Advanced Characterization of High-k Gate Stack by Internal Photo Emission (IPE): Interfacial Dipole and Band Diagram in Al/Hf(Si)O₂/Si MOS Structure

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1. Introduction

For the choice of a new high-k material to replace SiO₂, both the dielectric constant and the barrier height (Φ) at the high-k interfaces have to be considered. Indeed, this second parameter must be sufficiently high to reduce the electron transport between metal gate and silicon. In this context, a clear knowledge of the energy band diagram is needed. Through the determination of Al/HfO₂-and-HfSiO₂/SiO₂/Si electron band diagrams, we will see in this paper that Internal Photo Emission (IPE) is an appropriate tool. In the first part, Φ (Al/HfO₂) and Φ (Si/HfO₂) are deeply studied showing the possibility to characterize interfacial dipole in the structure. In the second part we analyze the effect of silicon incorporation inside HfO₂ films on the electronic structure.

2. Experiment

 $H\bar{f}O_2$ and $Hf_{(1-x)}Si_xO_2$ films (4-15nm) (x=15, 50 and 70%) were deposited on HF-treated *n*-Si (100) wafers by co-sputtering of $H\bar{f}O_2$ and SiO_2 targets in Ar ambient at room temperature. PDA was made at 400°C in 0.1% $O_2 + N_2$ ambient. Thin Al gates (15nm) were deposited, thin enough to allow photo-excitation of electrons during the IPE experiment. At the end of the process, an unintentional SiO₂ interfacial layer (IL) of about 1nm exists between the Si and the high-k layer. For the sake of comparison, identical metal electrode was evaporated onto thermal SiO₂ layers.

The capacitors were studied by IPE in the photon energy range from 1.2eV to 4eV. This technique [1] allows a direct measurement of the conduction band (CB) offset between the metal Fermi level and the dielectric CB (under V_G<0) and between the Si substrate valence band (VB) and the dielectric CB (under V_G>0). The IPE quantum yield (Y) is defined as the photocurrent normalized to the incident photon flux. $Y^{1/2}(hv)$ and $Y^{1/3}(hv)$ were used to extract $\Phi(metal/oxide)$ and $\Phi(silicon/oxide)$ respectively. Quantitatively, this technique is more accurate than XPS/UPS ones [2]-[3], since the electron band offset is directly measured.

2. Conduction band offsets of HfO₂

The spectral IPE curves obtained on the HfO₂ samples are presented in Fig. 1 for Si injection (V_G>0) and in Fig. 2 for Al metal gate injection (V_G<0). To obtain the exact barrier energies, the spectral thresholds were measured at different electric fields and extrapolated to the zero field in the Schottky plot (Fig. 3). The resulting Φ (Si-VB/HfO₂) is 3 ± 0.1eV (which corresponds to a CB offset (Δ Ec) of 1.9 ± 0.1eV) and Φ (Al/HfO₂) is 2.3 ± 0.1eV. As seen in Fig. 3, the spectral thresholds at HfO₂ interfaces are independent of the applied electric field. This obstruction of the image force barrier lowering at the HfO₂ interfaces may be related to defects inside the high-k.

To know the influence of the unavoidable SiO₂ IL on the extracted Φ value, SiO₂ thickness has been varied from 2nm to 17nm by thermal oxidation previous to the HfO₂ deposition. The IPE spectra from Al injection (Fig. 4a) indicate that, despite a reduction of the IPE yield intensity with the increase of the IL thickness, the $\Phi(AI/HfO_2)$ is not impacted up to a SiO₂ thickness of 4-5nm (Fig. 4b). On the other hand, $\Phi(Si/HfO_2)$ can only be extracted with an IL of about 1nm maximum since the spectral curves (data not shown) become similar to the IPE into SiO₂ for IL \geq 2nm [4]. From Al injection, photo-excited electrons are injected in the HfO₂ CB and can tunnel in the thin SiO₂ layer or/and can be re-excited by the constant photon emission above the SiO₂ barrier height (cf. Fig. 5). From Si injection, electrons have to tunnel into the SiO₂ barrier before reaching the HfO₂ CB. When the IL thickness increases, the tunneling probability exponentially

decreases, leading to the reflection of the excited electrons back into Si for Si injection and the decrease of the IPE yield for Al injection. With a fixed IL thickness, $\Phi(Al/HfO_2)$ appears to be the same for an HfO₂ thickness in the range of 5-15nm (Fig. 4b).

With these extractions, the electron energy band diagram of the Al/HfO₂/Si structure can be build (Fig. 5) and compared with the Al/SiO₂/Si band diagram (Φ (Al/SiO₂)=3.25 ± 0.05eV, cf. Fig. 2, 3). By comparing the oxide band offset with the Si and with the Al, we observe a 0.3eV difference between the SiO₂ and the HfO₂ case. Considering the SiO₂ electron affinity of 0.9eV and the vacuum alignment model in the SiO₂ case [5], we deduce that the Al work-function (WF) is 4.15 ± 0.1eV. In the HfO₂ case, the effective Al WF is enhanced of 0.3eV. This observation indicates the presence of an interfacial dipole in the Al/HfO₂/SiO₂/Si stack. As the Al/high-k interface is not affected by MIGS [6], we think that this dipole is associated with the high-k/SiO₂ interface, where a dipole was demonstrated to decrease the metal effective WF [7], in HfO₂ case, the dipole is in the opposite direction leading to an enhancement of the metal effective WF.

3. Impact of the Si doping in HfO₂ on the band diagram

The electron IPE spectra for Al/ $Hf_{(1-x)}Si_xO_2/Si$ MOS structures with x = 0, 15, 50, 70 and 100% are shown in Fig. 6 for Al injection and in Fig. 7 for Si injection. Barrier height values obtained from Schottky plots are summarized in Fig. 8. We can see that the electron CB offset is not a linear function of the silicon concentration in the hafnium silicate films: the hafnium silicate film with 15% of Si does not exhibit higher electron barrier heights compared to the pure HfO₂ case. The Al/oxide barrier height is even lower which can be explained by a decrease of the interfacial dipole by adding Si in the HfO₂ film. In the same way, for $Hf_{(1-x)}Si_xO_2$ with 70% of Si, the barrier height is close to the one of SiO_2 . To be able to represent the complete band diagram, the optical band gap was determined by Spectroscopic Ellipsometry (SE) on thick (\approx 35nm) as deposited oxides (Fig. 9). The HfO₂ band gap was determined at 5.5eV. With increasing the Si content in the hafnium silicate film from 0% up to 50%, the band gap value is almost unchanged (from 5.5eV to 5.75eV). The deduce band diagram of $Hf_{(1-x)}Si_xO_2$ films are schematized in Fig. 10.

Discussion (see Fig. 10): In SiO₂, the minimum CB states are related to the Si s states, whereas the maximum VB states are formed by the nonbonding O 2p states. For HfO₂, the minimum CB states are mostly composed of Hf 5d states, and the maximum VB states of O 2p states [8]. Hf-rich silicate films exhibit barrier heights close to pure HfO₂ and Si-rich silicate films exhibit the same barrier heights as pure SiO₂. This result indicates that the resulting minimum CB in the hafnium silicate is not a mixing of the Si and the Hf networks. On the contrary, these networks present independent contributions to the CB with the density of states proportional to the concentration of the particular element.

4. Conclusions

We have analyzed the electron band offsets at the HfO₂ interfaces with the Al metal gate and with the Si substrate using IPE. The quantitative comparison of the extracted energies on both sides of the hafnium oxide, compared with SiO₂ case, reveals an interfacial dipole at the HfO₂/SiO₂ interface which becomes less significant by adding Si inside the HfO₂ film. Through the combination of IPE and SE experiments, the band diagram of Hf_(1-x)Si_xO₂ films was determined for different silicon concentrations. It reveals that Si 3s and Hf 5d states give independent contributions to the conduction band.

Acknowledgements

The work was partly supported by The Mitsubishi Foundation. J. Widiez is grateful to the Japan Society for the Promotion of Science (JSPS) for financial support.



Fig 1 – Cube root of the IPE yield from the VB of the Si ($V_G > 0$) as a function of photon energy in Al/HfO2/Si structure.



V_G<0 HfC E=0.3MV/cm (IPE yield)^{1/2} (a.u.) 3 2 $\Phi_{\rm B}$ (Al/HfO₂)= Sin 2.3eV 0 600 1.5 2 2.5 3 3.5 Photon Energy (eV)

Fig 2 - Square root of the IPE yield from the Al metal gate (V_G<0) into HfO₂ and into SiO₂ as a function of photon energy.



3.5 V_>0 HfO 3 <0 HfO_ - V_<0 1.5 0.5 0 1.5 1 (Electric Field)^{1/2} (MV/cm)^{1/2}

Fig 3 - Schottky plot of the spectral thresholds of electron IPE from Al into HfO_2 and SiO₂ (filled symbols) and from Si into HfO₂.



Fig 4 – Influence of the SiO₂ IL thickness on the $\Phi_B(Al/HfO_2)$ extraction. (a): IPE spectra from Al injection for 1nm (non intentional), 2nm, 3.8nm, 5nm and 17nm of SiO₂. (b): $\Phi_B(Al/HfO_2)$ in function of the IL thickness with a 5nm HfO₂ thickness (circle) and in function of the HfO2 thickness with IL=1nm (square).



Fig 6 - Square root of the IPE yield from Al in function of photon energy for $Hf_{(1-x)}Si_xO_2$ with x=15, 50, 70% compared with pure HfO₂ and SiO₂ spectra at E=0.3MV/cm.



Fig 9 – $(\alpha h\nu)^{1/2}$ vs hv plot for HfO_2 and Hf_(1-x)Si_xO₂ films (x=15, 50 and 70%). α =absorption coef.=4 $\pi k/\lambda$. with k=extinction coefficient.



Fig 7 – Cube root of the IPE yield from Si as a function of photon energy $Hf_{(1-x)}Si_xO_2$ MOS structures with x=15, 50, 70% and HfO2 at E=1.5MV/cm (for x=15%, E=0.4MV/cm).



Fig 10 - Schematic band edge electronic diagram for SiO₂, hafnium silicate films with 70% and 15% of Si and HfO₂.

Fig 5 - Electron energy band diagram for the Al/HfO₂/Si MOS structure on the left compared to the Al/SiO₂/Si band structure on the right.



Fig 8 - Conduction band offset between Al/oxide (circle) and Si/oxide (square) in function of the Si concentration in the $Hf_{(1-x)}Si_xO_2$ dielectric.

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