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Photoemission study on electrical dipole at SiO₂/Si and HfO₂/SiO₂ interfaces

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Electrical dipole at SiO₂/Si and HfO₂/SiO₂ interfaces have been investigated by X-ray photoelectron spectroscopy (XPS) under monochromatized Al K α radiation. From the analysis of the cut-off energy for secondary photoelectrons measured at each thinning step of a dielectric layer by wet-chemical etching, an abrupt potential change caused by electrical dipole at SiO₂/Si and HfO₂/SiO₂ interfaces has been clearly detected. Al-gate MOS capacitors with thermally-grown SiO₂ and a HfO₂/SiO₂ dielectric stack were fabricated to evaluate the Al work function from the flat band voltage shift of capacitance–voltage (C–V) characteristics. Comparing the results of XPS and C–V measurements, we have verified that electrical dipole formed at the interface can be directly measured by photoemission measurements. © 2017 The Japan Society of Applied Physics

1. Introduction

A clear insight into the inner potential changes in the MOS structure, such as the electrical dipoles caused by metallic bonding states at the metal gate/high-*k* dielectric interface,¹⁾ the areal density difference of oxygen atoms at the high-*k* dielectric/SiO₂ interface,^{2,3)} and oxygen vacancies in the dielectric,^{4,5)} is strongly required to control the threshold voltages of advanced MOS transistors. The formation of electrical dipole has been often discussed from the flat band voltage shift of capacitance–voltage (C–V) characteristics.^{2,6,7)} However, if some electrical dipoles exist in a gate stack, it is not so easy to distinguish the amount of each electrical dipole by C–V analysis. To overcome this difficulty, we focused on the evaluation of electrical dipole by photoemission measurements.

Photoemission measurements such as X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are one of the powerful tools for evaluating the energy band alignment including that in the electrical dipole of a gate stack structure.^{8–11)} We have so far studied such potential changes in TiN/HfSiON and Ru/HfSiON gate stacks by back-side XPS measurements, and we have confirmed the work function (WF) change due to the dipole formation near the metal/high-*k* interface and the relief from the Fermi level pinning phenomena by oxygen incorporation into HfSiON.¹²⁾ In addition, photoemission measurements enable us to know the energy level difference between the vacuum level (VL) and the valence band (VB) top for the materials of interest from the dataset of the onset of VB signals and the cut-off energy for secondary photoelectrons taking excitation energy into consideration.^{13–15)} It is interesting to note that the energy difference of VL between the different materials indicates the potential change including electrical dipole formation. Using this measurement technique of VL, the evaluation of electrical dipole between two different materials by UPS has been reported.^{13,14)} Thanks to the higher excitation energy of X-ray as compared with ultraviolet, XPS analysis can measure not only the energy position of VL but also the electric potential of materials of interest from the peak energy of core-line signals.

The purpose of this work is to verify the evaluation of electrical dipole using XPS measurements and to quantify the

dipole at the SiO₂/Si and HfO₂/SiO₂ interfaces. By high-resolution XPS analysis under monochromatized Al K α X-ray radiation ($h\nu = 1486.6$ eV), the inner potential change and electrical dipole formation in the region near the SiO₂/Si and HfO₂/SiO₂ interfaces have been investigated. Electrical dipole was also examined from the flat band voltage shift of Al-gate MOS capacitors.

2. Experimental procedure

P- and n-type Si(100) substrates with a resistivity of ~ 10 Ω -cm were wet-chemically cleaned with an NH₄OH : H₂O₂ : H₂O = 0.15 : 3 : 7 solution at 80 °C for 10 min. Subsequently, the Si surface was terminated with hydrogen by dipping in 4.5% HF solution and a pure-water rinse. For the growth of a SiO₂ layer, dry oxidation at 850 °C in pure O₂ was conducted. In some samples, a HfO₂ layer was deposited at 280 °C by an atomic-layer controlled chemical vapor deposition (CVD) method using TEMA-Hf and O₃. Then, post deposition annealing (PDA) was performed at 850 °C in O₂ ambient for 30 s to densify the dielectric layers. In some samples, dielectric layers were thinned repeatedly by dipping in a dilute HF solution.

At each step of thinning the dielectric layers, XPS measurements under monochromatized Al K α radiation ($h\nu = 1486.6$ eV) at a photoelectron take-off angle of 90° were performed. The emitted photoelectrons from a sample were collected in a hemispherical analyzer with a pass energy of 20 eV. Potential changes and electrical dipole in the region near the SiO₂/Si and HfO₂/SiO₂ interfaces were evaluated by the combination of cut-off energy for secondary photoelectrons and the peak position of core-line signals. To detect secondary photoelectrons on the lower kinetic energy side with high sensitivity, a negative bias was applied to the sample during the measurements. Then, the depth profiling of chemical bonding features of the HfO₂/SiO₂/Si structure was investigated by HArD X-ray Photo-Emission Spectroscopy (HAXPES: $h\nu = 7939$ eV) at a beam line (BL) of 47XU in Super Photon ring-8 GeV (SPring-8).^{16,17)} Photoelectrons emitted at different photoelectron take-off angles were collected at the same measurement time using objective lens with wide solid angles ($\pm 30^\circ$) to minimize the change in the spectral shape caused by the charge-up effect during the measurements. For a comparative study, Al-gate MOS capacitors were fabricated by the evaporation of the Al gate

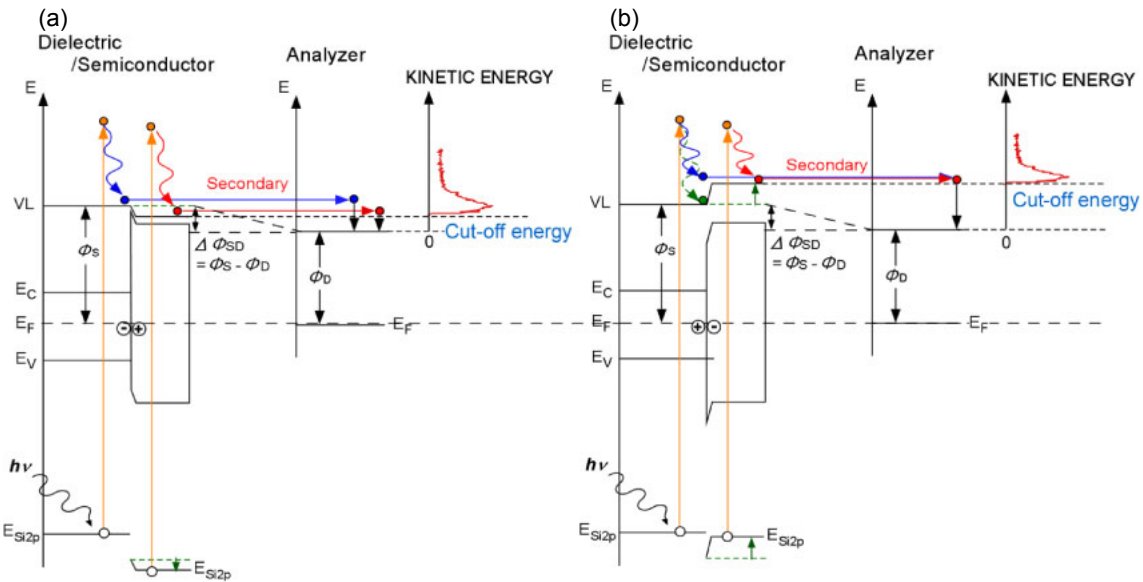


Fig. 1. (Color online) Schematic illustration of photoemission from dielectric/semiconductor and relationship between the cut-off energy for secondary photoelectrons and (a) potential drop or (b) raise of dielectric layer caused by the electrical dipole at the interface.

electrode with an area of $\sim 2.1 \times 10^{-3} \text{ cm}^2$ on dielectric layers, and electrical dipole and Al WF were also investigated from *C-V* characteristics.

3. Results and discussion

Figure 1 show a schematic view of the photoemission from the dielectric/semiconductor stacked structure with the electrical dipole under flat band condition and the correlation among the cut-off energy for secondary photoelectrons detected using the analyzer and the potential change due to the electrical dipole of the sample.

Ideally, the Fermi level (E_F) becomes the same as the energy level between the sample and the detector, because they were electrically grounded during the measurements. Secondary photoelectrons corresponded to the photo-excited electrons losing the energy with some electronic excitations due to inelastic scatterings. If the kinetic energy of secondary photoelectrons was below the energy between the VL and the VB top of a material of interest, such a low-energy electron can no longer emit to the outside. Thus, the energy level of VL was investigated from the cut-off energy for secondary photoelectrons near the lower limit in the kinetic energy scale. When an electrical dipole exists at the interface between a dielectric and a semiconductor, the resultant abrupt potential change causes the change in the measured cut-off energy for secondary photoelectrons. In the case of a dielectric/semiconductor with the potential drop of the dielectric layer caused by the interfacial electrical dipole [as shown in Fig. 1(a)], the cut-off energy from the dielectric/semiconductor was decreased as compared with that from the semiconductor, where the detected energy of photoelectrons was calibrated by the energy position of the semiconductor. On the other hand, when an opposite electrical dipole exists in the dielectric/semiconductor interface, an increase in cut-off energy can be observed, as seen in Fig. 1(b). In order to accurately evaluate electrical dipole, the band bending of each layer during the measurements should be estimated from the energy shift of core-line signals. This measurement technique has the advantage of simply evaluating electrical

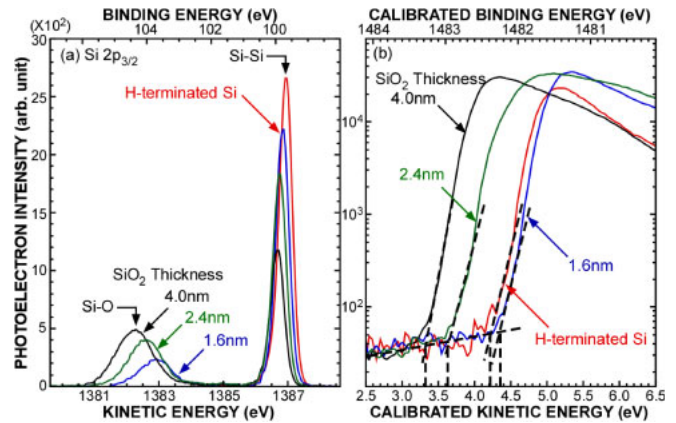


Fig. 2. (Color online) (a) Si 2p_{3/2} signals and (b) cut-off energy for secondary photoelectrons taken for thermally-grown SiO₂/Si structure with the SiO₂ layer thinned by dipping in a dilute HF solution.

dipole as compared with the discussion of dipole formation from the energy shift of core-line signals, because the energy shift of core-line signals is mainly derived from not only the change in the potential but also the changes in chemical bonding features. In addition, electrical dipole at dielectric/dielectric interfaces such as the HfO₂/SiO₂ interface can be evaluated by the same method as that shown in Fig. 1.

Firstly, we applied this technique to the evaluation of the potential change and electrical dipole in a thermally-grown SiO₂/Si structure. Figures 2(a) and 2(b) show Si 2p_{3/2} spectra and signals from secondary photoelectrons measured at each thinning step of the SiO₂ layer with an initial thickness of 4.0 nm by dipping in 0.1% HF solution. In Fig. 2(a), Si 2p_{3/2} signals were obtained by the spectral deconvolution of a measured Si 2p spectrum into two components in accordance with the spin-orbit splitting, where the energy splitting of 0.61 eV and the intensity ratio of Si 2p_{3/2} : 2p_{1/2} = 2 : 1 were used.^{18–21} The remaining SiO₂ layer thickness after the thinning was roughly estimated from the Si 2p_{3/2} intensity ratio of Si-O to Si-Si signals

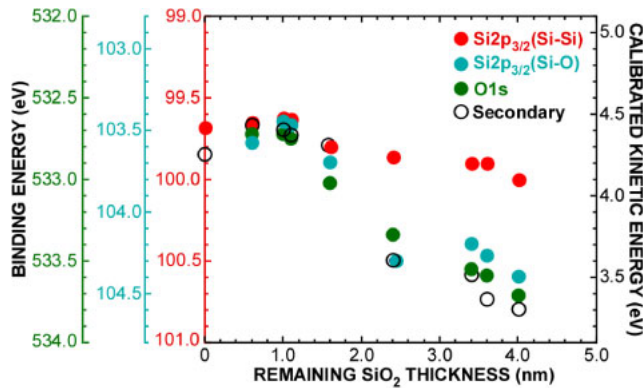


Fig. 3. (Color online) Energy position of core-line signals and cut-off energy for secondary photoelectrons as functions of remaining SiO₂ thickness.

($I_{\text{top}}/I_{\text{bottom}}$) using the following equation, where the top and bottom layers were responsible for the SiO₂ layer and Si substrate, respectively.

$$d_{\text{top}} = \lambda_{\text{top}} \cdot \sin \theta \cdot \ln \left(\frac{n_{\text{bottom}} \cdot \sigma_{\text{bottom}} \cdot \lambda_{\text{bottom}}}{n_{\text{top}} \cdot \sigma_{\text{top}} \cdot \lambda_{\text{top}}} \cdot \frac{I_{\text{top}}}{I_{\text{bottom}}} + 1 \right) \quad (1)$$

In the calculation, the atomic concentration [n , n_{SiO_2} : $0.0367N_D$, n_{Si} : $0.0832N_D$, $N_D = 6.022 \times 10^{23} \text{ mol}^{-1}$ (Avogadro constant)], photo-ionization cross section (σ , $\sigma_{\text{Si}2p_{3/2}}$: 0.541), and photoelectron escape depth of Si 2p photoelectrons (λ , λ_{SiO_2} : 3.4 nm, λ_{Si} : 2.7 nm) were used.^{22,23} With the thinning of the SiO₂ layer, the cut-off energy for secondary photoelectrons and the energy position of Si 2p_{3/2} signals originating from Si–O and Si–Si bonding units were gradually shifted toward the higher kinetic energy side. Note that, after the complete removal of the remaining SiO₂ layer with a thickness of 1.6 nm, an opposite energy shift in the direction for the cut-off energy for secondary photoelectrons was observed as compared with the shift of Si 2p_{3/2} signals from Si–Si bonding units. These observed energy shifts can be explained by the potential change at the Si surface and near the SiO₂/Si interface. Then, to obtain a clear insight into the potential change in the depth direction, energy peak positions of Si–Si bonding units from Si 2p_{3/2} spectra, Si–O bonding units from Si 2p_{3/2} and O 1s spectra, and cut-off energy for secondary photoelectrons were plotted as a function of remaining SiO₂ thickness, as shown in Fig. 3. In the remaining SiO₂ thickness region from 4 to 1 nm, the observed energy shift of the signals for secondary photoelectrons was almost the same as the shift of Si 2p_{3/2} and O 1s signals from Si–O bonding units, indicating that these secondary photoelectrons were mainly emitted from the SiO₂ layer. In the case of SiO₂ thickness below 1 nm, significant energy shifts of the signals for secondary photoelectrons and core-levels were hardly detected. This result implies that the band bending of SiO₂ and the Si surface is small. In Fig. 4, to quantify the electrical dipole at the SiO₂/Si interface, the cut-off energy for secondary photoelectrons was replotted as a function of remaining SiO₂ thickness, where kinetic energy was calibrated using Si–Si bonding units from Si 2p_{3/2} signals because the potential of the Si surface was set at the same level. Note that, the cut-off energy for secondary photoelectrons was reduced by $0.15 \pm 0.1 \text{ eV}$ after the

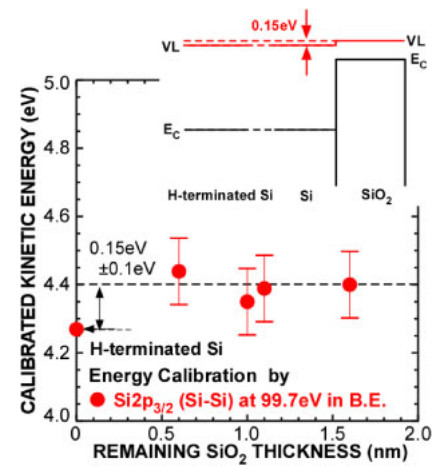


Fig. 4. (Color online) Cut-off energy for secondary photoelectrons as a function of remaining SiO₂ thickness. Energy was calibrated using Si 2p_{3/2} signals from Si–Si bonding units in the Si substrate. An energy band diagram of the SiO₂/Si structure before and after removal of SiO₂ layer is shown in the inset.

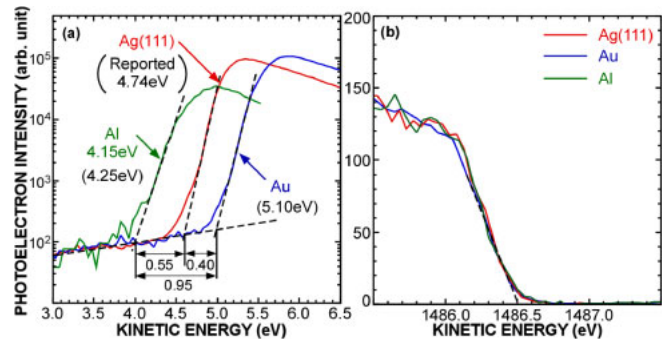


Fig. 5. (Color online) (a) Signals for secondary photoelectrons and (b) VB signals taken for thermally-evaporated Al after surface cleaning by Ar⁺ ion sputtering. Results of Au plate and epitaxial Ag(111) on Si(100) after surface cleaning are shown as references.

removal of SiO₂, which suggests a difference in the electrical dipole at SiO₂/Si interface and at H-terminated Si surface, as shown in inset of Fig. 4.

To check the observed potential change in the thermally-grown SiO₂/Si structure, Al-gate MOS capacitors with different SiO₂ thicknesses were fabricated, and Al WF was investigated using XPS and C–V measurements. Figures 5(a) and 5(b) show the measured cut-off signals for secondary photoelectrons and the VB spectrum of a thermally-evaporated 0.5-μm-thick Al film on the SiO₂ (~5 nm)/Si structure after surface cleaning by Ar⁺ ion sputtering. The results of surface cleaned Au plate and epitaxial Ag(111) on Si(111) are also shown as references. As seen in Fig. 5(a), an energy shift in the signals from secondary photoelectrons was observed because of the WF difference of these element metals. On the other hand, the difference in the onset of VB signals for the samples was hardly detected [shown in Fig. 5(b)], since the E_F between the sample and the detector becomes the same, as discussed in Fig. 1. Moreover, by fitting a straight line to measured spectra, the vacuum WF difference between Ag(111) and Au were found to be 0.40 eV with an accuracy of 0.05 eV. It was confirmed that the observed vacuum WF difference between Au and Ag(111)

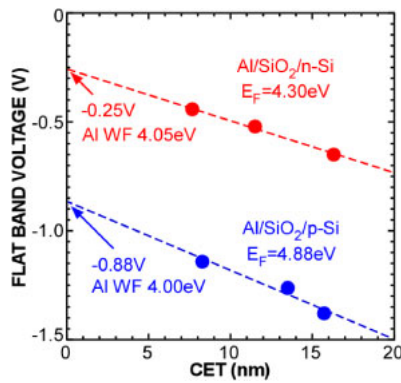


Fig. 6. (Color online) SiO₂ thickness dependence of flat band voltage shift for Al-gate MOS capacitors with thermal SiO₂ grown at 850 °C in dry-O₂. Si substrates with a donor concentration of $\sim 4.0 \times 10^{14} \text{ cm}^{-3}$ and an acceptor concentration of $\sim 1.0 \times 10^{15} \text{ cm}^{-3}$ were used.

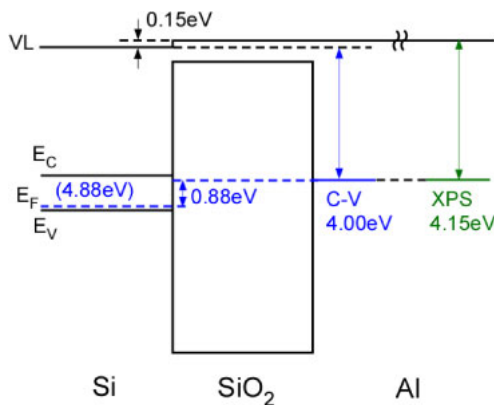


Fig. 7. (Color online) Energy band diagram of Al/SiO₂/Si structure.

was in good agreement with the reported values for Au (5.10 eV) and Ag(111) (4.74 eV).^{24,25} Taking into account of the measured cut-off energy in each sample and the reported vacuum WFs of Au and Ag(111), the vacuum WF of Al was determined to be $4.15 \pm 0.05 \text{ eV}$, which was slightly smaller than reported value for Al (4.25 eV).²⁶ Al WF was also evaluated from Al gate MOS capacitors with different SiO₂ thicknesses, where Si substrates with a donor concentration of $\sim 4.0 \times 10^{14} \text{ cm}^{-3}$ and an acceptor concentration of $\sim 1.0 \times 10^{15} \text{ cm}^{-3}$ were used. *C-V* curves for MOS capacitors were measured at 100 kHz and room temperature, and hysteresis was hardly detected. The obtained flat band voltage was plotted as a function of SiO₂ thickness (calculated equivalent oxide thickness: CET), which was calculated from accumulation capacitance as seen in Fig. 6. By fitting a straight line to the measured flat band voltages by the least squares method, the energy differences between Al WF and E_F of the Si substrate were obtained to be -0.25 eV for n-type Si ($E_F = 4.30 \text{ eV}$) and -0.88 eV for p-type Si ($E_F = 4.88 \text{ eV}$), and Al WF was determined to be $4.00 \pm 0.05 \text{ eV}$. From the obtained results of Al WF, an energy band diagram of the Al/SiO₂/Si structure was described in Fig. 7. The observed Al WF difference evaluated from XPS and *C-V* measurements can be explained by the abrupt rise in SiO₂ potential due to the electrical dipole at the SiO₂/Si interface as discussed in Fig. 4. A similar result of electrical dipole at the SiO₂/Si interface has been so far reported from both experimental and

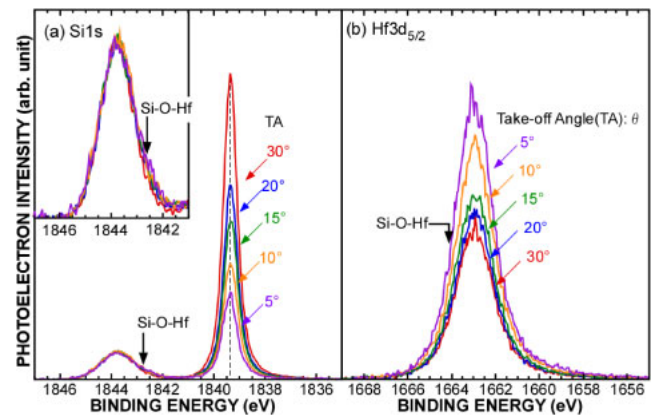


Fig. 8. (Color online) (a) Si 1s and (b) Hf 3d_{5/2} HAXPES core-line spectra of HfO₂ (1.6 nm)/SiO₂ (2.5 nm)/Si structure. These spectra were measured at different photoelectron take-off angles in the range from 30 to 5° at 5° steps. In each spectrum, binding energy calibration and photoelectron intensity normalization were made by using Si 1s signals from SiO₂ components.

calculation.^{27–29} From the UPS analysis of the 0.5 nm-thick SiO₂ grown on Si(100) by plasma oxidation, the electrical dipole at SiO₂/Si interface was found to be $0.2 \pm 0.14 \text{ eV}$.²⁷ In addition, theoretical calculations suggested that the origin of the electrical dipole at the SiO₂/Si interface caused by the charge transfer of 0.18 electron/bond in the Si–SiO₂ interface due to the difference in the electro-negativities of SiO₂ and Si.²⁸

Next, the electrical dipole at the HfO₂/SiO₂ interface was investigated using the same method described above. Firstly, the chemical bonding features in the region near the interface between HfO₂ and SiO₂ for the HfO₂ (1.6 nm)/SiO₂ (2.5 nm)/n-type Si(100) structure after PDA at 850 °C were investigated from the photoelectron take-off angle dependence of HAXPES core-line spectra such as Si 1s and Hf 3d_{5/2} as shown in Figs. 8(a) and 8(b). In each spectrum, the binding energy and photoelectron intensity were normalized using Si 1s signals originating from SiO₂ components at 1843.8 eV. With decreasing photoelectron take-off angle for surface sensitive analysis, the Si 1s signals of Si–Si bonding unit originating from underlying Si substrate were decreased. On the other hand, the observed increase in Hf 3d_{5/2} signals without any change in the spectral shape indicated the formation of HfO₂ on SiO₂. Moreover, Si 1s and Hf 3d_{5/2} signals from Si–O–Hf bonding units were hardly detected. From these results, it was confirmed that an abrupt HfO₂/SiO₂ interface was formed, in other words, the compositional mixing between HfO₂ and SiO₂ was quite small.

Then, to evaluate the electrical dipole at the HfO₂/SiO₂ interface, XPS measurements were performed at each thinning step of the HfO₂ layer by dipping in 0.1% diluted HF solution. Figure 9 shows the changes in the core-line spectra and the signals from secondary photoelectrons with the thinning of the HfO₂ layer measured at a photoelectron take-off angle of 90°. In each spectrum, kinetic energy was calibrated by Si 2p_{3/2} signals from SiO₂ component. The remaining HfO₂ thickness after the thinning was crudely estimated from the relative photoelectron intensities of Hf 4f signals from HfO₂ (I_{Hf4f}) to Si 2p_{3/2} signals from SiO₂/Si (I_{Si2p}).

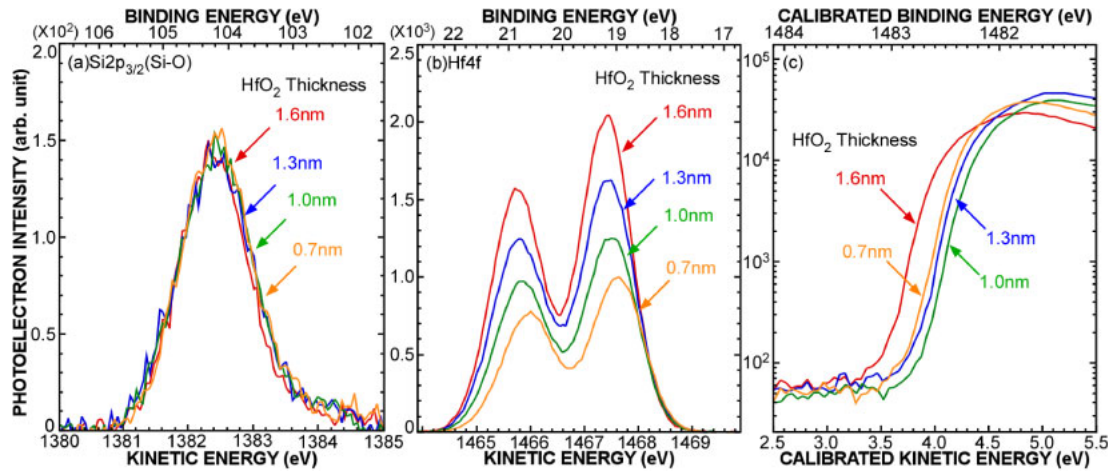


Fig. 9. (Color online) (a) Si 2p_{3/2} and (b) Hf 4f spectra, and (c) the signals from secondary photoelectrons taken for HfO₂/SiO₂/Si structure with the HfO₂ layer thinned by dipping in dilute HF solution. Kinetic energy was calibrated using Si 2p_{3/2} signals originating from SiO₂ component.

$$I_{\text{Hf4f}} = \sin \theta \cdot n_{\text{HfO}_2} \cdot \sigma_{\text{Hf4f}} \cdot \lambda_{\text{Hf4f-in-HfO}_2} \left[1 - \exp \left(- \frac{d_{\text{HfO}_2}}{\lambda_{\text{Hf4f-in-HfO}_2} \sin \theta} \right) \right] \quad (2)$$

$$I_{\text{Si2p}} = \sin \theta \cdot n_{\text{Si}} \cdot \sigma_{\text{Si2p}} \cdot \lambda_{\text{Si2p-in-Si}} \exp \left(- \frac{d_{\text{HfO}_2}}{\lambda_{\text{Si2p-in-Si}} \sin \theta} \right) \quad (3)$$

Assuming that the escape depth from Si 2p and Hf 4f signals in HfO₂ were equal as shown in Eqs. (2) and (3), HfO₂ thickness was evaluated using the following equation.

$$d_{\text{HfO}_2} = \lambda_{\text{Hf4f-in-HfO}_2} \cdot \sin \theta \cdot \ln \left(\frac{n_{\text{Si}} \cdot \sigma_{\text{Si2p}} \cdot \lambda_{\text{Si2p-in-Si}}}{n_{\text{HfO}_2} \cdot \sigma_{\text{Hf4f}} \cdot \lambda_{\text{Hf4f-in-HfO}_2}} \cdot \frac{I_{\text{Hf4f}}}{I_{\text{Si2p}}} + 1 \right), \quad (4)$$

where n , σ , and λ of the top layer (HfO₂) were set at $n_{\text{HfO}_2} = 0.0632N_D$, $\sigma_{\text{Hf4f}} = 7.52$, and $\lambda_{\text{HfO}_2} = 2.9$ nm,³⁰⁾ respectively, and n , σ , and λ of the bottom layers (SiO₂/Si) were simply set at values of Si as discussed in Eq. (1). With the thinning of the HfO₂ layer, the Hf 4f signals and cut-off energy for secondary photoelectrons mainly shifted toward the higher kinetic energy side. It was confirmed that the observed energy shift of Hf 4f signals with the HfO₂ thinning was almost the same as the shift of the signals for secondary photoelectrons, except for the sample with a HfO₂ thickness of 1.6 nm, which showed that the large energy shift of cut-off energy is probably due to surface contaminants. The observed cut-off energy for secondary photoelectrons were replotted as a function of remaining HfO₂ thickness as shown in Fig. 10, in which the energy calibration of cut-off energy was made by Si–O bonding units from Si 2p_{3/2} signals. The cut-off energy for secondary photoelectrons was decreased by $\sim 0.15 \pm 0.1$ eV as compared with that of the thermally-grown SiO₂/Si structure. This result indicates an abrupt potential drop of HfO₂ layer near the HfO₂/SiO₂ interface, in other words, an electrical dipole exists at the HfO₂/SiO₂ interface, as schematically illustrated in the energy band diagram shown in the inset of Fig. 10. MOS capacitors of Al/HfO₂/SiO₂ (2.5 nm)/n-type Si(100) with different HfO₂ thicknesses in the range from 0.8 to 1.6 nm were fabricated, and C – V curves were obtained of measurement frequencies of 100 and 200 kHz by two frequency method.³¹⁾ The observed flat band voltage shifts of MOS capacitors are

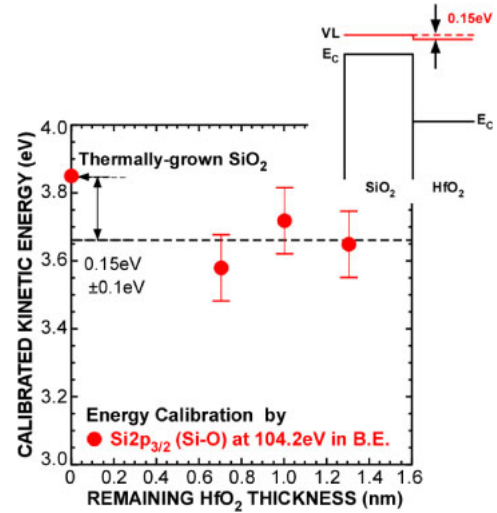


Fig. 10. (Color online) Energy position of cut-off energy for secondary photoelectrons as a function of remaining thickness of HfO₂ layer thinned by dipping in a dilute HF solution and energy band diagram at HfO₂/SiO₂ interface. Kinetic energy was calibrated using Si 2p_{3/2} signals from Si–O bonding units.

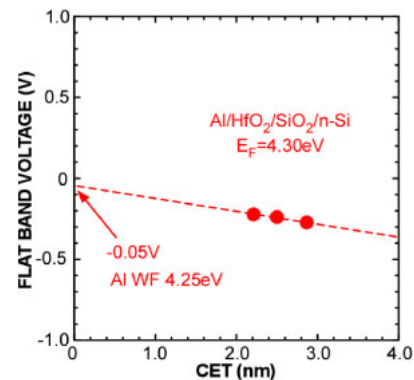


Fig. 11. (Color online) Flat band voltage for Al/HfO₂/SiO₂/n-type Si MOS capacitors as a function of CET. C – V curves were obtained at measurement frequencies of 100 and 200 kHz using the two-frequency method.

summarized as a function of CET in Fig. 11. By fitting a straight line, the WF of Al on the HfO₂/SiO₂ stack was evaluated to be 4.25 eV taking the E_F of the Si substrate in

consideration, which increased by 0.20 eV as compared with the WF of Al on the thermally grown SiO₂/n-Si structure. Taking into account the fact that the potential change in HfO₂/SiO₂/Si structure by electrical dipole moments at SiO₂/Si and at HfO₂/SiO₂ interface as discussed in Figs. 4 and 10 is canceled, the observed work function difference of Al obtained by XPS measurements of the Al surface (Fig. 5) and by the C–V characteristics of the Al-gate MOS capacitor with HfO₂/SiO₂ stack (Fig. 11) is likely to be responsible for the electrical active defects in HfO₂ and/or electrical dipole at Al/HfO₂ interface presumably caused by oxygen vacancies in HfO₂. We demonstrated that this measurement technique was effective for evaluating electrical dipoles at the interface between different materials.

4. Summary

The evaluation method of measuring electrical dipole at the interface between different materials by XPS has been studied. From the SiO₂ thickness dependence of the cut-off energy for secondary photoelectrons after energy calibration by the Si substrate, an abrupt potential change of SiO₂ due to electrical dipole between SiO₂/Si and H-terminated Si was detected to be ~0.15 eV. The difference between Al WF values measured by XPS and from C–V characteristics also indicates electrical dipole at the SiO₂/Si interface. In HfO₂ near the abrupt HfO₂/SiO₂ interface, a potential drop of ~0.15 eV was evaluated by XPS analysis.

Acknowledgments

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