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X-ray photoelectron spectroscopy study of dipole effects at $HfO_2/SiO_2/Si$ stacks

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1. Introduction

The control of flat-band voltage (V_{FB}) is currently one of the most serious problems in high-k gate stacks. Recently, the dipole model was proposed to explain anomalous V_{FB} observed experimentally [1-4]. In order to investigate the physical insight of the dipole layer formation, a physical characterization is required in addition to electrical characterizations. In this work, we report the applicability of x-ray photoelectron spectroscopy (XPS) measurements to detect the dipole behaviour at $HfO_2/SiO_2/Si$ stacks [5, 6].

2. Experiment

HfO_2 with different thickness (1.8nm, 2.4nm and 3nm) were prepared on both surface oxidized N-type (8~10Ω·cm) and P-type (1~5Ω·cm) Si substrates by sputtering of HfO_2 targets in Ar ambient at room temperature. All the stacks were received RTA at 500°C for 30s in N_2+0.1%O_2 ambient. **Fig.1** illustrates the simplified band diagram of the $HfO_2/SiO_2/Si$ stack with taking account of the dipole at HfO_2/SiO_2. In the case that there is a dipole at HfO_2/SiO_2 interface, the Hf4f core levels (CLs) will shift correspondingly. The increased (or decreased) Hf4f CL binding energy means the dipole downward (or upward) from SiO_2 side to HfO_2 side. This is our guideline for characterizing the dipole.

3. Results and discussion

Firstly, the time dependence of CL shifts have been excluded by taking Si2p or O1s spectra for Si/SiO_2 stacks with different X-ray exposure time (20min~120min) (**Fig.2**). For metal/HfO_2/SiO_2/Si stack, a schematic model of the possible charge locations and dipoles is illustrated in **Fig.3.** In electrical characterization, the V_{FB} is described by both dipoles at interface (Δ_2, Δ_1 *and* Δ_0) and the fixed charges in the stacks (ρ_1, ρ_0, Q_1 *and* Q_0). Similarly, if we calibrate the energy scale to Si Fermi level, Hf4f CL for $HfO_2/SiO_2/Si$ stacks will be:

$$BE = \Delta BE(Q_0) + \Delta BE(Q_1) + \Delta BE(\rho_0) + \Delta BE(\rho_1) + \Delta_1 + \Delta_0 + BB_{Si} + BE_0 \quad (1)$$

, where BE_0 (depending on Si Fermi level) is the ideal Hf4f CL for no band bending, no fixed charge and no dipole case, while BE is the measured Hf4f CL. Here, we assume the followings.

(i) Band bending in Si substrate (BB_{Si}) : By measuring the BE referring to Si2p signal from Si substrate, the effects of BB_{Si} on the Hf4f CLs can be eliminated by setting such Si2p CLs at certain position (~99.47eV).

(ii) Dipole at SiO_2/Si interface (Δ_0) : It is believed that there is no dipole at SiO_2/Si interface, so we neglected this term (Δ_0= 0).

(iii) Interface charges at SiO_2/Si interface ($\Delta BE(Q_0)$) : It is also believed to have no charges at SiO_2/Si interface ($\Delta BE(Q_0)$= 0).

Note that both $\Delta BE(Q_1)$ and $\Delta BE(\rho_0)$ are functions of t_{SiO2}, whereas $\Delta BE(\rho_1)$ is a function of both t_{HfO2} and t_{SiO2}. First, we investigated the HfO_2-thickness-dependence of BE. As shown in **Fig. 4**, for HfO_2 on 3nm SiO_2, there is almost no dependence of Hf4f CLs (located at ~18.5eV) on HfO_2 thickness. From this result it is concluded that the effects of the fixed charge in HfO_2 on Hf4f CLs can be ignored ($\Delta BE(\rho_1)$= 0).

Fig. 5 illustrates the shifts of Hf4f CLs as a function of SiO_2 thickness for 3nm HfO_2/x nm SiO_2/ Si(100) stacks with N- and P-Si substrates. Firstly, we find that there are increased Hf4f CLs with increased SiO_2 thickness. Such increase is ~0.8eV for both N- and P-Si. These quite significant shifts of BE depending on SiO_2 thickness consist of 3 terms, $\Delta BE(Q_1)$, $\Delta BE(\rho_0)$, and Δ_1, since we can regard other terms negligibly small. Dipole term (Δ_1) does not show the dielectric layer thickness dependence in the usual situation, however, here we include a change of the dipole strength with SiO_2 layer thickness change.

In order to evaluate the impact of $\Delta BE(\rho_0)$, $\Delta(Si_{2p}^{si\ oxides}-Si_{2p}^{0})$ vs. t_{SiO2} in SiO_2/Si stacks without HfO_2 over layer are plotted as shown in **Fig. 6**, where $\Delta(Si_{2p}^{si\ oxides}-Si_{2p}^{0})$ is composed of both charging and the chemical shift of Si2p in sub-oxide. There is increased $\Delta(Si_{2p}^{si\ oxides}-Si_{2p}^{0})$ values for ~0.3eV from ~2nm to above 3nm. This should be attributed to the effects of fixed charges in SiO_2 layer ($\Delta BE(\rho_0)$). The decreased $\Delta(Si_{2p}^{si\ oxides}-Si_{2p}^{0})$ value for very thin SiO_2 thickness (below 1.5nm) is also due to the increased contribution of the sub-oxide to $Si_{2p}^{si\ oxides}$ and it does not contribute to Hf4f CL shift. After taking account of these results, the impact of the charging effects in SiO_2 on Hf4f CLs shown in **Fig. 5** is estimated to be around 0.3 eV. On the other hand, the impact of interfacial fixed charges at HfO_2/SiO_2 interface ($BE(Q_1)$) on the shift of Hf4f CLs in **Fig. 5** is hard to evaluate quantitatively only from XPS measurements. However, $Q_1 < 1\times10^{12}$, which is a reasonable assumption from the electrical characteristics of $HfO_2/SiO_2/Si$ stacks, will result in a shift of BE ~0.05 eV/EOT, *i.e.* less than 0.2 eV shift even by the change of SiO_2 thickness from 1 nm to 5 nm. The observed slope in **Fig. 5** is significantly larger than what is expected from the change of $BE(Q_1)$.

From above discussions, it can be concluded that the anomalously large shift of Hf4f CLs by changing the SiO_2 thickness cannot be interpreted only by the terms of $\Delta BE(\rho_1)$, $\Delta BE(\rho_0)$, and $\Delta BE(Q_1)$. This fact suggests that there is a shift of the magnitude of dipole at HfO_2/SiO_2 interface (Δ_1). It will be reasonable to consider that the change of Δ_1 is no less than a few hundreds of meV, and Δ_1 is enhanced by increasing the SiO_2 thickness. It is reported that a dipole at HfO_2/Si direct interface increases by decreasing SiO_2 below 1 nm [7]. We think, however, our result is attributable to the dipole at HfO_2/SiO_2 interface, because we observe the shift of Δ_1 for SiO_2 much thicker than 1 nm. It is also noted that the charge transfer between HfO_2 and Si substrate with the decrease of the SiO_2 thickness is not the reason for the change of Δ_1, because the change of Δ_1 with SiO_2

thickness is quite similar for both N-Si and P-Si with different Si Fermi level. We believe that this is a first good example of observing the existence of the interface dipole at HfO_2/SiO_2, and change of it with SiO_2 thickness, without electrical characteristics measurements.

4. Conclusions

We analyzed factors to affect the Hf4f CLs in XPS results, and found that a significant Hf4f CLs shift by changing SiO_2 thickness which cannot be explained only by the charges in the stack. This anomalous shift might be attributed to the change of the dipole effects at HfO_2/SiO_2 interface. The present study suggests that XPS can be a tool to investigate physical insights of dipole formation mechanisms at high-k/SiO_2 interfaces, though further investigation is obviously needed.

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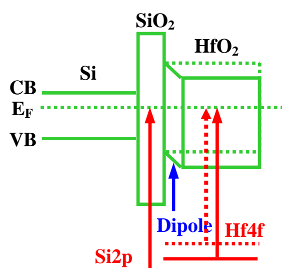

Fig.1 Simplified band diagram of $HfO_2/SiO_2/Si$ stack. The increased Hf4f CL binding energy will be related to the dipole downward from SiO_2 side to HfO_2 side.

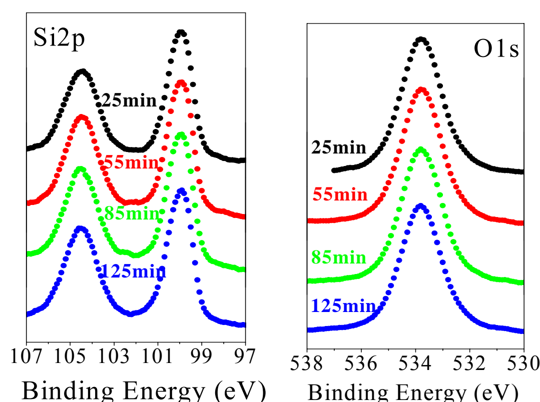

Fig.2 Time dependent XPS Si2p and O1s spectra for ~3.0nm SiO_2/Si stack. There are no observable CL binding energy shifts in both Si2p and O1s spectra within two hours X-ray exposure, indicating no time dependence of XPS spectra.

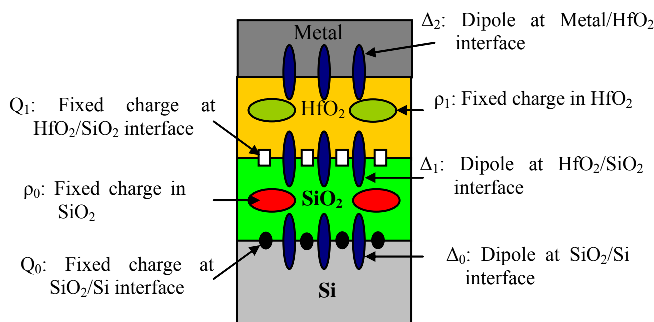

Fig.3 Schematic model of possible fixed charges and dipole locations.

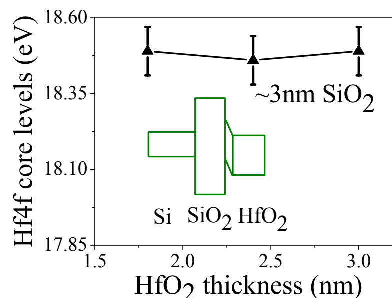

Fig.4 The effects of HfO_2 thickness on Hf4f CLs for HfO_2/SiO_2 stacks. All the CLs are calibrated to Si2p at 99.47eV.

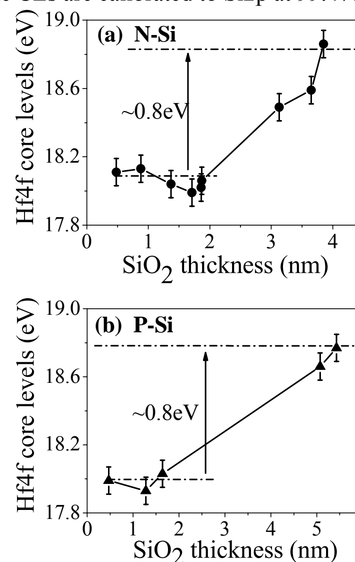

Fig.5 Hf4f CLs as a function of SiO_2 thickness for (a) HfO_2/SiO_2/N-Si(100) stacks and (b) HfO_2/SiO_2/P-Si(100) stacks. All the CLs are calibrated to Si2p at 99.47eV.

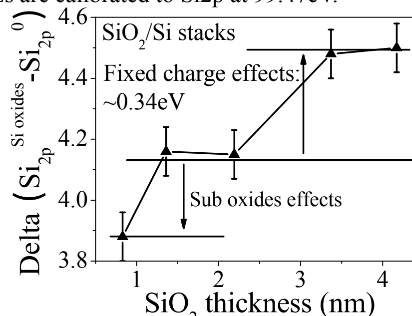

Fig.6 $\Delta(Si_{2p}^{si\ oxides}-Si_{2p}^{0})$ vs t_{SiO2} for SiO_2/Si stacks. This trend was taken into consideration for estimating the dipole at HfO_2/SiO_2 interface.