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Electrically induced change in HfO₂/1-monolayer TiO₂/SiO₂ metal-oxidesemiconductor stacks: capacitance-voltage and hard X-ray photoelectron spectroscopy studies

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Metal-oxide-semiconductor capacitors with HfO2/1-monolayer TiO2/SiO2 stacks were examined to explore the origin of the interface dipole modulation. The capacitance-voltage (C-V) measurements exhibited that the polarity of the interface dipole layer changes depending on the gate bias. The hard X-ray photoelectron spectroscopy measurements demonstrated that an applied gate voltage induces small changes in the Ti–O chemical bonding and potential profile around the HfO₂/SiO₂ interface. © 2021 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

he material HfO₂ is used as a gate dielectric layer in a current type of advanced MOS field-effect transistors (FETs), and it has a high material affinity with semiconductor device technology.^{1–3)} There are many studies on emerging HfO₂-based memory devices, such as a resistance-change random-access memory using oxygen vacancies in the HfO₂ and a ferroelectric FET (FeFET) with a thin ferroelectric HfO_2 layer.^{2,4–8)} One advantage of these devices is the capability to fabricate high-density memory devices via the current semiconductor manufacturing platform. In particular, the technical hurdles of HfO2-based FeFETs are expected to be low, as it has essentially the same device structure as the current MOS FETs. The key issue is the precise control of the ferroelectric crystal phase, which involves the annealing procedure, the selection of dopant atoms, and the dopant concentration.^{7–11)} On the other hand, an amorphous-HfO₂-based MOS memory device, which can be fabricated by a low-temperature process, was recently proposed.^{12,13)} Amorphous HfO_2/SiO_2 MOS capacitors with an atomically thin interfacial TiO₂ layer have been reported to exhibit C-V hysteresis similar to that of ferroelectric MOS capacitors. The hysteresis width induced by a single HfO_2/SiO_2 stack is too small (~0.3 V) to be sufficient for memory applications, so a multi-stack HfO2/1-ML TiO2/SiO2 structure has been proposed.^{12,14,15} As for the mechanism of these C-V characteristics, an interface dipole modulation (IDM) induced by Ti-O bond breakage/repair or bonding configuration change has been proposed.^{12,14)} However, there have been few reports on IDM mechanism, and our understanding of it is not sufficient. In this study, we examine single HfO₂/1-ML TiO₂/SiO₂ MOS stacks, which are the simplest IDM structures, by using the C-V and HAXPES methods.

First, a 10 nm thick SiO₂ layer was formed on an n-type Si (100) substrate by a thermal oxidation method. Second, by immersing the substrate in a diluted HF solution, the SiO₂ layer was etched and thinned to about 7 nm. Third, the sample was introduced into an ultra-high vacuum chamber and heated at above 350 °C for longer than 10 min to desorb the adsorbed molecules of species such as water. After cooling down to room temperature, 1-ML TiO₂ and HfO₂ layers were deposited by an EB evaporation method.^{12–14)} To provide a sample for C-V measurements, an HfO₂ layer with a thickness of 2–7 nm was deposited on the same substrate by gradually moving a shutter between the EB evaporator and the substrate. Finally, the post-deposition annealing was performed at 350 °C for 30 min, and 50 nm thick Al was then deposited as a gate electrode by using a stencil mask. To provide a HAXPES sample, 1-ML TiO₂ and 2 nm thick HfO₂ layers were also deposited on a 10 nm thick SiO₂/n-Si substrate. Because the gate electrode has to be thin enough to enable detection of photoelectrons emitted from the oxide stack underneath, 16,17 a 15 nm thick Ir layer was deposited on the HfO2. The HAXPES measurements were performed with synchrotron radiation ($h\nu = 7940 \text{ eV}$) in the BL47XU at SPring-8.^{18,19)}

As seen in Fig. 1(a), a transmission electron microscopy (TEM) image of the prepared MOS stack showed that the HfO₂ and SiO₂ were amorphous and the reaction at their interface was negligible. Note that the TEM contrasts of TiO₂ and SiO_2 are at the same level. The high-frequency C-Vcurve shown in blue in Fig. 1(b) indicates a counterclockwise hysteresis, which is the same as the IDM operation reported in previous papers.^{12–15)} Those studies used Ir and Au, which are metals with a large work function ($\Phi_M > 5 \text{ eV}$), as the gate electrode. The present C-V data is the first demonstration with Al, a metal with a low work function $(\Phi_M$ \sim 4.25 eV). In high-frequency C-V measurements for an ntype Si substrate, it is well known that a sufficient oxide electric field in the negative bias range is not produced because of the formation of a depletion layer.²⁰⁾ The red curves in Fig. 1(b) show the C-V hysteresis measured at 5 kHz under laser-light illumination (730 nm) in which the sufficient minority carriers were supplied to overcome the above issue.^{12,13)} A C-V shift starting from the initial curve was found towards both the positive and negative biases. Here, the flat-band voltage, $V_{\rm fb}$, was estimated; it is shown by the dotted green curves in Fig. 1(b), and its bias dependence is plotted in Fig. 1(c). There was a saturation tendency at a



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Fig. 1. (Color online) C-V measurements of HfO₂/1-ML TiO₂/SiO₂ MOS capacitors. (a) TEM image of a typical MOS capacitor. Position of 1-ML TiO₂ layer is indicated by green arrow. (b) C-V hysteresis curves measured under high-frequency and light-illuminated conditions. (c) Gate-voltage-induced $V_{\rm fb}$ shifts estimated by light-illuminated C-V method. (d) Maximum and minimum $V_{\rm fb}$ values measured for MOS capacitors with various HfO₂ thicknesses.

bias range wider than ± 4 V, and estimated maximum hysteresis width is about 0.3 V.

The oxide thickness dependence is well known to provide information about the electric charge position in a MOS stack,²⁰⁻²²⁾ so we examined the effect of the HfO₂ thickness on the switched $V_{\rm fb}$, i.e. the maximum and minimum $V_{\rm fb}$ values, as shown in Fig. 1(d). The HfO₂ thickness $[t_{HfO_2}]$ (nm)] was estimated from the equivalent oxide thickness determined from the high-frequency C-Vmeasurements.²²⁻²⁴⁾ In the following discussion, we assume that two of electric at types charges the HfO₂/1ML-TiO₂/SiO₂ interfaces were changed by the gate voltage: a unipolar sheet charge $[qS_I \text{ (cm}^{-2})]$ and a dipole layer with positive and negative changes, respectively, on the HfO₂ and SiO₂ sides [Φ_{dipole} (V)]. This means that the electric charges near the electrode/HfO2 and the SiO2/Si interfaces are ignored. The $V_{\rm fb}$ value can be expressed by the following equation:^{20–22)}

$$V_{\rm fb} = \Phi_{\rm MS} - \frac{q S_I t_{\rm HfO_2}}{\varepsilon_{\rm HfO_2}} + \Phi_{\rm dipole}, \qquad (1)$$

where, Φ_{MS} (V) is the work function difference between Si and the Al gate metal, and $\varepsilon_{\rm HfO_2}$ is the dielectric constant of the HfO₂ layer with the relative dielectric constant of approximately $20^{23,24}$ Ignoring the interface dipole, the switching betw $(4.1 \times 10^{12} \text{ cm}^{-2})$ between the positive sheet charge negative and the sheet charge $(3.2 \times 10^{12} \,\mathrm{cm}^{-2})$ produced the dotted lines shown in Fig. 1(d). This calculated tendency is different from the experimental data. In contrast, the solid lines in Fig. 1(d) were calculated by considering both types of charges, and this result is suitable for explaining the experimental data. In this case, the sheet charge density, S_I , was estimated to be low ($<3 \times 10^{11}$ cm⁻²) and the interface dipole, Φ_{dipole} , switched between -0.14 and +0.18 V. This indicates that the polarity reversal of the interface dipole was the main contribution to the observed hysteresis characteristics.

A similar analysis was reported for IDM MOS capacitors with Ir gate electrodes,^{13,14)} and those results have been proposed to provide one reasons for the IDM mechanism. However, the maximum and minimum $V_{\rm fb}$ for the Irelectrode samples were always smaller than the ideal $V_{\rm fb}$, so the strength of the interface dipole was considered to have changed. This is different from the dipole polarity reversal of the present Al-electrode samples. We consider that this difference is related to the charge distribution around the metal/HfO2 interface. From Al/HfO2/SiO2/Si MOS capacitors without interface Ti oxide, Φ_{dipole} was estimated to be about 0.02 V, which was almost consistent with that estimated for Al/SiO₂/Si MOS capacitors. This means that the dipole at the Al/HfO₂ interface is negligibly small. On the other hand, Φ_{dipole} of Ir/HfO₂/SiO₂ stacks was reported to be larger than 0.2 V.^{13,22} This dipole is probably present at the Ir/HfO₂ interface rather than at the HfO₂/SiO₂ interface. In fact, several groups have proposed dipole formation at the contact between HfO2 and a metal with a large work



Fig. 2. (Color online) HAXPES measurements of a HfO₂/1-ML TiO₂/SiO₂ MOS capacitor. (a) Schematic illustration of the MOS sample measurement. (b) Hf 3d, Si 1s, and Ti 1s photoelectron spectra measured under the gate voltage conditions of (I) $V_g = 0$ V, (II) $V_g = -5$ V, and (III) $V_g = 0$ V after $V_g = -5$ V. (c) Ti 1s photoelectron spectra of (II), and fitting curves of (I) and (III).

function.^{25,26)} Therefore, we concluded that the initial dipole at the HfO_2/SiO_2 interface is small in both electrode samples, and in the IDM operation, interface dipoles with opposite polarities are formed depending on the induced electric field direction.

In the HAXPES measurements, the gate electrode was connected to the ground and a voltage was applied to the Si back contact, as illustrated in Fig. 2(a). For convenience of comparison with the above C-V measurements, the substrate voltage is denoted as $-V_g$ (V) in the following explanation. The curves indicated (I) in Fig. 2(b) are the Hf 3d, Si 1s, and Ti 1s photoelectron spectra observed before applying the voltage. These curves show that the HfO₂, SiO₂, and TiO₂ were major components and each suboxide was small.^{16,27–30)} This result is consistent with previous standard X-ray photoelectron spectroscopy results for the HfO₂/1-ML TiO₂/SiO₂ structure without an electrode.¹³⁾ Thus, we conclude that the formation of the Ir electrodes does not induce defects in the oxide stack.

The curves indicated by (II) in Fig. 2(b) show that an applied voltage of $V_{\rm g} = -5.0$ V caused a large binding energy shift and spectral change in the Si 1s photoelectron spectrum, but the Hf 3d and Ti 1s spectra were only slightly changed. This behavior can be mostly explained via the change in the band diagrams shown in Fig. 3. The peak shift of the Si substrate reached about 4 eV, suggesting that about 4 V was applied to the HfO₂/1-ML TiO₂/SiO₂ stack structure. This is reasonable given the Si surface band bending and the parasitic series capacitance. The spectral shape for the oxide components at $V_{\rm g} = -5.0 \,\rm V$ is obviously different from the spectral shape at $V_g = 0$ V. This can be explained by the inclined SiO_2 band shown in Fig. 3(b). Even if the chemical composition is the same, the binding energy shifts according to the potential drop. The Si oxide spectrum is the integration of the photoelectrons emitted from such an inclined SiO₂ band.¹⁶⁾ Therefore, we can conclude that the applied voltage caused the large spectral change, especially in the SiO₂ layer. Note that a small peak indicated by "*" in Fig. 2(b) (II) remained at the binding energy of Si substrate. This is presumed to be due to stray photoelectrons from the area not covered by the Ir. On the other hand, the Hf 3d peak shift is as small as 0.1 eV. This is consistent with the band diagram in Fig. 3(b), where the band slope of the HfO_2 layer with a



Fig. 3. (Color online) Band diagrams for the HAXPES measurements of the HfO₂/1-ML TiO₂/SiO₂ MOS capacitor. (a) $V_g = 0$ V conditions, and (b) negative V_g conditions.

high dielectric constant must be smaller than that of the SiO_2 layer. The peak shift of Ti 1s is also small, which is consistent with the small potential drop of the interfacial Ti oxide as shown in Fig. 3(b).

When the gate voltage was returned to $V_g = 0$ V, all the spectra returned to being almost the same as before applying the voltage. On the other hand, we can find a slight difference in the Ti 1s spectra, i.e. the full width at half maximum (FWHM) changes from 2.2 to 2.5 eV by applying -5 V. The spectral change shown in Fig. 2(c) could be related to the Ti-O bonding configuration (bond length and angle) and the formation of Ti₂O₃. A more elaborate measurement with higher resolution and higher sensitivity is required to identify the structural change. On the other hand, FWHM returned to 2.2 eV after applying voltage of +3 V (not shown). Therefore, we considered that the above Ti 1s spectral change is a reversible phenomenon similar to the IDM operation. In addition, the above speculation is consistent with the previously reported IDM mechanism with Ti-O structural change.^{12,14)}

Figure 4(a) shows the Si 1s (4+) and Hf 3d (4+) spectra at $V_{\rm g} = 0$ V, which reveal that the peak binding energy difference, $BE_{Si1s-Hf4d} = Si 1s (4+)-Hf 4d (4+)$, decreased slightly after applying a voltage of -5 V. The change in BE_{Si1s-Hf4d}, $\delta BE_{Si1s-Hf4d} = BE_{Si1s-Hf4d} - BE_{Si1s-Hf4d}$ (initial), is plotted in Fig. 4(b). As indicated by the blue circles, large $\delta BE_{Si1s-Hf4d}$ shifts took place naturally when the voltage was applied. The red rhombuses show the behavior for $V_{g} = 0$ V, zero-voltage $\delta BE_{Si1s-Hf4d}$, indicating that the $\delta BE_{Si1s-Hf4d}$ decreased after applying voltage of -3 and -5 V. These changes can be explained by the change in the interface dipole, as shown in Fig. 3(a). Here, we assume an interface dipole with positive changes on the HfO_2 side and negative changes on the SiO_2 side. If this dipole polarity switches, $\delta BE_{Si1s-Hf4d}$ is expected to become small. This behavior is also consistent with the above C-V characteristics, i.e. the C-V curve is shifted toward a positive bias by applying a negative voltage. On the other hand, $\delta BE_{Si1s-Hf4d}$ decreased by about 0.2 eV after applying a voltage of -5 V, which is slightly smaller than the maximum C-V hysteresis mentioned above. This difference



Fig. 4. (Color online) Effect of the applied voltage V_g on the binding energy difference between the Si 1s (4+) and Hf 3d (4+) photoelectron peaks (BE_{Si1s-Hf3d}). (a) Si 1s and Hf 3d photoelectron spectra before and after applying a voltage of -5 V. (b) Difference from initial BE_{Si1s-Hf3d}, δ BE_{Si1s-Hf3d} = BE_{Si1s-Hf3d}-BE_{Si1s-Hf3d} (*initial*). The blue circles show the voltage dependence. The red rhombuses show zero-voltage δ BE_{Si1s-Hf3d}, which shows the changes induced by applying the voltage.

© 2021 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd can be explained by the band diagram in Fig. 3(a). Even at $V_g = 0$ V, the energy bands of the SiO₂ and HfO₂ layers are expected to be slightly tilted. The Si 1s (4+) and Hf 4d spectra are the integration of photoelectrons emitting from these SiO₂ and HfO₂ layers, respectively. The spectral peak position can be roughly estimated to be the photoelectron binding energy at the center of the oxide layer. Therefore, it is reasonable that the peak energy difference is smaller than the potential change at the SiO₂/HfO₂ interface. From the above results, we conclude that the same phenomenon was detected in both the *C*–*V* and HAXPES measurements. On the other hand, the interface dipole was already formed before applying the voltage in the HAXPES measurement. We consider that the interface dipole has already been produced by the X-ray irradiation.

Finally, we discuss the other mechanisms that could produce the above counterclockwise C-V hysteresis: (1) mobile electric charges in the oxide stack, and (2) carrier transfer between the gate electrode and the carrier traps in the oxide stack. We first consider the defect-related mobile charges or carrier traps around the interfacial Ti atoms. In this case, $V_{\rm fb}$ must be proportional to the HfO₂ thickness, as expected from Eq. (1). Our experimental data rejects this scenario. If mobile charges or carrier traps are formed in the HfO_2 near the electrode, the measured V_{fb} shifts can be explained. In this case, a usual HfO2/SiO2 MOS stack without an interfacial TiO_2 layer should have a similar C-Vhysteresis. In addition, if the metal/HfO₂ contact induces such defects, the hysteresis characteristics are expected to depend on the electrode material. Furthermore, as seen in Fig. 4(a), the peak shift of Hf 3d is much smaller than that of Si 1s, suggesting that the change in the potential distribution of the HfO₂ layer is small. Therefore, from the above C-Vand HAXPES measurements, we conclude that the polarity of the interface dipole in the $HfO_2/1$ -ML TiO_2/SiO_2 structure is switched by applying the voltage. The structural change observed for the interfacial Ti oxide described above is considered to induce the polarity reversal of the interface dipole.

In conclusion, the C-V measurements of the HfO₂/1-ML TiO₂/SiO₂ MOS stack revealed that polarity reversal of interface dipole produces the $V_{\rm fb}$ shift of about 0.3 V. The HAXPES measurement exhibited a small change in the Ti–O chemical bonding and supported the potential change between the HfO₂ and SiO₂ layers.

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