Direct observation of the site-specific valence electronic structure at SiO₂/Si(111) interface

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(Received 17 January 2006; Accepted 15 February 2006; Published 24 March 2006)

For today's silicon based devices, understanding the SiO₂/Si(111) interface on atomic level is an important subject for fabricating superior devices. However, despite of many studies on the SiO₂/Si(111) interface, the interfacial valence electronic states have been typically evaluated as the average and not as individual states. In the present study, we successfully observed valence electronic states of particular atoms at the SiO₂/Si(111) interface for the first time using soft x-ray absorption and emission spectroscopy. In addition, comparing the experimental results to first-principles calculations revealed local interfacial properties. [DOI: 10.1380/ejsnt.2006.280]

Keywords: silicon; silicon oxides; semiconductor-insulator interfaces; X-ray emission; density functional calculations; interface

I. INTRODUCTION

Over the last 30 years, the active element density in integrated circuits has doubled roughly every 18 months as embodied in Moore's law. The smallest, but crucial, controlling feature of these circuits is the gate oxide (amorphous SiO₂) layer, which is the basis for metal-oxide-semiconductor field effect transistors (MOSFET's). Currently, industry can produce MOSFET's with a gate shorter than 50 nm and an SiO₂ gate oxide less than 2 nm thick [1]. If the present reductions continue, the thickness will soon be a few atomic layers. This implies that an atomic level understanding of the properties at the SiO₂/Si interface is important for fabricating devices with an ultra-thin oxide layer. Therefore, we have focused on measuring the occupied electronic states projected at particular atoms of the SiO₂/Si(111) interface.

Recently, several groups reported that the conduction band edge was lower at the interface compared to bulk SiO₂ [2–4]: Muller, *et al.* reported that the oxygen *K*-edge was 3 eV lower at the interface using electron energy loss spectroscopy (EELS) in a scanning transmission microscope [2]. Based on this finding, the selective photo-absorption at the interface is realized by tuning the incident photon energy to only allow the electronic excitation from the O 1s level to the lowered conduction band levels. Once the O 1s core level at the interface is excited, the core hole is filled by an electron from an occupied valence level accompanied with soft X-ray emission. Since the O 1s state is localized on a particular oxygen site, the emit-

ted photon spectrum allows an atom-specific projection of the valence electronic states. Using this method, we successfully observed site-specific occupied states at the SiO₂/Si(111) interface for the first time.

II. EXPERIMENTAL

SiO₂/Si(111) samples were prepared from phosphorus-doped *n*-type Si(111) wafers that have a resistivity of 0.001 Ωcm. After standard RCA cleaning, a native oxide layer was etched away by a 1% HF solution and then the wafers were immersed in a 40% NH₄F solution for 15 min to form an atomically smooth silicon surface [Si(111)(1 × 1)-H] [5, 6]. A 1.8 nm-oxide-layer was prepared in 0.1 M Pa of oxygen at 600 K for 5 min.

The synchrotron radiation experiments were performed using BL-27SU at SPring-8. The oxygen *K*-edge absorption spectroscopy was performed by detecting O KVV Auger electrons at 510 eV and an instrumental energy resolution of 50 meV. Soft X-ray emission (SXE) spectra were measured with an 800 meV energy resolution. The design and performance of the SXE spectrometer is described in detail elsewhere [7]. Si 2*p* core level spectra were measured with incident photon energy of 800 eV and a Gammatdata Scienta SES2002.

Atomic force microscopy (AFM) measurements were performed with a JEOL SPM 4200 using contact mode. The H-terminated Si(111) surface and the surface after the etch of the oxide layer of SiO₂ on Si(111) away with a 0.5% HF solution were investigated. The measurements were performed in nitrogen atmosphere.

First-principles calculations based on the density functional theory with a generalized gradient approximated correction were performed to evaluate the local density of states of the valence level and the interface structure

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FIG. 1: AFM images: (a) the H-terminated Si(111) surface and (b) after the etch of the oxide layer on Si(111) away. Each area is $300 \times 300 \text{ nm}^2$ and the measurements were performed in nitrogen atmosphere.

and properties [8]. A six Si-layer thick slab model was used with a periodic boundary condition: the unit cell contains four dangling bonds of a clean Si(111) surface in its initial configuration. The oxidized structures were then obtained by inserting O atoms one by one with structure relaxation. We prepared three models obtained by a different insertion order of oxygen atoms.

III. RESULTS AND DISCUSSION

Figure 1 shows AFM images of the H-terminated Si(111) surface and after the etch of the oxide layer on Si(111) away. After the etch of the oxide layer, steps are clearly observed indicating that the interface is atomically flat after the oxidation. This is consistent with the previous studies [6, 9].

Figures 2(a) and (b) show the oxygen *K*-edge absorption spectra of SiO₂/Si(111) structures with 1.8-nm and 8-nm thick SiO₂ layers, respectively. The latter is considered to represent the bulk SiO₂ spectrum since the mean

FIG. 2: Oxygen *K*-edge absorption spectra of (a) 1.8-nm-thick SiO₂/Si(111) and (b) 8-nm-thick SiO₂/Si(111) structures. The spectrum (c) shows the magnified spectrum of (a). Incident photon angle was 36° from surface normal and *p*-polarized photon was used.

free path of the Auger electron is $\sim 1.5 \text{ nm}$ at 510 eV [10], which is much shorter than the SiO₂ layer thickness. An absorption spectrum of the 1.8-nm-thick SiO₂/Si(111) structure is strikingly different from the bulk SiO₂ spectrum. The 1.8 nm spectrum has a lower onset and exhibits edge structures at 530 and 531.5 eV. Muller et al. used EELS and reported that the oxygen *K*-edge was lowered by 3 eV at the interface compared to the bulk SiO₂ [2]. Thus, the edge structures in the spectrum are explained by unoccupied O *2p* states at the interface, and the lowered edge exhibits a reduced band gap at the interface. Note that the peak at 537.5 eV is attributed to unoccupied O *2p* states bound with Si *3s* and *3p* states of bulk SiO₂ [11, 12].

Figure 3 shows the Si *2p* core level spectrum for the 1.8-nm-thick SiO₂/Si(111) structure. A peak fitting procedure was referred to the previous studies [5, 6, 13]. In these figures, Si⁰ and Si⁴⁺ denote the Si substrate and SiO₂ respectively, and Si¹⁺ and Si³⁺ denote Si atoms bound to one and three oxygen atoms, respectively. Note that Si²⁺ due to an Si atom bound to two oxygen atoms was very weak for the 1.8-nm-thick SiO₂/Si(111) structure. It is found from emission angle dependence of Si *2p* spectra that these suboxide species, i.e. Si¹⁺, Si²⁺, and Si³⁺, were dominantly formed at the interface. In addition, analysis of the Si *2p* photoelectron spectra for the 1.8-nm-thick SiO₂/Si(111) structure revealed that the relative intensities of the suboxide species were $Si^{1+} : Si^{2+} : Si^{3+} = 0.563 : 0.003 : 0.434$. Thus the interface predominantly consists of Si¹⁺ and Si³⁺ and these results are in good agreement with the previous results [5].

Wallis, *et al.* reported using theoretical calculations that the oxygen *K*-edge of the intermediate states in the amorphous silicon shifted to lower energy as the oxidation number of the adjacent silicon atoms decreased [3].

FIG. 3: Si 2p core level spectrum for (a) 1.8-nm-thick SiO₂/Si(111) and (b) the magnified spectrum of (a). The spectrum was measured at the photon energy of 800 eV and take-off angle of 45°.

Thus, the absorption edges at 530 and 531.5 eV are assigned to an O atom bonding to Si¹⁺ and Si³⁺ at the interface, respectively (hereafter, the O atom bonding to Si¹⁺ and Si³⁺ at the interface is denoted to P1 and P3, respectively). Therefore, site-specific SXE spectra of particular oxygen atoms at the interface can be obtained by choosing excitation energies, i.e., 530 eV for P1, 531.5 eV for P3, and 537.5 eV for SiO₂.

Figures 4(a)-(c) show the O *K*-edge SXE spectra for the 1.8-nm-thick SiO₂/Si(111) structure. The electronic states at the interface are noticeably different from those of bulk SiO₂ and the interfacial electronic states strongly depend on the intermediate oxidation states at the interface. With a photon energy of 537.5 eV, the occupied O 2p states of bulk SiO₂ predominantly contribute to the SXE spectrum (Fig. 4(a)). In this spectrum, the peak at 7.25 eV and the shoulder at 8.65 eV are attributed to the O 2p non-bonding states, while the peaks at 11.75 and 14.33 eV are due to the bonding states between O 2p and Si *sp*³ orbitals [14]. When the incident photon energy is 533 eV in order to excite P3 (Fig. 4(b)), the peaks due to non-bonding states become broader and shift towards a higher binding energy compared to bulk SiO₂. In addition, a new, small, broad peak around 4 eV is observed. For P1 (Fig. 4(c)), the peak at 6.50 eV, which is at-

FIG. 4: O *K*-edge SXE spectra for the 1.8-nm-thick SiO₂/Si(111) structure and the calculated O-2p density of states (DOS) obtained from the model presented in this figure. For the SXE spectra shown as the black lines, incident photon energies were (a) 537.5 eV, (b) 533 eV, and (c) 530 eV. Incident photon angle was 60° from surface normal and a *p*-polarized photon was used. Note that in order to selectively excite P3, we used 533 eV as the incident photon energy. Red lines show the calculated O-2p DOS for (d) SiO₂, (e) P3 atoms of SiO₂/Si(111) interface with P3, and (f) P1 atoms of SiO₂/Si(111) interface with P1. The calculated DOS spectrum was the average of each oxygen atom spectrum for amorphous SiO₂ and that of each interface oxygen atom spectrum in the case of P1 and P3. Gaussian broadening was applied for the O-2p DOS using experimental and lifetime broadening (total 1.1 eV). Red balls and yellow balls correspond to oxygen and silicon atoms, respectively.

tributed to the non-bonding states of O 2p, is very sharp and does not have a shoulder, indicating that an uniform structure is formed at the interface. Note that P1 should be also excited as well as P3 when the incident photon energy is 533 eV because the absorption edge of P3, i.e. 531.5 eV, could overlap with that of P1 (see Fig. 2(c)). However, intensity of P1 decreased as increasing incident photon energy; the relative intensity of P1 was less than 10% judging from the P1 derived peak intensity at 6.50 eV. Thus, the occupied O 2p states of P3 predominantly contribute to the SXE spectrum (Fig. 4(b)) when the incident photon energy is 533 eV.

A straightforward way to quantitatively evaluate the interface states is to combine the experimental results with theoretical calculations, providing the interface properties such as the structure, conducting and dielectric behavior. For the SiO₂/Si(111) interface, the interface is abrupt, and Si¹⁺ and Si³⁺ species dominate as described above. Therefore, the atomically flat SiO₂/Si(111) interface only consisting of Si¹⁺ or Si³⁺ is calculated as the interface model. Figures 4(d)-(f) show the oxygen projected density of states (O-2p DOS) for SiO₂, P3, and P1, respec-

FIG. 5: Calculated energy band gap variation in the structures with P1 and P3 along the normal direction to the interface. Black and red solid lines exhibit the structure with P3 and P1 interfaces, respectively. The solid lines in the interface model structures show the origin of the distance.

tively, calculated with the model structures illustrated in the right.

It is clear that the calculated DOS for amorphous SiO_2 produces SXE spectrum of the oxide region well (Figs. 4(a)(d)). The Si-O-Si angle and Si-O bond length in the theoretically optimized structure are predominantly distributed from 140° to 155° and 0.155 nm to 0.165 nm, respectively, which are consistent with previous experimental results [15]. As for the P3 interface layer, the Si-O-Si angle is distributed from 131.6° to 151.6° and the Si-O bond length from 0.158 nm to 0.176 nm in the theoretically optimized structure. The local variation from the amorphous SiO_2 results in the appearance of a shoul-

der at 4 eV and the broadening of the non-bonding state from 7.75 eV to 9.13 eV (Figs. 4(b)(e)). On the other hand, for the P1 interface layer, the Si-O-Si angle and Si-O bond length should be maintained near 180° and 0.19 nm, respectively, in order to reproduce the non-bonding sharp peak at 6.50 eV (Figs. 4(c)(f)).

Next we investigated how the structure with P1 or P3 interface exhibits the interface properties, which would enable us to understand atomic scale transport properties of carrier. Figure 5 shows the calculated conduction band minimum (CBM) and valence band maximum (VBM) of the structure with P1 or P3 interface in the interfacial region. For the P1 interface, since the Si-O-Si bond angle and the Si-O bond length are near 180° and 0.19 nm, the orbital of the non-bonding state is along the parallel to the interface. In this case, our calculations clearly show that the non-bonding state of P1 hardly interacts with Si atoms, and the CBM and VBM in the interface region are attributed to penetration from DOS of the silicon substrate. Therefore the P1 interface exhibits a similar band gap to the bulk Si in the interfacial region from 0 nm to 0.2 nm. For the P3 interface, on the other hand, the non-bonding state of the P3 interacts with Si atoms because the Si-O-Si bond angle and the Si-O bond length are distributed as described above. Thus the gap of the P3 interface gradually becomes large in the interfacial region from 0 nm to 0.2 nm. These results indicate that the P1 interface is relatively more conductive. Thus, the interface characteristics strongly depend on the local interface structures, which implies that performance of MOSFET with an extremely small gate width is essentially affected by the suboxide composition at the interface. In future MOSFET, it is determined that controlling the interfacial states on atomic level is crucial for not only SiO_2 less 1nm thick, but high-dielectric constant materials and silicon oxynitride used as alternatives to SiO_2 [16, 17]. In this study, we present our approach using SXE, which successfully detects the electronic states of particular atoms at the interface. Therefore, this approach is applicable to interfacial states for various kinds of gate oxides and will be indispensable for evaluating and designing nm-scale superior devices.

IV. CONCLUSIONS

Site-specific valence electronic states at the $\text{SiO}_2/\text{Si}(111)$ interface were successfully observed by SXA and SXE spectroscopy. We found that the interfacial valence electronic states were noticeably different from those of bulk SiO_2 and strongly depended on the chemical states of each atom at the interface. In addition, comparison of the experimental results with first-principles calculations quantitatively revealed not only the interface structure but also the interface electronic properties in atomic-scale.

Acknowledgments

We wish to thank Professors Hattori and Nohira for their useful discussion and gratefully acknowledge the help by Dr. Tamenori of JASRI. This work was supported

by the Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology. The synchrotron radiation experiments were performed

at the SPring-8 with the approval of JASRI (Proposal No. 2003B0209-Nsa-np-Na and 2004A0345-Nsa-np-Na).

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