Characterization of the Interlayer between a Nanolaminate Gate Oxide and SiGe(001)

INTRODUCTION

SiGe is considered to be the leading materials for channels on p-FET devices for the 7 nm node. SiGe is a more challenging material than silicon because of its oxide can contain GeOx which is a defective an unstable material. When high-k dielectric such as HfO2 are deposited on silicon, a few angstroms on SiO2 are intentional maintained between the Si channel and the HfO2 to reduce interfacial defect density (Dit) and to reduce remote phonon scattering which decrease channel mobility. It is shown by density functional theory molecular dynamics (DFTMD) simulations that the ideal interface between a-HfO2 oxide and SiO2 is again silicon oxide. Experimentally, a sub 1nm SiOx interlayer could be deposited by ALD but this is challenging due to the induction period in most ALD process. Here we show that carefully annealing of the SiGeOx interlayer using projector augmented-wave (PAW) pseudo potentials between a-HfO2 and a fully-stoichiometric nitride interlayer (a-HfO2 ALD but this is challenging due to the induction period in most ALD process. We compare here that carefully annealing of the SiGeOx interlayer results in a nearly pure SiOx layer between the gate oxide and SiGe consistent with SiOx between the thermodynamically most stable state. Transmission electron microscope (TEM)

Formation of high-k gate oxide/SiGe interfaces is challenging since germanium suboxide (GeOx<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-SiOxNy: a-SiO2N0.8, a-SiO2N0.4, a-SiNx, a-SiNxN4, a-SiO2, and a-SiO2 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-HfO2 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 functional [8].

For silicon nitride passivation, a comparison was made between a sub-stoichiometric N-deficient interlayer (a-HfO2/a-Si1xN2y/SiGe) and a fully-stoichiometric nitride interlayer (a-HfO2/a-SiNxNy/SiGe). While the a-HfO2/a-Si1xN2y/SiGe has multiple Ge-N bonds, the a-HfO2/a-SiNxNy/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-HfO2/a-Si1xN2y/SiGe stack has several pinning states (Fig 1b). Even for the most ideal interface observed at short annealing times, there are dangling bonds on the three-fold coordinated Ge atoms which induce band edge states (Fig 1c). The pinning states are localized at the a-SiNxNy/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.

For silicon sub-oxynitride (a-SiOxNy: a-SiO2N0.8) and oxynitride (a-SiOxNy: a-SiO2N0.4) passivation, DFT-MD shows a better passivation than pure silicon nitride and silicon nitride (Fig 2). Again, the sub-stoichiometric interlayer produces a better interface than the stoichiometric interface as shown by a larger band gap and a more centered Fermi level. For SiO2 passivation, a stoichiometric interlayer, a-HfO2/a-

Figure 1: DFTMD of a-HfO2/a-Si1xN2y/SiGe and a-HfO2/a-Si1xN2y/SiGe. (a) Atomic structure of the best interface with short annealing times of a-HfO2/a-Si1xN2y/SiGe. Note no Ge-O nor Ge-N bonds. (b) DOS of best a-HfO2/a-Si1xN2y/SiGe and a-HfO2/a-Si1xN2y/SiGe after about 2000 time steps. The SiNxN4 interface has a shifted Fermi level (red) and even the Si1xN2y has band gap states. (c) Most common defect of sub-stoichiometric interface is a Ge dangling bond which produces band edge states.

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Figure 2: DOS of best a-HfO2/a-Si1xN2y/SiGe and a-HfO2/a-Si1xN2y/SiGe after about 2000 time steps. The SiNxN4 interface has a shifted Fermi level (red) and even the Si1xN2y has band gap states. (c) Most common defect of sub-stoichiometric interface is a Ge dangling bond which produces band edge states.
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.

The DFTMD simulations suggests that an ideal a-HfO$_2$/Si(001) avoids both direct bonding of a-HfO$_2$ to Si(001), avoids formation of Ge-O bonds, and contains an interface of SiO$_x$. Furthermore, the DFTMD simulations show that the SiO$_x$ 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$_x$. Note Ge-O bonds and numerous undercoordinated Ge atoms; (b) DOS of best a-HfO$_2$/a-SiO$_x$/SiGe and a-HfO$_2$/a-SiO$_x$/SiGe after about 2000 time steps. The SiO$_2$ 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$_x$/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 band gap with no Fermi-level shifting (Fig. 3b). The high quality of this interface can be explained by almost perfect coordination of interfacial atoms.

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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 SiO$_x$ likely intermixed with HfO$_x$ and contains no Ge.