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Band Offset Energies in Zirconium Silicate Alloys

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1. Introduction

Zr and Hf silicate alloy satisfy many requirements as gate dielectrics for advanced Si and SiC devices. This paper combines our studies using X-ray absorption spectroscopy (XAS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), with previously published studies of photoconductivity (PC) and vacuum ultra-violet photoemission spectroscopy (UPS) to determine for the first time conduction and valence band offset energy for the entire range of alloy compositions. These new results and then integrated into an empirical model for the direct tunneling that demonstrates that the minimum tunneling current is not obtained at the end member ZrO_2 with the highest dielectric constant, but rather at alloys $[(ZrO_2)_x(SiO_2)_{1-x}]$ with x less than 0.5.

2. Experimental Results

Zr(Hf) silicate alloys were prepared by low temperature, 300°C, remote plasma enhanced chemical vapor deposition using silane as the Si-atom source gas, and Zr t-butoxide as the Zr-atom source gas. These were injected downstream from a remote O₂/He plasma, and excited O-atom species extracted from the plasma were used to initiate the remote plasma-assisted chemical vapor deposition. Alloys compositions were determined by Rutherford backscattering.

A summary of XAS, XPS and AES results is presented below:

i) studies of Zr-atom $M_{2,3}$ ($3p_{1/2}$, $3p_{3/2}$ to 4d* and 5s*) transitions by X-ray absorption spectroscopy (XAS) have established that energies of 4d* and 5s* states do not change with alloy content, x, or with the degree of crystallinity [1], confirming the predictions of *ab-initio* theory with respect to atomic scale localization of the 4d* and 5s* states;

ii) studies of O-atom K_1 transitions for silicate alloys terminate in the lowest conduction band states, and indicate that the energy difference between the Zr 4d* states that define the lowest conduction, and the conduction band associated with Si 3s* states is independent of alloy composition (see Fig. 1);

ii) Zr $3d_{5/2}$ and Si 2p binding energies derived from X-ray photoelectron spectroscopy (XPS) show similar non-linear behaviors as a function of x (see Fig. 2(a)) with the

difference in the respective binding energies between the alloy end members, SiO_2 and ZrO_2 , being the same (1.8 eV); this XPS behavior is *equivalent* to the O-atom K₁ XAS discussed in ii); the O1s binding energy shows a non-linear behavior with a difference in binding energy of ~2.8 eV between the end member oxides [2]; and

iv) kinetic energies of OKVV and ZrMVV Auger electrons show a non-linear compositional dependence *different from* that observed in XPS studies [2] (see Fig. 2(b)).



Fig. 1. Oxygen-atom K_1 spectra for XrO_2 and a silicate alloy with x ~0.2. The dashed lines are relative conduction band energies from *ab-initio* calculations.



Fig. 2(a). XPS binding energies for Zr 3d states as function of alloy composition.



Fig. 2(b) Kinetic energy of OKVV AES electrons as a function of alloy composition.

3. Interpretation of Experimental Results

The following conclusions are drawn from these results: i) localization of Zr d*-states on these atoms explains the absence of any dependence of Zr $M_{2,3}$ to $N_{4,5}$ transition energies on Si alloy content, or crystallinity; similar behaviors and explanations also apply to XAS results for Hf silicate alloys;

ii) non-linear behaviors of the Xr $3d_{5/2}$ and Si 2p binding energies for x < 0.5 are consistent with changes in a Zr-atom disrupted SiO₂ network in which network oxygen donor/Zr-acceptor pair bonds contribute at low x; these non-linear behaviors identify the microscopic origin of the enhanced dielectric constants reported in low concentration Zr (and Hf) silicate alloys [3];

iii) non-linear behaviors of the OKVV and ZrMVV AES kinetic energies reflect changes in the valence band energies with respect to vacuum, and therefore in the band offset energies between the Zr (and Hf) silicate alloy and semiconductor valence bands as well [2];

iv) the combination of XPS and AES establish that (a) bandgaps of Zr(Hf) silicate alloys decrease monotonically, but non-linearly between those of SiO₂ and ZrO₂, and (b) that conduction band offset energies with respect to c-Si are associated with the lowest Zr and Si anti-bonding states are independent of alloy composition, but valence band offsets (wrt c-Si) decrease monotonically with increasing O-atom coordination, N: from ~ 4.5 eV in SiO₂ (N=2), to 3.8 eV in the silicate compound, x = 0.5 (N=3), and to 3.1 eV in ZrO₂ (N~4) [2]; and

v) the connection between these spectroscopic results and effective tunneling barriers in metal-oxide-semiconductor structures has not as yet been determined from the *ab-inito* theory; however, tunneling current densities are sufficiently low for microelectronic applications. If it is assumed that tunneling barriers are correlated with either photoconductive or IPE band gaps [4], then analysis of tunneling in terms of empirical models developed for SiO_2 yields an *unrealistically low* electron mass. It is proposed that the increased current defined by this mass results from tunneling pathways that strongly couple to localized Zr (Hf) anti-bonding d*-states.

4. Conclusions

The tunneling current displays a minimum value in $(SiO_2)_{1-x}(Si_3N_4)_x$ pseudo-binary allo system at x ~0.5, rather than at the end-member Si_3N_4 composition which corresponded to the highest k, ~7.6, and physically-thickest film for a given EOT. This is due to a linear scaling of the effective barrier height, tunneling mass, and dielectric constant. Using the same empirical model for Zr9Hf) silciates also gives a non-linear behavior with this dependence being displayed in Fig. 3 [5].



Fig. 3. Direct tunneling at 1.0 V for Zr(Hf) silicate alloys.

Values of the direct tunneling current for x = 0.0 (SiO₂), $x \sim 0.2$ -0.3, and $x = \sim 1$ (HfO₂/ZrO₂) suggest that this dependence is obeyed experimentally. The plots in Fig. 3 do not take into account an enhancement of the dielectric constant for low values of $x_{1} \sim 0.1$ to 0.3 which would lead to additional decreases in the tunneling current in that composition region. Combined with high thermal stability and reduced interfacial fixed charge, low Zr(Hf)O₂ content alloys emerge as a strong candidates for advanced devices.

Acknowledgements

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