DENSITY FUNCTIONAL THEORY MOLECULAR DYNAMICS SIMULATIONS AND EXPERIMENTAL MEASUREMENTS OF A-HfO_2/A-SIO/SIGE(001) AND A-HfO_2/A-SiO_2/SIGE(001) INTERFACES.

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INTRODUCTION

To determine the optimal interface between a-HfO_2 oxide and $Si_{0.5}Ge_{0.5}$(001), density functional theory molecular dynamics (DFTMD) simulations of several amorphous stoichiometric and sub-stoichiometric SiOxNy interlayers (a-$SiO_{0.8}N_{0.8}$, a-$SiO_{0.4}N_{0.4}$, a-Si_3N_2, a-Si_3N_4, a-SiO, and a-SiO_2,) were performed. In general the sub-stoichiometric interlayers had superior electrical properties because they minimized Ge-O and Ge-N bond formation and had low internal bond strain. The stack with oxygen deficient a-SiO interlayer demonstrated superior electric properties because it avoided all dangling bond formation. Experimental studies confirmed that a nearly pure SiOx interface between a-HfO2 and SiGe(001) could be formed which correlated with a low interface state density.

Formation of high-k gate oxide/SiGe interfaces is challenging since germanium suboxide (GeO_x<2 containing Ge^{+2}) is known to induce electronic defects, and it is nearly impossible to fully oxidize or nitride Ge to Ge^{+4} in the presence of Si since both O and N make stronger bonds to Si than Ge. An alternative approach is to form a monolayer or bilayer of amorphous SiOxNy between the high-k dielectric and the SiGe channel. This can be done by either ALD of silicon monolayers/bilayer or annealing of a SiGeON interface to form a purely SiON layer [1-3]. However, the ideal composition of the SiON layer is unknown. A fully stoichiometric layer has the advantage of the widest possible bandgap but its formation in the presence of excess Ge atoms in the channel is problematic.

RESULTS

DFT-MD simulations were employed to form bilayers of a-$SiO_{0.8}N_{0.8}$, a-$SiO_{0.4}N_{0.4}$, a-Si_3N_2, a-Si_3N_4 a-SiO, and a-SiO_2 interlayers on SiGe(001) by random placing O and N atoms on SiGe(001), annealing stacks at 800K, cooling to 0K and relaxing to the ground state configuration below force tolerance level of 0.05 eV/Å. The 3 bottom SiGe layers were fixed in the bulk-like positions and passivated by H atoms to simulate continuous bulk. After interlayer formation, the a-HfO_2 sample [4-6] was stacked on the relaxed interlayer/SiGe stacks and annealed-cooled-relaxed as described previously. For these studies, for each interface, 6 to 8 different annealing times were tested. The sample with the best density of states (widest band gap) and annealing-cooling-relaxation was chosen for comparison to other interfaces. The DFT-MD simulations were performed using the VASP plane-wave simulation package using projector augmented-wave (PAW) pseudopotentials (PP) and Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [7]. The density of states was calculated with HSE06 exchange-correlation hybrid-functional [8].

For silicon nitride passivation, a comparison was made between a sub-stoichiometric N-deficient interlayer (a-HfO_2/a-Si_3N_2/SiGe) and a fully-stoichiometric nitride interlayer (a-HfO_2/a-Si_3N_4/SiGe). While the a-HfO_2/a-Si_3N_4/SiGe has multiple Ge-N bonds, the a-HfO_2/a-Si_3N_2/SiGe has no Ge-N bonds (Fig 1a) since there are sufficient Si atoms in the interface to satisfy all N bonding. However, the sub-stoichiometric a-HfO_2/a-Si_3N_2/SiGe stack has several pinning states (Fig 1b). Even for the most ideal interface observed at short annealing times, there are stained Si-Ge bonds which have conductance and valance band states. (Fig 1c). The pinning states are localized at the a-Si_3N_4/SiGe interface and consistent with the interface deformation. In sum, for both purely nitride interfaces, the ridged, strong bonds in the SiNx interlayer induced deformations in the top layer of SiGe which pinned the Fermi level.

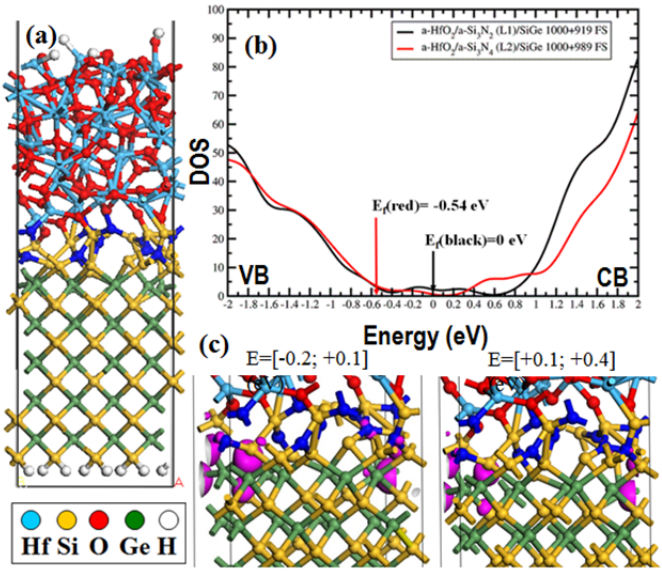

Figure 1: DFTMD of a-HfO_2/a-Si_3N_2/SiGe and a-HfO_2/a-Si_3N_4/SiGe. (a) Atomic structure of the best interface with short annealing times of a-HfO_2/a-Si_3N_2/SiGe. Note no Ge-O nor Ge-N bonds. (b) DOS of best a-HfO_2/a-Si_3N_2/SiGe and a-HfO_2/a-Si_3N_4/SiGe after about 2000 time steps. The Si_3N_4 interface has a shifted Fermi level (red) and even the Si_3N_2 has band gap states. (c) Most common defect of sub-stoichiometric interface is stained Si-Ge bonds.

For silicon sub-oxynitide (a-$SiO_{0.8}N_{0.8}$) and oxynitride (a-$SiO_{0.4}N_{0.4}$) passivation, DFT-MD shows a better passivation than pure silicon subnitride and silicon nitride (Fig 2). Again, the substiochiometric interlayer produces a better interface than the stiochiometric interface as shown by a larger band gap and a more centered Fermi level.

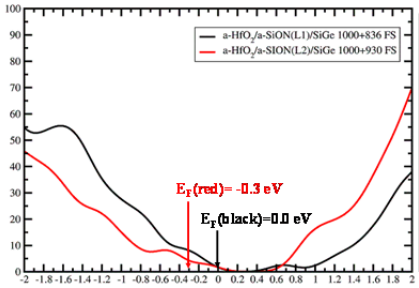

Figure 2: DOS of best a-HfO_2/ a-$SiO_{0.4}N_{0.4}$/SiGe (black) and a-HfO_2/ a-$SiO_{0.8}N_{0.8}$/SiGe (red) after about 2000 time steps. The a-$SiO_{0.8}N_{0.8}$ interface has a highly shifted Fermi level (red).

For SiO_2 passivation, a stoichiometric interlayer, a-HfO_2/a-SiO_2/SiGe stack was simulated (Fig 3). There are multiple Ge-O bonds; however, there are also dangling bonds. Even in the best interface simulated (Fig 3a), there are two Ge atoms which are only 3 fold coordinated and one Ge atoms which is 2 fold coordinated. The calculated HSE06 DOS (red) has zero band gap and is completely pinned (Fig 2c). The projected density of the VB states and CB states show they are distributed among all the interfacial Ge atoms.

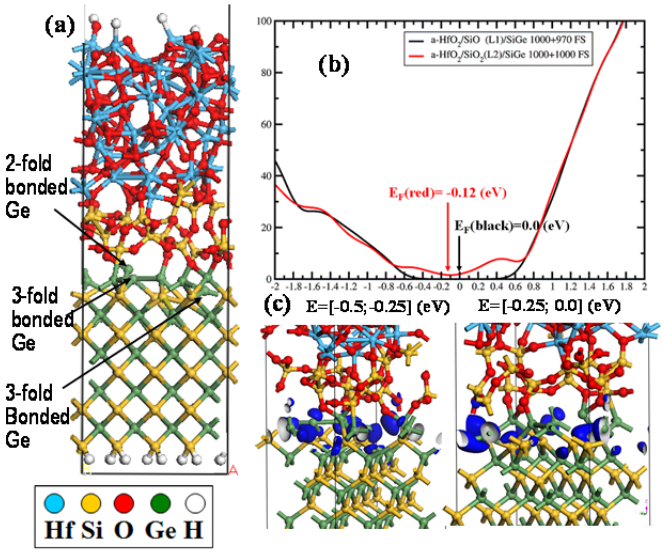

Figure 3: DFTMD of a-HfO_2/a-SiO_2/SiGe and a-HfO_2/a-SiO/SiGe. (a) Atomic structure of the best interface of a-HfO_2/a-SiO_2/SiGe. Note Ge-O bonds and numerous undercoordinated Ge atoms; (b) DOS of best a-HfO_2/a-SiO_2/SiGe and a-HfO_2/a-SiO/SiGe after about 2000 time steps. The SiO interface is nearly ideal. (c) Band decomposed charge density of the SiO_2 interface shows band edge states on nearly all interfacial Ge atoms.

For silicon suboxide passivation, a sub-stoichiometric O-deficient interlayer, the a-HfO_2/a-SiO/SiGe stack was simulated; there is just one Ge-O bond since there are sufficient Si atoms in the interface to satisfy nearly all O bonding (not shown). The calculated HSE06 DOS is nearly ideal and demonstrates unpinned bandgap with no Fermi-level shifting (Fig. 3b). The high quality of this interface can be explained by almost perfect coordination of interfacial atoms.

The DFTMD simulations suggests that an ideal a-HfO_2/SiGe(001) avoids both direct bonding of a-HfO_2 to SiGe(001), avoids formation of Ge-O bonds, and contains an interface of SiOx. Furthermore, the DFTMD simulations show that the SiOx interface can be only 2 monolayers thick, about 0.4 nm. To test this hypothesis, several dozen ALD recipes were evaluated for deposition of HfO_2 on $Si_{0.7}Ge_{0.3}$(001) (Applied Materials). $Si_{0.7}Ge_{0.3}$(001) was chosen instead of $Si_{0.5}Ge_{05}$(001) since there is a higher quality regrowth for $Si_{0.7}Ge_{0.3}$(001)/Si(001) than $Si_{0.5}Ge_{05}$(001)/Si(001). The SiGe samples were cleaned in HF(aq) and $(NH_4)_2S$. An Al_2O_3-HfO_2 alloy was deposited to increase the yield using $HfCl_4$, TMA, and H_2O at 300 ^oC. A Ni gate was thermally evaporated along with an Al back contact. FGA was performed at 300 ^oC. As shown in Fig 4, this procedure produces a high quality interface characterized by (a) a low interfacial trap density (small Dit bump in C-V near threshold), (b) low boarder trap density ($N_{BT,}$ small frequency dispersion in accumulation C-V), near zero threshold voltage (Vth ~ 0 in C-V), and (d) low leakage (flat G-V in accumulation).

Cross sectional scanning TEM with energy-dispersive x-ray spectroscopy (STEM-EDX)) was performed on the sample. The high-angle annular DF STEM clearly shows an interlayer of low atomic number between the AlHfOx and the SiGe (Fig 5). EDX spectra of the sub 1 nm interlayer shows that it consists of SiOx likely intermixed with HfOx and contains no Ge.

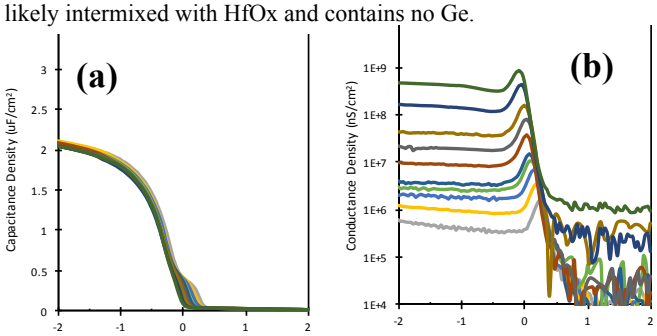

Figure 4: Electrical Characterization of ~10% Al_2O_3 and ~90% HfO_2/ $Si_{0.5}Ge_{05}$(001)/Si(001). (a) C-V shows Dit ~ $2x10^{12}$ /cm^2-eV using the conductance method. (b) G-V shows low leakage

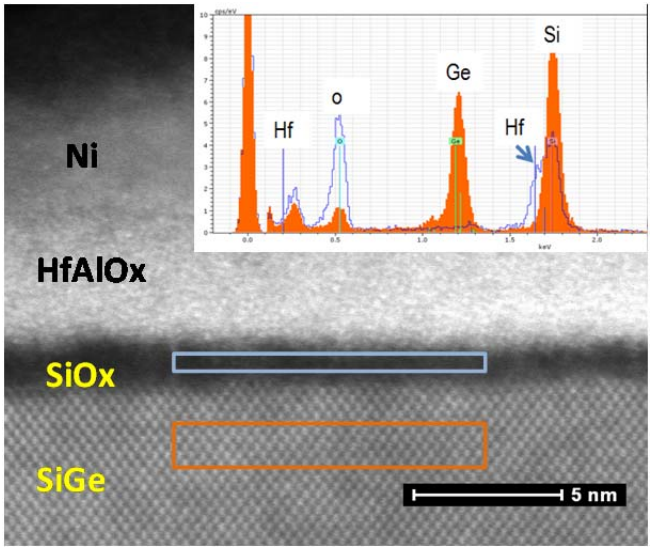

Figure 5: STEM-EDX characterization of ~10% Al_2O_3 and ~90% HfO_2/ $Si_{0.5}Ge_{05}$(001)/Si(001). Blue box shows a region of interlayer for EDX analysis revealing a Ge-free SiOx interlayer. The orange box is a control region in the SiGe. The EDX spectra of the interlayer is in blue while the spectra on the SiGe control region is in orange. Note the absence of Ge in the interlayer.

SUMMARY

To determine the optimal interface between a-HfO_2 igh-K oxide and $Si_{0.5}Ge_{0.5}$(001), density functional theory molecular dynamics (DFTMD) simulations of several amorphous stoichiometric and sub-stoichiometric SiOxNy interlayers were performed. The stack with oxygen deficient a-SiO interlayer demonstrated superior electric properties because it avoided all dangling bond formation. Experimental studies confirmed that a nearly pure SiOx interface between a-HfO2 and SiGe(001) could be formed which correlated with a low interface state density.

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