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Nonlinear Al Concentration Dependence of the $HfAlO_x$/Si Conduction Band Offset Studied by Internal Photoemission Spectroscopy

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1. Introduction

In high dielectric constant materials considered for replacement of a SiO_2 gate dielectric in CMOS devices, a high energy barrier height at the conduction band of Si surface is needed. Internal photoemission (IPE) is a reliable method for the evaluation of the band offset,[1] as the energy band diagram is schematically shown in **Fig. 1**. Afanas'ev *et.al.*[2] reported the IPE results on the dependence of Al concentration in $HfAlO_x$ on the band offset, and concluded that the conduction band of $HfAlO_x$ was derived mostly from the states of Al atom. On the other hand, a small amount of Al in $HfAlO_x$ can successfully modulate the V_{FB} thanks to the modulation of the Fermi-level pinning.[3] Hence, a more accurate understanding of the electronic properties of $HfAlO_x$ is required for optimizing and designing Hf-based high-k dielectrics. In this paper, effects of Al concentration on the conduction band edge of $HfAlO_x$ have been carefully studied, particularly focusing on the low Al concentration region. The conduction band offset for N-doped HfO_2 is also presented.

2. Sample preparation and IPE measurement

IPE specimens were fabricated as follows. 1.3-nm- thick SiO_2 interfacial layers (ILs) were thermally grown on low doped p-type (100) Si substrates, followed by $HfAlO_x$ film deposition with thickness of 6.4 nm using Layer-by-Layer Deposition and Annealing (LL-D&A) method.[4] Semitransparent 13-nm-thick Al electrode was deposited at room temperature without PMA to avoid any interfacial reaction.[5] Al electrode was used in order to accurately evaluate the band offset, because the IPE spectra for electron injection in Al/$HfAlO_x$ should give a distinct threshold due to high photoemission efficiency. The electric field dependence of the offset was taken into account for estimating the intrinsic band offset value.

IPE spectra were measured in the photon energy range of 1.3 eV to 3.2 eV with a spectral resolution of 2 nm. A monochromatic light with square shape was irradiated on MOS capacitors with an area of 200 μm×200 μm. Typical photon flux was $1\text{-}5\times10^{11}$ photons·s^{-1}. Steady state IPE current was measured under negative voltages on the Al electrode to avoid the interference of the transient current.

3. Conduction band offset for HfO_2 and Al_2O_3

Figures 2 (a) and **3 (a)** show the square root plots of IPE spectra for an Al/HfO_2 and for an Al/Al_2O_3, respectively. The quantum yield Y, is defined by the photocurrent per the incident photon flux. **Fig.2 (b)** and **Fig.3 (b)** show that the offset energy Φ_e was plotted as a function of $(V_g\text{-}V_{fb})^{1/2}$ for both samples. A good linear dependence of Φ_e was obtained after taking account of the photo-assist tunneling and the Schottky barrier lowering at Al/high-k interface. From these results, $\Phi_e|_{Vg=Vfb}$ =1.68 eV, and 1.94 eV can be quantitatively evaluated for Al/HfO_2 and Al/Al_2O_3. The Al/SiO_2 case was also measured to check the present procedure, and $\Phi_e|_{Vg=Vfb}$ = 3.2 eV was obtained. **Table 1** compares those band offset values for HfO_2/Si and Al_2O_3/Si with previously measured results,[2,6-9] together with theoretical work.[10] It is confirmed that the present results are in the reasonable range of the reported values.

4. Effect of Al concentration on $HfAlO_x$ band offset

The dependence of $\Phi_e(V_g)$ on $(V_g\text{-}V_{fb})^{1/2}$ for an Al/$HfAlO_x$ with different Al concentration is shown in **Fig.4**. HfO_2 and 7% Al-doped HfO_2 show a smaller gate voltage dependence and the lower $\Phi_e|_{Vg=Vfb}$ values than the higher Al-doped HfO_2 samples, which exhibit almost the same gate voltage dependence and approximately equal $\Phi_e|_{Vg=Vfb}$ values, including pure Al_2O_3. **Figure 5** shows the dependence of ΔE_C between $HfAlO_x$ and Si evaluated from $\Phi_e|_{Vg=Vfb}$ for Al/$HfAlO_x$ on Al concentration in $HfAlO_x$, as well as previously reported values by IPE from Si to $HfAlO_x$.[2] At 19 % Al in $HfAlO_x$, ΔE_C abruptly increase, and then remains almost constant. On the other hand, the change in band offset evaluated from IPE spectra from Si to $HfAlO_x$[2] is smaller than that in the present study. The overlap of direct optical transitions in the Si substrate and another IPE from Si to IL-SiO_2 on the spectra might affect evaluation accuracy. In the present study, distinct IPE spectra due to the usage of Al electrode of high photoemission efficiency should make it possible to reliably evaluate band offset.

The abrupt change of Φ_e on Al concentration in our IPE measurements is interpreted in the terms of the conduction process in ternary oxides different from binary oxides. Namely, in pure HfO_2, the conduction band bottom is mainly derived from 5*d*-states of Hf, while in Al_2O_3 it is from 3*s*-states (or mixing with 3*p*) of Al.[11] Since *d*-states of transition metals are easily localized, the 5*d*-states of Hf do not contribute to the band conduction anymore by Al replacement for a small amount of Hf in HfO_2. On the other hand, 3*s*-states of Al are delocalized at higher energy levels than the 5*d*-states of Hf, and Φ_e is relatively insensitive to Al concentration. This also explains the fact that a small amount of Al in $HfAlO_x$ can significantly reduce the leakage current.[4]

5. Effect of N doping into HfO_2

Effect of nitrogen introduced into HfO_2 on the band offset was also studied using IPE. **Fig.6 (a)** and **(b)** shows the square root plots of IPE spectra for an Al/HfO_2, and for an Al/HfON with [N]/([O]+[N])=0.21 under various negative gate voltages, and the dependence of $\Phi_e(V_g)$ on $(V_g\text{-}V_{fb})^{1/2}$. Almost the same value of $\Phi_e|_{Vg=Vfb}$ around

1.7 eV is obtained for HfO_2 and HfON. Because non-bonding O 2*p*-states mainly contribute to the valence band edge,[11] it is quite reasonable that the substitution of oxygen by nitrogen does not affect the conduction band offset.

6. Conclusions

The result of IPE measurements for Al/$HfAlO_x$ structures has shown that the abrupt change of the band offset occurs at Al contents over 19%. On the other hands, for N doping to HfO_2, no change of the conduction band offset was observed. This is explained by the idea that the conduction band bottom *d*-states of Hf is localized by a small amount of Al replacement, while N doping in HfO_2 only modulate the valence band states.

Acknowledgements

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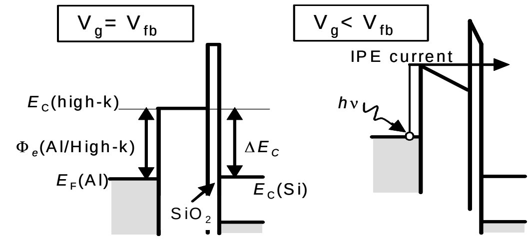

Fig. 1 Schematic band diagram for high-k/IL-SiO_2 gate stack under flat band condition and under negative bias condition.

Table 1 Comparison of reported values for conduction band offset, ΔE_C for high-k/Si substrate

	This study (ϕ_M(Al)=4.1 eV)	IPE	XPS	Theoretical work
HfO_2	1.63 (eV)	2.0[2]	1.2[6] 1.91[7] 1.50-1.85[8]	1.3[10]
Al_2O_3	1.89 (eV)	2.1[2]	2.37[7] 2.08[9]	2.4[10]

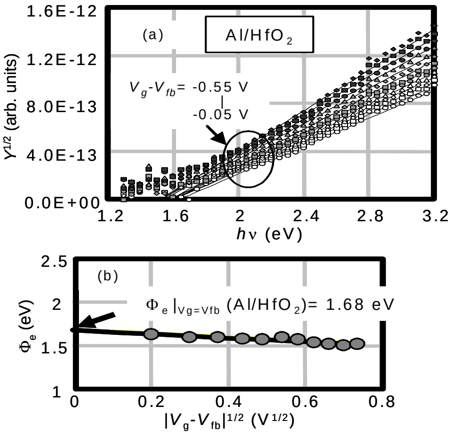

Fig. 2 (a) Square root plots of quantum yield *Y* against photon energy for an Al/ 6.4-nm-thick HfO_2/IL-SiO_2/p-Si capacitor under various gate voltage conditions.
(b) Dependence of $\Phi_e(V_g)$ obtained from Fig.2 (a) on $(V_g-V_{fb})^{1/2}$.

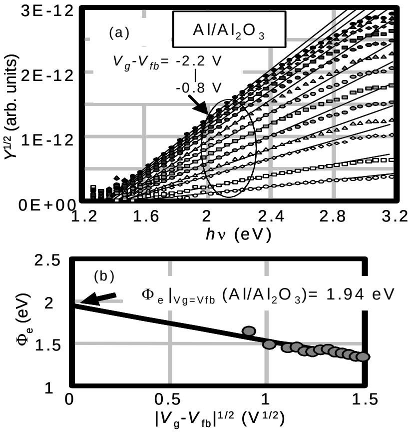

Fig. 3 (a) Square root plots of quantum yield *Y* against photon energy for an Al/ 6.4-nm-thick Al_2O_3/IL-SiO_2/p-Si capacitor under various gate voltage conditions.
(b) Dependence of $\Phi_e(V_g)$ obtained from Fig.3 (a) on $(V_g-V_{fb})^{1/2}$.

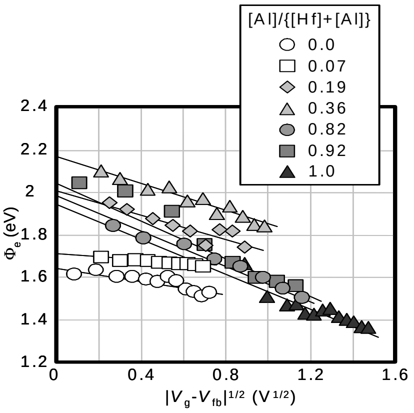

Fig. 4 Dependence of $\Phi_e(V_g)$ on $(V_g-V_{fb})^{1/2}$ for an Al/6.4-nm-thick $HfAlO_x$/1.3-nm-thick IL-SiO_2/p-Si capacitor with various Al concentrations.

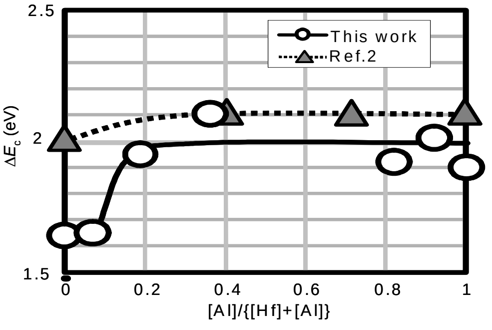

Fig. 5 Dependence of ΔE_C between $HfAlO_x$ and Si on Al concentration in $HfAlO_x$. ΔE_C was evaluated from $\Phi_e|_{Vg=Vfb}$ for Al/$HfAlO_x$ in Fig. 4. For comparison, previously reported values evaluated from IPE for electron injection from Si to $HfAlO_x$ were also plotted.[2]

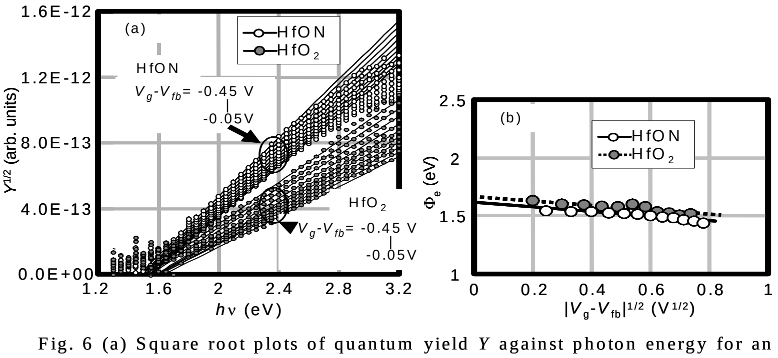

Fig. 6 (a) Square root plots of quantum yield *Y* against photon energy for an Al/6.4-nm-thick HfO_2/IL-SiO_2 /p-Si capacitor, and for an Al/14.4nm-thick HfO_2N/IL-SiO_2/p-Si capacitor under various gate voltage conditions.
(b) Dependence of $\Phi_e(V_g)$ obtained from Fig.6 (a) on $(V_g-V_{fb})^{1/2}$.