Valence-band offset variation induced by the interface dipole at the SiO_2/Si(111) interface

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X-ray photoelectron spectroscopic evaluation of the SiO_2/Si(111) interface reveals that the valence-band offset differs by about 0.19 eV between two types of atomic structures that contain Si atoms in different intermediate-oxidation states. The difference in the valence-band offset is reproduced by a first-principles molecular orbital calculation for model clusters ($Si_{17}O_4H_{36}$ and $Si_{17}O_3H_{36}$) of the two interface structures. It is concluded that the valence-band offset at the interface with more Si atoms in the 3+ oxidation state than in the 1+ oxidation state is larger than the valence-band offset at the interface with more Si atoms in the 1+ oxidation state. This is thought to be a result of the depolarization effect making the interface dipole smaller at the interface with more Si atoms in the 3+ oxidation state.

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I. INTRODUCTION

The atomic structure in the vicinity of the SiO_2/Si interface has recently become a fundamental issue because the current device technology demands a dramatic reduction in the size of metal-oxide semiconductor field-effect transistors (MOSFET's): a reduction that results in gate oxide films only 1 nm thick, corresponding to three layers of SiO_2 molecules.[1] The only way the atomic structure of such ultrathin interfaces can be characterized is by using x-ray photoelectron spectroscopy (XPS) and theoretical studies based on first principles. These techniques have recently been used to evaluate the Si-O-Si bond angle, Si-O bond length, carrier traps, and intermediate-oxide states.[2–11]

Another aspect of great interest is the valence-band offset at the interface because this offset determines the electrical properties of the MOSFET's. More than 30 years ago, Williams determined the energy band diagram of the SiO_2/Si interface by measuring internal photoemission.[12] This technique, however, cannot be used to evaluate the valence-band offset at an ultrathin SiO_2/Si interface because the properties of such an interface can be altered by the processes involved in preparing samples and because the measured photoemission is affected by the tunneling current flowing through the SiO_2 layer. Grunthaner and Grunthaner therefore measured the valence-band spectra of an ultrathin SiO_2/Si(111) interface by using XPS and found the valence-band offset to be 4.5 eV,[13] while Himpsel *et al.* measured the valence-band spectrum of an ultrathin SiO_2/Si(100) interface by using synchrotron-radiation photoemission spectroscopy and found the valence-band offset to be 4.3 eV.[14]

The valence-band offset has recently been found to depend on the atomic structure at the SiO_2/Si interface. Alay and Hirose used high-resolution XPS to evaluate the valence-band offsets at ultrathin SiO_2/Si interfaces and found that for oxide thicknesses ranging from 1.6 to 4.4 nm the valence-band offset for the SiO_2/Si(100) interface is 4.43–4.49 eV and the valence-band offset for the SiO_2/Si(111) interface is only 4.36 eV.[15] Keister *et al.* confirmed, with better energy resolution, that the valence-band offsets of the SiO_2/Si(100) and SiO_2/Si(111) interfaces are different and did so using a device-proven oxidation process: for oxide thicknesses between 0.8 and 1.2 nm, they obtained a valence-band offset of 4.35 eV for the SiO_2/Si(100) interface and of 4.54 eV for the SiO_2/Si(111) interface.[16] They speculated that the difference is due to the different orientation of the interface bond relative to the surface normal, since the interface dipole induced by the interface bond would contribute to the valence-band offset. On the other hand, Nohira and Hattori demonstrated that the valence-band offset at the SiO_2/Si(111) interface changes periodically during the progress of layer-by-layer oxidation.[17] They thought that this periodic change is caused by a periodic change in the orientation of the interface bond. But if the charge transfer across the interface is estimated from the electronegativity difference between silicon and oxygen atoms, the interface dipole derived from the product of the surface charge density calculated from the charge transfer and the interplanar distance is the same for the interfaces whose interface bonds have different orientations.

This paper describes our study using XPS and a first-principle molecular orbital (MO) calculation for SiO_2/Si(111) model clusters—$Si_{17}O_4H_{36}$ and $Si_{17}O_3H_{36}$—to clarify the correlation between the valence-band offset and the atomic structure at the interface. We conclude that the valence-band offset at the interface containing Si atoms in the 3+ oxidation state is larger than that at the interface containing Si atoms in the 1+ oxidation state because the depolarization effect makes the interface dipole smaller at the former interface.

II. EXPERIMENT

Silicon substrates were oxidized in an extremely uniform way by using procedures we have described elsewhere.[18–20] Briefly, after SiO_2 layers 200 nm thick were formed on *n*-type Si(111) substrates (resistivity = 10–20 Ω cm) in dry O_2 at 1000 °C and then removed by hydrofluoric acid, the

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surfaces were rinsed in 40% NH_4F solution. The Si(111) surfaces thus prepared were terminated with hydrogen atoms and were atomically flat. Their reflection high-energy electron diffraction (RHEED) pattern showed clear 1×1 structure. The Si substrates were loaded into an oxidation chamber connected to an XPS chamber. Heating the hydrogen-terminated Si surfaces with an infrared light under 4 torr dry oxygen at 300 °C for 360 min formed a preoxide layer 0.5 nm thick without breaking the surface H-Si bonds. SiO_2 layers with thicknesses ranging from 0.58 to 1.80 nm were then formed by oxidizing the substrate at temperature between 600 and 850 °C under dry oxygen at 1 torr.

The samples were studied by high-resolution XPS (Scienta ESCA-300). The valence-band spectrum and Si $2p$ core-level spectrum were measured at a photoelectron take-off angle of 15° by using a monochromatic Al $K\alpha$ x-ray source. The energy resolution of the XPS measurements was 0.39 eV. We measured a difference between valence-band spectra for two SiO_2/Si(111) samples with different oxide thicknesses so that we could subtract the valence-band spectrum of the Si substrate. From this analysis could be obtained the valence-band spectrum of SiO_2 layers between two certain distances from the Si surface.

The electronic structures for the SiO_2/Si(111) interface were calculated using a first-principles MO method. We used the Hartree-Fock-Slater method using the discrete variational (DV) $X\alpha$ code.[21] Molecular orbitals were constructed by linear combination of atomic orbitals (LCAO) that were generated numerically and the basis functions of Si, O, and H were $1s$-$3d$ for Si, $1s$-$3d$ for O, and $1s$-$2p$ for H. The $Si_{17}O_4H_{36}$ and $Si_{17}O_3H_{36}$ clusters shown in Fig. 1 were used to represent the SiO_2/Si(111) interface structures. The 36 hydrogen atoms were arranged so as to terminate the dangling bonds of the surrounding 12 silicon atoms. We used the constant interatomic distances of 0.162 nm for Si and O and 0.148 nm for Si and H, which are in consistent with those used in Refs. 22 and 23. In addition, we used a bond angle of 180° for the Si-O-Si angle after Ref. 24. The cluster model with four oxygen atoms represents the interface which contains Si atoms in the 1+ oxidation state (Si^{1+} atoms), while the cluster model with three oxygen atoms represents the interface which contains Si atoms in the 3+ oxidation state (Si^{3+} atoms). We hereafter call these interfaces the Si^{1+} interface and the Si^{3+} interface.

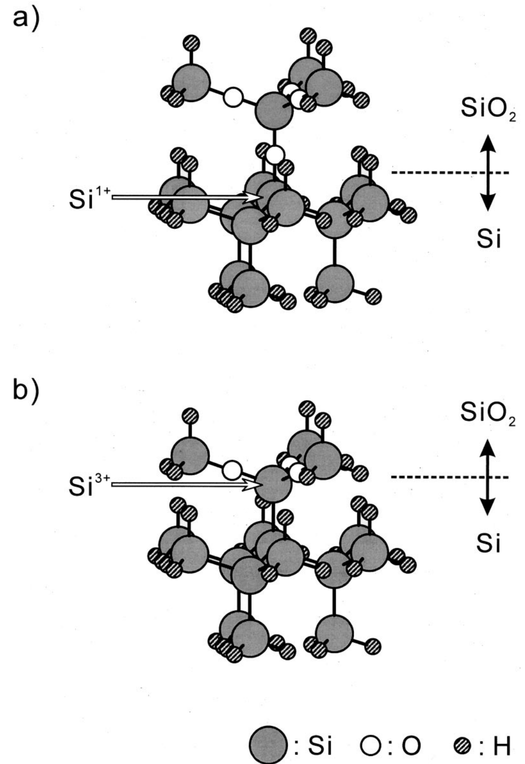

FIG. 1. SiO_2/Si(111) interface models: (a) $Si_{17}O_4H_{36}$ cluster representing the Si^{1+} interface and (b) $Si_{17}O_3H_{36}$ cluster representing the Si^{3+} interface.

III. RESULTS AND DISCUSSION

After removing the total background,[25] the observed Si $2p$ core-level spectrum is decomposed into $2p_{1/2}$ and $2p_{2/3}$ spin-orbit partner lines. In this decomposition we assumed that the spin-orbit splitting of the Si $2p$ photoelectron spectrum is 0.60 eV with a branching ratio of 0.5. We also assumed that the intermediate oxidation states were Si^{1+}, Si^{2+}, and Si^{3+} as defined by Himpsel *et al.*[14] The areal densities of the Si^{1+}, Si^{2+}, and Si^{3+} atoms are shown as a function of oxide thickness in Fig. 2, where it is clear that with increasing thickness the areal densities of the Si^{1+} and Si^{3+} atoms change periodically—with a period of about 0.7 nm—in opposite directions. The 0.7-nm period corresponds to the thickness of two molecular layers of SiO_2. In addition, it is found that the total of these areal densities of the intermediate oxidation states is constant and equivalent to that calculated for an abrupt interface. These findings confirm that, as reported earlier,[18] the interface structure changes periodically as oxidation progress. Here we pay special attention to the inter-

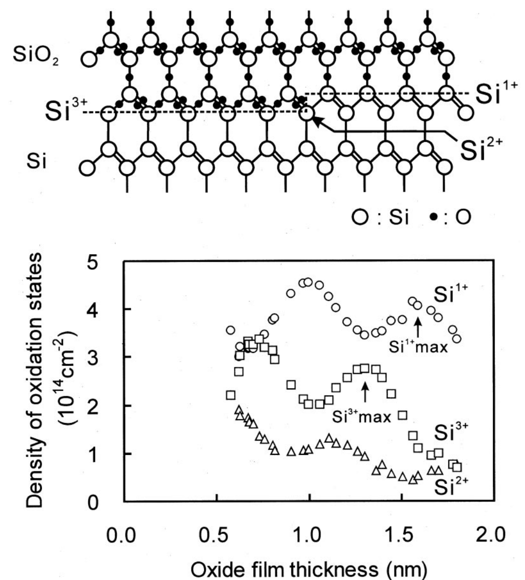

FIG. 2. Areal densities of intermediate-oxidation states (Si^{1+},Si^{2+},Si^{3+}) at the SiO_2/Si(111) interface.

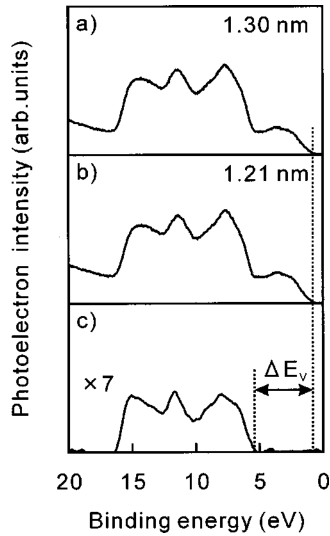

FIG. 3. Photoelectron spectra of the valence-band region for the Si^{3+} interfaces with different oxide thicknesses: (a) 1.30 nm and (b) 1.21 nm. The spectrum in (c) is the difference between those in (a) and (b).

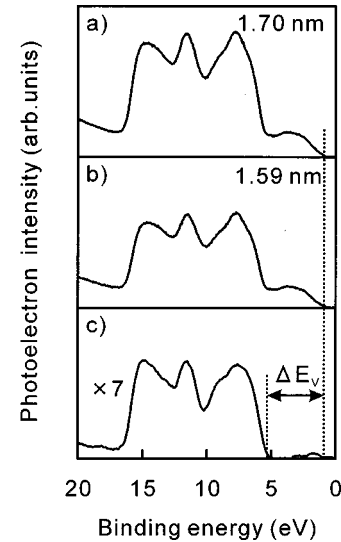

FIG. 4. Photoelectron spectra of the valence-band region for the Si^{1+} interfaces with different oxide thicknesses: (a) 1.70 nm and (b) 1.59 nm. The spectrum in (c) is the difference between those in (a) and (b).

face structures of the SiO_2/Si(111) samples whose oxide thicknesses were 1.21–1.30 and 1.59–1.70 nm (indicated in Fig. 2 by arrows labeled Si^{3+}max and Si^{1+}max). The former samples have the interface structure which contains the most Si^{3+} atoms, while the latter samples have the interface structure which contains the most Si^{1+} atoms.

Figures 3(a) and 3(b) show the valence-band spectra for a SiO_2/Si(111) sample with 1.30-nm-thick oxide and for a SiO_2/Si(111) sample with 1.21-nm-thick oxide, respectively. Figure 3(c) shows the spectrum obtained by subtracting the one shown in Fig. 3(b) from the one shown in Fig. 3(a) in order to eliminate the valence-band spectrum of the Si substrate. Thus the valence-band spectrum shown in Fig. 3(c) represents the valence band of the oxide surface in a SiO_2/Si(111) sample with the average oxide thickness: namely, 1.26 nm. Assuming that the top of the valence-band is obtained by fitting the lower-binding-energy part of the spectrum with a straight line, we define the valence-band offset at the Si^{3+} interface as the energy difference between the tops of the valence bands of the oxide surface and the Si substrate.

We measured the valence-band offset for the SiO_2/Si(111) interfaces corresponding to the Si^{1+} interface similarly. Figures 4(a) and 4(b) show the valence-band spectra for a sample with 1.70-nm-thick oxide and for a sample with 1.59-nm-thick oxide, respectively. Figure 4(c) shows the spectrum obtained by subtracting the one shown in Fig. 4(b) from the one shown in Fig. 4(a). It thus represents the valence band of the oxide surface in a sample with the average thickness: namely, 1.65 nm. And we again define the valence-band offset at the Si^{1+} interface as the energy difference between the tops of the valence bands of the oxide surface and the Si substrate. The results obtained from Figs. 3 and 4 are summarized in Table I: the valence-band offset ΔE_V is 4.42 eV at the Si^{1+} interface and 4.61 eV at the Si^{3+} interface. These values are close to those others have reported for the SiO_2/Si(111) interface.[13,15,16] Note that the valence-band offset at the Si^{3+} interface is 0.19 eV larger than that at the Si^{1+} interface. This difference is consistent with the values ranging from 0.12 to 0.20 eV we obtained in a separate experiment.[17,26]

To evaluate the validity of our cluster models, we calculated the core-level shifts of the Si $2p$ core level at the SiO_2/Si(111) interfaces. We obtained the Si $2p$ core level of the Si^{1+} atom in the $Si_{17}O_4H$ cluster model and of the Si^{3+} atom in the $Si_{17}O_3H_{36}$ cluster model. We took as a reference the Si $2p$ core level of the Si atoms in the bulk Si, i.e., the Si atoms in the second Si layer in each cluster. The Si $2p$ core-level shifts, shown in Fig. 5 as a function of oxidation state, are very close to those obtained by Pasquarello *et al.* (also plotted in Fig. 5),[24] who used the pseudopotential method rather than the total electron method we used. The agreement is not surprising, since the shifts calculated using the two methods are the same when the shift is small.[23,27] In addition, the values of the shifts obtained by Pasquarello *et al.* agreed well with experimental values when core-hole relaxation effects were taken into account.[28] The cluster models we used therefore seem to be appropriate for the Si^{1+} and Si^{3+} interfaces.

We also calculated the valence-band offset by using a method often used for determining the valence-band offset at heterojunctions.[6,29,30] As shown in Fig. 6, the valence-band offset is given by

TABLE I. Valence-band offset at the Si^{1+} and Si^{3+} interfaces and the difference between them.

	ΔE_V (eV)	$\delta\,\Delta E_V$ (eV)
Si^{1+} max	4.42 ± 0.01	
Si^{3+} max	4.61 ± 0.01	0.19 ± 0.01

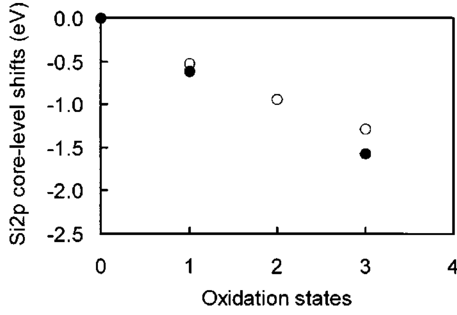

FIG. 5. Relation between oxidation state and the Si $2p$ core-level shifts at the SiO_2/Si(111) model interfaces: present work (solid circle) and Ref. 24 (open circle).

$$\Delta E_V = E_{V\text{-Si}2p}(\text{Si}) + \Delta E_{\text{Si}2p} - E_{V\text{-Si}2p}(\text{SiO}_2), \quad (1)$$

where $\Delta E_{\text{Si}2p}$ (influenced by the interface dipole) is the energy difference between the Si $2p$ energies in Si and SiO_2 $[= E_{\text{Si}2p}(\text{Si}) - E_{\text{Si}2p}(\text{SiO}_2)]$, and $E_{V\text{-Si}2p}(\text{Si})$ and $E_{V\text{-Si}2p}(\text{SiO}_2)$ are the Si $2p$ energies with respect to the tops of the valence bands in Si and SiO_2. So we can obtain the difference between the valence-band offsets at the two interfaces as

$$\delta \Delta E_V = \delta \Delta E_{\text{Si}2p}. \quad (2)$$

We used constant values for $E_{V\text{-Si}2p}(\text{Si})$ and $E_{V\text{-Si}2p}(\text{SiO}_2)$, supposing that these values depend only on the bulk properties of SiO_2 and Si and are independent of the interface structure. This approximation is reasonable, since even when an ultrathin SiO_2/Si(100) structure undergoes a thermal relaxation only 20% of the change in the valence-band offset is due to the change in $E_{V\text{-Si}2p}(\text{Si})$ and $E_{V\text{-Si}2p}(\text{SiO}_2)$.[6] Thus we used the same parameters (e.g., Si-O bond length and Si-O-Si bond angle) for the two cluster models and obtained almost the same Mulliken charges for the oxygen atoms in SiO_2, which results in constant values of $E_{V\text{-Si}2p}(\text{SiO}_2)$ for the two models. We also used the same parameters (e.g., Si-Si bond length and Si-Si-Si bond angle) for the two cluster models and obtained almost the same Mulliken charges for silicon atoms in Si, which results in constant values of $E_{V\text{-Si}2p}(\text{Si})$ for the two models. The same procedures were also used to evaluate the Si $1s$ and Si $2s$ core levels, and the differences between the valence-band offsets of the Si^{1+} and Si^{3+} interfaces deduced from analysis of each core-level energy are summarized in Table II. The valence-band offset at the Si^{3+} interface is 0.18–0.23 eV (average 0.21 eV) larger than that at the Si^{1+} interface due to the change in $\Delta E_{\text{Si}2p}$ or the interface dipole. This result is in good agreement with the experimental results as shown in Table I, although the absolute values are hard to compare because the interface that contains the most Si^{3+} atoms also contains some Si^{1+} atoms and the interface that contains the most Si^{1+} atoms also contains some Si^{3+} atoms. On the other hand, the influence of an interface dipole on the valence-band offset at SiO_2/Si(111) interfaces is quantitatively in good agreement with what has been found experimentally by Perfetti *et al.*[31] They demonstrated that the valence-band offset can be modified as much as 0.25–0.5 eV by inserting an interlayer (of atoms such as H or Cs atoms). They explained the dramatic changes by considering an additional interface dipole induced by the interlayer. More evidence for the influence of the interface dipole was later reported by Ohmi *et al.*[32] They studied the effect of impurities on the valence-band offset at SiO_2/Si(100) interfaces and found that impurities such as hydrogen or nitrogen atoms increase the valence-band offset by 0.2–0.6 eV. They thought that the effects of impurities were due to a reduction in the strength of interface dipoles. Our calculated change in the valence-band offset is in good agreement with these reports, so we conclude from the results of our first-principles calculation that the difference between the valence-band offset at the Si^{1+} and Si^{3+} interfaces is due to the different interface dipoles there.

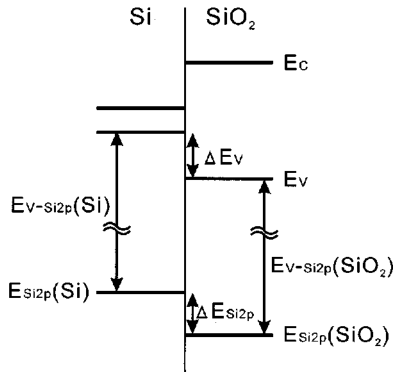

FIG. 6. Energy band diagram of the SiO_2/Si(111) interface.

TABLE II. Differences between the valence-band offsets at the Si^{1+} and Si^{3+} interfaces deduced from analysis of each core-level energy.

	Si $2p$	Si $2s$	Si $1s$	Ave.
$\delta \Delta E_V$ (eV)	0.23	0.23	0.18	0.21

To find the reason for the different interface dipoles at the two interfaces, we used a simple condenser model. Figure 7 shows condensers that model the Si^{1+} and Si^{3+} interfaces. The corresponding interface dipole is calculated from the surface charge density for each plane ($\sigma_{\text{Si1+}}, \sigma_{\text{Si3+}}$), the interplanar distance ($d_{\text{Si1+}}, d_{\text{Si3+}}$), and the average ($\varepsilon_{\text{ave}}$) of the Si and SiO_2 dielectric constants. We used interplanar distances of 0.324 nm for the Si^{1+} interface and 0.108 nm for the Si^{3+} interface. The surface charge density was obtained from the calculated charge transfer between the SiO_2 and Si sides of the clusters—that is, from the difference between the sums of Mulliken charges for the atoms in the SiO_2 and Si sides of each cluster. The calculated interface dipoles are 3.99 eV for the Si^{1+} interface and 3.76 eV for the Si^{3+} interface, or the interface dipole at the Si^{3+} interface is 6% smaller than that at the Si^{1+} interface.

The effective moment of a dipole close to other dipoles at an interface is smaller than that of an isolated dipole, and this "depolarization effect" is caused by mutual energy between dipoles. We estimated the strength of this effect by using the classical model of Krueger and Monch, who explained a work function difference by attributing it to a surface dipole

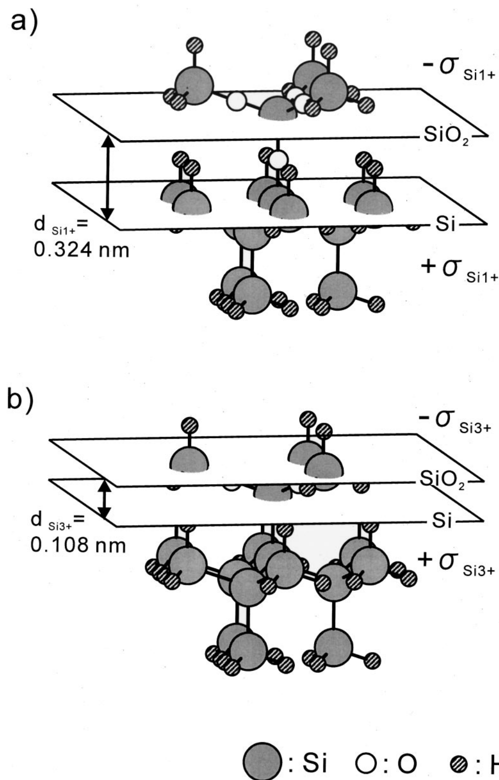

FIG. 7. Condenser models for (a) the Si^{1+} interface and (b) the Si^{3+} interface.

change due to the depolarization effect.[33] Using interdipole distances of 0.38 nm for the Si^{1+} interface and 0.27 nm for the Si^{3+} interface, we estimated the reduction due to the depolarization effect to be 3% at the Si^{1+} interface and 8% at the Si^{3+} interface. This five-percentage-points larger depolarization effect at the Si^{3+} interface is in good agreement with the difference we calculated from first principles. Therefore we conclude that the valence-band offset is larger at the Si^{3+} interface than at the Si^{1+} interface because the depolarization effect makes the interface dipole smaller at the Si^{3+} interface.

IV. SUMMARY

High-resolution XPS measurements of uniform ultrathin layers of SiO_2 formed by oxidizing Si(111) substrates revealed that the valence-band offset differs by 0.19 eV between interfaces with different atomic structures. The difference in the valence-band offset was reproduced by a first-principles molecular orbital calculation for model clusters ($Si_{17}O_4H_{36}$ and $Si_{17}O_3H_{36}$) of the two interface structures. It was concluded that the valence-band offset at the interface with more Si atoms in the 3+ oxidation state than in the 1+ oxidation state is larger than the valence-band offset at the interface with more Si atoms in the 1+ oxidation state. This was thought to be a result of the depolarization effect making the interface dipole smaller at the interface with more Si atoms in the 3+ oxidation state.

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