that the thickness of the thin SiO_2 layers formed on Si substrates is uniform enough so that XPS measurements are able to identify the electronic structures for the vicinity of the SiO_2/Si interface. Structural changes in the transition layer should therefore be directly reflected in the changes in electronic structures in ultrathin oxide formed on Si substrates by such uniform oxidation. The purpose of the present work is to reveal differences in electronic structure of the transition layer and the bulk SiO_2 by high-resolution XPS. For the transition layer and the bulk SiO_2, we measure the energy differences between the valence band and the O 2s core level, which is more sensitive to structural distortion than the O 2p-related levels.[14] The experimental study is accompanied by a theoretical study on the energy difference using a first-principle molecular-orbital (MO) method. Comparisons of the experimental data and the molecular-orbital calculations will enable us to deduce the structural deformation in the SiO_2 transition layers near the SiO_2/Si interfaces.

II. EXPERIMENT

Extremely uniform oxidation of Si substrates was performed by the following procedures.[11–13] First, 200-nm thick

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SiO_2 layers were formed on 10–20-Ω cm *n*-type Si(100) substrates in dry O_2 at 1000 °C. Second, after removing the SiO_2 layers by buffered hydrofluoric acid, nearly 5-μm-thick undoped Si layers were grown epitaxially by the gaseous reaction of $SiHCl_3$ at 1100 °C in hydrogen atmosphere. Third, the Si substrates were cooled down to less than 400 °C in hydrogen atmosphere. The Si(100) surfaces thus prepared were terminated with hydrogen atoms and their reflection high-energy electron diffraction pattern exhibited a clear 2×1 structure.[15] The native oxides formed on the Si substrates, after being kept in nitrogen atmosphere for a long time, were removed by dipping in 0.5% hydrofluoric solution at room temperature, followed by a rinse in deionized water. The measurement of C 1*s* and O 1*s* XPS spectra showed that contaminations on these surfaces were negligibly small. Then, the Si substrates were loaded into an oxidation chamber through an introduction chamber. The base pressures of the introduction and the oxidation chambers were 6×10^{-5} and 4×10^{-8} Pa, respectively. By heating the hydrogen-terminated Si surfaces with an infrared light in 4-torr dry oxygen (the dew point of the oxygen gas was below −95 °C) at 300 °C for 360 min, preoxide was formed without breaking the H-Si bonds on the surfaces[16,17] up to the thickness of 0.5 nm. Through this preoxide, 0.61- to 1.5-nm thick SiO_2 was formed at 600 to 830 °C in 1-torr dry oxygen. Further oxidation up to 10 nm was performed at 800 °C. The SiO_2 thicknesses were determined by the Si 2*p* peak intensity in XPS spectra.

The samples were studied by high-resolution XPS, Scienta ESCA-300.[18] The XPS chamber (with a base pressure of 4×10^{-8} Pa) is connected by a gate valve to the oxidation chamber. The valence band and the O 2*s* core-level spectra were measured by using a monochromatic AlKα x-ray source at a photoelectron take-off angle of 15° with an acceptance angle of 3.3°. We measured differences between valence-band spectra for SiO_2 layers with two different thicknesses in order to subtract the valence-band spectrum of the Si substrate. The subtraction was performed by normalizing the Si valence-band intensity without making an energy correction. From this analysis the valence-band spectrum can be obtained for SiO_2 layers, which exist between two certain distances from the Si surface. The other experimental details are described elsewhere.[19]

The electronic structures for the valence band and the O 2*s* core level of SiO_2 were calculated using a first-principles MO method. In the present study, we used the Hartree-Fock-Slater method using the discrete variational (DV)-Xα code.[20] MO's were constructed by linear combination of atomic orbitals, which were numerically generated. Basis functions of Si, O, and H were $1s-3d$ for Si, $1s-3d$ for O, and $1s-2p$ for H. In this method, the exchange and correlation energies were taken into account by using the Xα potential given by

$$V_{X\alpha}(\mathbf{r}) = -3\alpha[(3/8\pi)\rho(\mathbf{r})]^{1/3},$$

where $\rho(\mathbf{r})$ is the local charge density. The parameter α was fixed at 0.7 for Si and O atoms.[20]

The $Si_2O_7H_6$ cluster as depicted in Fig. 1 was taken in this study to represent the structure of thermally grown SiO_2. The six hydrogen atoms were put so as to terminate the dangling bonds of the surrounding six oxygen atoms. It has already been confirmed that the valence band mainly consists of three peaks: two of them at higher binding energy are from bonding states between the O 2*p* and the Si 3*s*, 3*p* atomic orbitals, while one at lower binding energy is from nonbonding states of the O 2*p* atomic orbital.[10,21] Since the valence band as well as the O 2*s* core level has been revealed to have a predominant oxygen character, the local density of states of the center oxygen atom in the cluster was calculated using the Slater transition state procedure,[22] which is suitable for studying binding energy in XPS spectra. Analysis using such local density of states has been found to be effective for studying photoemission, by eliminating boundary effects, which may appear on the surrounding oxygen atoms.[23]

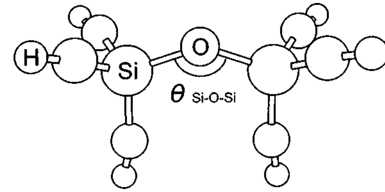

FIG. 1. A $Si_2O_7H_6$ cluster with C_{2v} point symmetry. The intratetrahedral bond angle, $\theta_{\text{O-Si-O}}$, and the Si-O interatomic distance, $\mathbf{r}_{\text{Si-O}}$, were taken to be constant; namely, 109.47° and 0.162 nm, respectively. The intertetrahedral bond angle, $\theta_{\text{Si-O-Si}}$, was used as a parameter in order to reproduce structural deformation in the transition layer at the SiO_2/Si interface. We used the O-H interatomic distance of 0.92 nm and the Si-O-H angle of 170°.

Deformation of the SiO_2 structure in the transition layer was investigated by referring to the following two reports. First, by using the photoemission-extended fine-structure measurement, Sieger *et al.*[24] clarified that the Si-O bond length near a 1-nm thick SiO_2/Si interface is identical to that in bulk SiO_2. Therefore, the Si-O interatomic distance, $\mathbf{r}_{\text{Si-O}}$, was taken to be constant; namely, 0.162 nm.[10,25] Second, using Monte Carlo simulations, Stixrude and Bukowinski[26] revealed that amorphous SiO_2 under a large stress does not change its intratetrahedral geometries substantially but decreases the intertetrahedral bond angle, $\theta_{\text{Si-O-Si}}$. The intratetrahedral bond angle, $\theta_{\text{O-Si-O}}$, was therefore set to 109.47° as for a SiO_4 tetrahedron in the bulk SiO_2.[25] On the other hand, the intertetrahedral bond angle, $\theta_{\text{Si-O-Si}}$, was used as a parameter in order to reproduce structural deformation in the transition layer under a large stress at the interface. We used $\theta_{\text{Si-O-Si}}$ of 144° for the bulk model and 130°, 135°, and 140° for the transition-layer model. The former angle is an average $\theta_{\text{Si-O-Si}}$ value in the bulk SiO_2,[27] while the latter angles were chosen to cover the possible range[28] of decreased bond angles under a large stress. In addition, we used the constant O-H interatomic distance of 0.92 nm and the Si-O-H angle of 170°.[25]

III. RESULTS AND DISCUSSION

Figure 2 compares the valence-band spectra between the bulk (10 nm thick) SiO_2 and the transition layer. The two spectra are shown by normalizing the highest peak in each spectrum without making an energy correction. The spectrum for the 10-nm thick SiO_2 was directly obtained without subtraction of two spectra for different thicknesses. This is

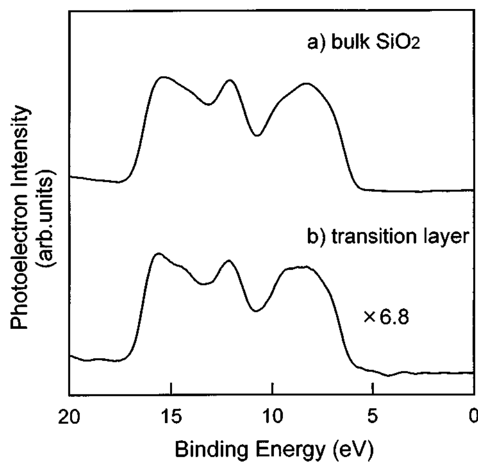

FIG. 2. A comparison of the XPS valence-band spectra from bulk SiO_2 and the transition layer. (a) Valence-band spectrum of the bulk SiO_2 (SiO_2 with film thicknesses of 10 nm). The spectrum was directly obtained without subtraction, since the Si substrate and the SiO_x interface components are not detected due to the small inelastic mean-free paths of 3.4 nm for photoelectrons with this energy. (b) Valence-band spectrum of the transition layer. The spectrum for the transition layer was obtained by subtracting the spectrum for 0.61-nm thick SiO_2 from that for 0.83-nm thick SiO_2.

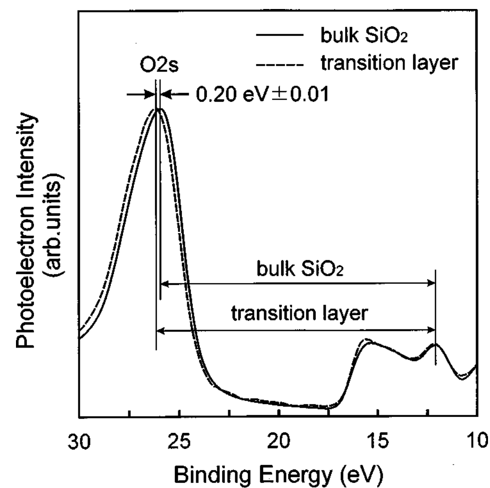

FIG. 3. A comparison between the bulk SiO_2 and the transition layer in terms of the energy difference between the O 2s core level and the lower binding-energy peak of the bonding states in the valence band. Both spectra are shown by normalizing the lower binding-energy peak of the bonding states.

because the Si substrate and SiO_x interface components were not detected because of the small effective escape depths of 0.8 nm for photoelectrons of this energy.[29] The valence band is found to be almost identical to that measured for bulk SiO_2 with film thicknesses larger than 10 nm.[30–33] Apparently, the valence band mainly consists of three peaks for which the original electronic structures were already identified; two of them at higher binding energy are bonding states between the O 2p and the Si 3s, 3p atomic orbitals, and one at lower binding energy is nonbonding states of the O 2p atomic orbital. On the other hand, the spectrum for the transition layer was obtained by subtracting the spectrum for 0.61-nm thick SiO_2 from that for 0.83-nm thick SiO_2. The obtained differential spectrum therefore represents the valence band of the SiO_2 layers existing between 0.61 and 0.83 nm from the Si surface, which means the obtained spectrum does not involve not only the valence bands of Si but also SiO_x suboxide, which exists within 0.5 nm from the interface.[3] Although the spectrum is acquired only for the very thin layers with a thickness of 0.22 nm, the obtained spectrum is clear enough to be compared with that for the bulk SiO_2. It should be noted that the overall shape and the relative intensities for these three peaks in the valence band are almost the same for the two spectra. This fact strongly suggests that the structural change of SiO_2 is only in the 4:2 coordination framework because a drastic change in relative intensities for the main three peaks in the valence-band spectra should be expected for different coordinations.[10]

Next, we will compare the bulk SiO_2 and the transition layer in terms of the energy difference between the O 2s core level and the lower binding-energy peak of the bonding states in the valence band. The energy differences were compared by normalizing the lower binding-energy peak of the bonding states in the valence band; that is, a change of the energy difference was obtained by measuring the energy difference between the two O 2s core-level peaks. As a result, the energy difference is found to increases by as much as 0.20 ± 0.01 eV as shown in Fig. 3. Likewise, we determined the energy differences in other differential spectra for SiO_2 layers, which exist at different distances from the Si surface. These differences were obtained with respect to the energy difference of the bulk SiO_2 and are listed in Table I. Although the energy difference for the layers that exist between 0.61 to 0.83 nm from the Si surface is 0.20 ± 0.01 eV larger than that for the bulk SiO_2, the energy differences for the layers that exist over 1.01 nm in thickness are the same (within 0.03 eV) as that for the bulk SiO_2. These facts clearly show that the larger energy difference is intrinsic to the transition layer that exists between 0.61 to 0.83 nm from the interface.

To investigate deformation of SiO_2 structure in the transition layer, we calculated the energy difference between the O 2s core level and the lower binding-energy peak of the bonding states in the valence band for the $Si_2O_7H_6$ clusters as depicted in Fig. 1. First, the energy levels for the cluster were calculated using $\theta_{\text{Si-O-Si}}$ of 144°. The calculated effective charges on the center O atom are $-0.73e$, which are in good agreement with previously reported values, $-0.67e$ to $-0.81e$, obtained by *ab initio* calculations for amorphous SiO_2.[25,34] Furthermore, we found a very good agreement between the XPS spectra and the calculated energy levels for

TABLE I. Energy differences between the O 2s core level and the lower binding-energy peak of the bonding states in the valence band for the SiO_2 layers that exist at different distances from the Si surface. These are obtained by subtraction of two spectrum for different SiO_2 thicknesses. The differences are obtained with respect to the energy difference of the bulk SiO_2.

SiO_2 thicknesses (nm)	Experiment (eV)
0.83−0.61	0.20 ± 0.01
1.50−1.30	0.00 ± 0.01
1.30−1.01	0.03 ± 0.01

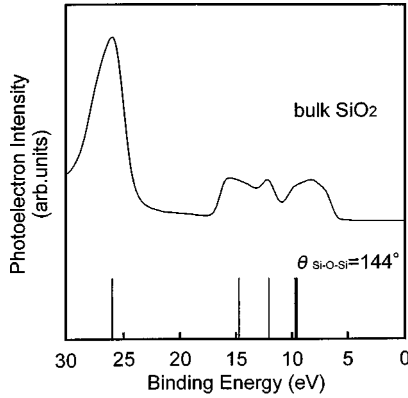

FIG. 4. A comparison between the XPS spectrum for the bulk SiO_2 and the calculated energy levels. The energy levels are obtained for the $Si_2O_7H_6$ cluster with $\theta_{Si\text{-}O\text{-}Si} = 144°$.

the O 2*s* core level and for the lower binding-energy peak in the bonding states as shown in Fig. 4. This agreement indicates that the present cluster size is large enough to investigate these energy levels that are mostly localized within the nearest-neighbor atoms. Besides, we confirmed that the calculated energy levels did not vary over a few tens of eV if we changed the configuration of the second nearest-neighbor (oxygen) and the third nearest-neighbor (hydrogen) atoms with respect to the center oxygen atom in the cluster. We, therefore, believe that the present cluster is a reasonable representative for discussing the observed energy change.

Next, we calculated the changes in the energy difference between the O 2*s* core level and the lower binding-energy peak of the bonding bands when the bond angle $\theta_{Si\text{-}O\text{-}Si}$ changes from the bulk SiO_2 value (144°) to smaller values including 130°, 135°, and 140°. These calculated energy differences are listed in Table II. Consequently, we find that the increases in the energy difference are 0.12, 0.27, and 0.33 eV for $\theta_{Si\text{-}O\text{-}Si} = 140°$, 135°, and 130°, respectively. This result shows that the transition layer of the 0.83-nm thick SiO_2/Si interface has a smaller $\theta_{Si\text{-}O\text{-}Si}$ bond angle (about 135° to 140°) than that (144°) observed in the bulk SiO_2.

Such a smaller $\theta_{Si\text{-}O\text{-}Si}$ bond angle was first suggested by Grunthaner *et al.*[9] They measured the Si 2*p* and the O 1*s* core level in 2.3-nm thick SiO_2 by high-resolution XPS and deconvoluted each measured core-level spectrum into two peaks separated by 0.6 eV using a unique reconstruction procedure. Based on a tight-binding calculation, the obtained peaks in each core-level spectrum were assigned to the bond angles ($\theta_{Si\text{-}O\text{-}Si}$) of 144° or 125°.[9,35] They concluded a smaller bond angle of 125° exists within 3 nm of the SiO_2/Si interface. Later, however, such an assignment was reexamined by Ching[14] using the first-principles effective-charge calculation. He found that such a decrease in bond angle $\theta_{Si\text{-}O\text{-}Si}$ would not produce a large core-level shift as shown by the deconvolution procedures. Therefore, the deconvolution procedures themselves are now in question. Recently, Miyazaki *et al.* proposed a smaller $\theta_{Si\text{-}O\text{-}Si}$ bond angle for the transition layer by considering their Fourier-transform infared (FT-IR) measurements.[36] They subtracted the FT-IR spectra for about 0.5-nm thick SiO_2 from the spectra for thicker SiO_2 layers in order to eliminate the influence of both the microroughness and suboxides on the LO phonon mode, and then they determined the LO phonon peak frequency. The results for SiO_2 grown at 1000 °C on Si(111) indicates that a distinct redshift of about 30 cm^{-1} still remains between 2- and 0.6-nm thick SiO_2. This result strongly indicates that a bond angle $\theta_{Si\text{-}O\text{-}Si}$ smaller than the bulk value (144°) exists in the interface region. According to a simple central force model,[37] the redshift of 30 cm^{-1} corresponds to a reduction of the Si-O-Si average bond angle by 7.7°, e.g., $\theta_{Si\text{-}O\text{-}Si} = 136.3°$, which is in very good agreement with the present results. We therefore, conclude that the $\theta_{Si\text{-}O\text{-}Si}$ is about 135° to 140°.

TABLE II. Energy differences of the O 2*s* core level and the lower binding-energy peak of the bonding states in the valence band calculated for the $Si_2O_7H_6$ clusters with $\theta_{Si\text{-}O\text{-}Si} = 130°$, 135°, and 140°. The differences are obtained with respect to the energy difference for $\theta_{Si\text{-}O\text{-}Si} = 144°$.

$\theta_{Si\text{-}O\text{-}Si}$ (degrees)	Calculation (eV)
140	0.12
135	0.27
130	0.33

Such a change in bond angle $\theta_{Si\text{-}O\text{-}Si}$, in turn, would affect several kinds of important characters for device designing, including the dielectric constant, the band gap, and the hole and electron barriers at the SiO_2/Si interface. Recently, one of these kinds of changes in electronic structures for the transition layer has been actually found by a valence-band study using high-resolution XPS.[38] We have found that the energy level of the top of the valence band, within about 1 nm from the present SiO_2/Si interface, is different from that of the bulk SiO_2. Further analysis of this energy difference will verify the bond-angle reduction in the transition layer.

IV. SUMMARY

Ultrathin SiO_2 was formed on Si substrates in a quite uniform oxidation process. High-resolution XPS measurements revealed that the energy difference between the valence band and the O 2*s* core level is larger in the transition layer within 1 nm from the SiO_2/Si interface than in the bulk SiO_2. A comparison of these experimental results with the calculated energy levels for $Si_2O_7H_6$ clusters by the DV-Xα method showed that the intertetrahedral bond angle, $\theta_{Si\text{-}O\text{-}Si}$, is about 135° to 140° in the structural transition layer.

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