X-ray photoelectron spectroscopy study of dipole effects at HfO2/SiO2/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 HfO2/SiO2/Si stacks [5, 6].

2. Experiment
HfO2 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 HfO2 targets in Ar ambient at room temperature. All the stacks were received RTA at 500°C for 30s in N2+0.1%O2 ambient. In the case that there is a dipole at HfO2/SiO2 interface, the Hf4f core levels (CLs) will shift correspondingly. The increased (or decreased) Hf4f CL binding energy means the dipole downward (or upward) from SiO2 side to HfO2 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/SiO2 stacks with different X-ray exposure time (20min~120min) (Fig.2). For metal/HfO2/SiO2/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 $d_1$ at HfO2/SiO2 interface, whereas $d_2$ at HfO2/Si direct interface. 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 HfO2/SiO2/Si stacks [5, 6].

$BE = \Delta BE(Q_1) + \Delta BE(Q_2) + \Delta BE(\rho_1) + \Delta BE(\rho_0) + \Delta_1 + \Delta_0 + BB_{\rho_1} + BB_{\rho_0}$ (1)

where $BB_{\rho_1}$ (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\rho): By measuring the BE referring to Si2p signal from Si substrate, the effects of BB\rho on the Hf4f CLs can be eliminated by setting such Si2p CLs at certain position (~99.47eV).

(ii) Dipole at SiO2/Si interface ($\Delta d$): It is believed that there is no dipole at SiO2/Si interface, so we neglected this term ($\Delta d = 0$).

(iii) Interface charges at SiO2/Si interface ($\Delta BE(\rho_0)$): It is also believed to have no charges at SiO2/Si interface ($\Delta BE(\rho_0) = 0$).

Note that both $\Delta BE(Q_1)$ and $\Delta BE(\rho_0)$ are functions of tSiO2, whereas $\Delta BE(\rho_1)$ is a function of both tHfO2 and tSiO2. First, we investigated the HfO2-thickness-dependence of BE. As shown in Fig. 4, for HfO2 on 3nm SiO2, there is almost no dependence of Hf4f CLs (located at ~18.5eV) on HfO2 thickness. From this result it is concluded that the effects of the fixed charge in HfO2 on Hf4f CLs can be ignored ($\Delta BE(\rho_1) = 0$).

Fig. 5 illustrates the shifts of Hf4f CLs as a function of SiO2 thickness for 3nm HfO2/SiO2/Si(100) stacks with N- and P-Si substrates. Firstly, we find that there are increased Hf4f CLs with increased SiO2 thickness. Such increase is ~0.8eV for both N- and P-Si substrates. These significant shifts of BE depending on SiO2 thickness consist of 3 terms, $\Delta BE(Q_1)$, $\Delta BE(\rho_0)$, and $\Delta d$, since we can regard other terms negligibly small. Dipole term ($\Delta d$) does not show the dielectric layer thickness dependence in the usual situation, however, here we include a change of the dipole strength with SiO2 layer thickness change.

In order to evaluate the impact of $\Delta BE(\rho_0)$, $\Delta (Si_{2p}^{SiO_2^{\delta\text{oxide}}}-Si_{2p}^{SiO_2^{\delta\text{ox}}})$ vs. tSiO2 in SiO2/Si stacks without HfO2 over layer are plotted as shown in Fig. 6, where $\Delta (Si_{2p}^{SiO_2^{\delta\text{oxide}}}-Si_{2p}^{SiO_2^{\delta\text{ox}}})$ is composed of both charging and the chemical shift of Si2p in sub-oxide. There is increased $\Delta (Si_{2p}^{SiO_2^{\delta\text{oxide}}}-Si_{2p}^{SiO_2^{\delta\text{ox}}})$ values for ~0.3eV from ~2nm to above 3nm. This should be attributed to the effects of fixed charges in SiO2 layer ($\Delta BE(\rho_0)$). The decreased $\Delta (Si_{2p}^{SiO_2^{\delta\text{oxide}}}-Si_{2p}^{SiO_2^{\delta\text{ox}}})$ value for very thin SiO2 thickness (below 1.5nm) is also due to the increased contribution of the sub-oxide to Si_{2p}^{SiO_2^{\delta\text{ox}}} and it does not contribute to Hf4f CL shift. After taking account of these results, the impact of the charging effects in SiO2 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 HfO2/SiO2 interface ($\Delta BE(Q_1)$) on the shift of Hf4f CLs in Fig. 5 is hard to evaluate quantitatively only from XPS measurements. However, $Q_1 < 1 \times 10^{13}$, which is a reasonable assumption from the electrical characteristics of HfO2/SiO2/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 SiO2 thickness from 1nm to 5nm. 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 SiO2 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 HfO2/SiO2 interface ($\Delta d$). It will be reasonable to consider that the change of $\Delta d$ is no less than a few hundreds of meV, and $\Delta d$ is enhanced by increasing the SiO2 thickness. It is reported that a dipole at HfO2/Si direct interface increases by decreasing SiO2 below 1nm [7]. We think, however, our result is attributable to the dipole at HfO2/SiO2 interface, because we observe the shift of $\Delta d$ for SiO2 much thicker than 1nm. It is also noted that the charge transfer between HfO2 and Si substrate with the decrease of the SiO2 thickness is not the reason for the change of $\Delta d$, because the change of $\Delta d$ with SiO2
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 HfO2/SiO2, and change of it with SiO2 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 SiO2 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 HfO2/SiO2 interface. The present study suggests that XPS can be a tool to investigate physical insights of dipole formation mechanisms at high-k/SiO2 interfaces, though further investigation is obviously needed.

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References


Fig.1 Simplified band diagram of HfO2/SiO2/Si stack. The increased Hf4f CL binding energy will be related to the dipole downward from SiO2 side to HfO2 side.

Fig.2 Time dependent XPS Si2p and O1s spectra for ~3.0nm SiO2/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 HfO2 thickness on Hf4f CLs for HfO2/SiO2 stacks. All the CLs are calibrated to Si2p at 99.47eV.

Fig.5 Hf4f CLs as a function of SiO2 thickness for (a) HfO2/SiO2/N-Si(100) stacks and (b) HfO2/SiO2/P-Si(100) stacks. All the CLs are calibrated to Si2p at 99.47eV.

Fig.6 Δ(Si2pSi oxides – Si2p0) vs tSiO2 for SiO2/Si stacks. This trend was taken into consideration for estimating the dipole at HfO2/SiO2 interface.