

GeO_x interface layer reduction upon Al-gate deposition on a HfO₂/GeO_x/Ge(001) stack

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The metallization of HfO₂/Ge by Al at room temperature was studied using photoemission and inverse photoemission. Upon deposition, Al reduces the GeO_x interfacial layer between Ge and HfO₂, and a thin Al₂O₃ layer is formed at the Al/HfO₂ interface. The band alignment across the Al/HfO₂/Ge stacks is also addressed. © 2008 American Institute of Physics.

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As SiO₂/Si based technology has scaled to the 45 nm device node, the need for subnanometer effective gate oxide thicknesses has resulted in unacceptably large leakage currents. This has led to the exploration of high- κ dielectrics, such as HfO₂, as replacements for SiO₂. High- κ dielectrics and metal gate electrodes integrated on a Si substrate appeared in the market in late 2007, following ten years of intensive research. The disappearance of SiO₂ has raised the question of the need to stay with Si as the semiconductor in high performance complementary metal oxide semiconductor (CMOS) devices. Ge has the potential for performance superior to Si in MOS device applications due to its higher mobility and carrier concentration.¹ Progress toward fabricating semiconductor devices using Ge had been slow because obtaining an effective insulating germanium oxide layer that exhibits electrical performance comparable to or better than the SiO₂/Si system has presented a major scientific and engineering challenge. However, as our understanding and control of high- κ dielectrics and metal gate electrodes on Si have developed, we find that we can bring this gate stack integration experience to Ge and III-V semiconducting substrates, hitherto, effectively ruled out for CMOS because of their poor quality intrinsic oxides.

To fabricate a MOS structure with a metal gate, one must have the proper work function for both *n*-type and *p*-type devices, and sufficient chemical and morphological stability of the interfaces. Some metal gates have been shown to chemically interact with high- κ oxides upon annealing, either by alloying or by drawing oxygen either out of the gate oxide or out of the interface oxide where the semiconductor and high- κ dielectric meet. For example, the presence of metal Hf during HfO₂ deposition even in an oxidizing ambient can lead to the decomposition of the interfacial SiO₂ oxide of a HfO₂/SiO₂/Si stacks.² In Ti/ZrO₂/SiO₂/Si stacks, annealing at 300 °C leads to reduction in the SiO₂ interface layer and oxidation of the Ti gate.³ In the case of Ti/HfO₂/SiO₂/Si stacks, annealing at 300 °C also leads to the reduction in the SiO₂ interface layer and to Ti oxidation, and slight changes in the HfO₂ layer are also observed.⁴ As

GeO_x is considerably less stable than SiO₂, the possibility for significant modification of the high- κ /Ge interface upon a metal gate deposition arises.

In this work, we report results on the stability of a HfO₂/GeO_x/Ge stacks upon Al deposition at 300 K, studied using synchrotron x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), and inverse photoemission spectroscopy (IPS). We have determined the valence band offset (VBO), conduction band offset (CBO), and the oxide band gap of the HfO₂/GeO_x/Ge system and found them to be in reasonable accord with those determined by earlier photoemission⁵ and internal photoemission⁶ measurements. In addition, we find that the Al immediately oxidizes upon deposition, but not at the expense of reducing the HfO₂ film. Rather, the interfacial GeO_x is reduced upon metallization. This process occurs even at room temperature. The deposition of additional Al results in elimination of the interface oxide, metallic overlayer growth, and appreciable band bending, but no apparent reduction in the HfO₂ film.

Synchrotron XPS measurements were performed on the U5UA beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. All spectra presented here were obtained using a photon energy of 150 eV and had an overall energy resolution of 0.1 eV.⁷ Measurements of the valence band and conduction band densities of states were performed in a unique UHV chamber that housed both UPS and IPS capabilities at Rutgers University. This enabled direct determination of the oxide band gap, and the band offsets between the oxide, the substrate, and the metal overlayer from the same sample subject to specific preparation conditions. The overall uncertainty in determination of the band edges is ± 0.1 eV. The sample consisted of a 30 Å HfO₂ film that was atomic layer deposition grown *ex situ* on a Ge(001) substrate that had a resistivity of 0.107 Ω cm.⁸ Upon insertion into the experimental chambers, the samples were degassed by resistive heating to about 600 °C for several minutes in UHV (the base pressure in the two UHV systems was in the low 10⁻¹⁰ Torr range). This treatment did not modify the film properties but removed possible surface contamination from exposure to the atmosphere. The Fermi level was established by measuring the photoemission or inverse photoemission spectra from an Au film that was in electrical

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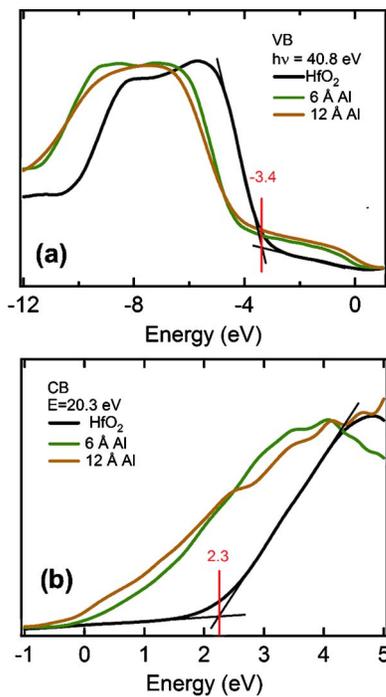


FIG. 1. (Color online) (a) Valence band and (b) conduction band of a clean and metallized 30 Å HfO₂ on Ge(001) obtained in the same UHV chamber in UPS and InPE. For the clean surface, band edges are obtained as the intersection of the linear fits of the HfO₂ edges and the Ge substrate edges. The position of the VB edges and CB edges are measured at -3.4 and 2.3 eV, respectively, with respect to the measured Fermi level.

contact with the sample. By working with HfO₂ films with a thickness of 30 Å, issues associated with sample charging were avoided. After the clean film properties were determined, the HfO₂/Ge(001) sample was subjected to sequential Al depositions from a thermal evaporation source in the UHV experimental chambers. The source was thoroughly outgassed and pressure during evaporation was better than 2×10^{-9} Torr. The Al thickness was determined using a quartz crystal monitor. The cleanliness of the source was verified by the absence of any contamination detectable either by Auger spectroscopy or synchrotron XPS on an Al film deposited on a clean silicon surface. After a freshly evaporated Al film was exposed to the residual gasses in the UHV systems for ~ 12 h, the amount of surface oxidation was determined to be less than 5% of a monolayer.

Valence band UPS spectra and conduction band IPS spectra from the clean 30 Å HfO₂/Ge(001) systems, obtained in the same UHV chamber, are displayed as the black curves in Figs. 1(a) and 1(b), respectively, as well as those obtained for two successive Al depositions (green and yellow). The electronic structure of HfO₂ is characteristic of a transition metal oxide: the valence band primarily being of O 2p character and the conduction band is dominated by Hf 5d states. To obtain the band edge positions, emission in the oxide gap region arising from the underlying Ge substrate, and the rising edges of the oxide valence and conduction bands, were approximated with linear fits, as shown in the figures. The intersection of these fits place the valence-band maximum (VBM) and conduction band minimum at -3.4 and 2.3 eV, respectively, from the Fermi level, giving a band gap of 5.7 eV. The same VBM position is obtained from the synchrotron radiation data in Fig. 2 (black curve). A linear fit locates the Ge valence band edge at -0.7 eV below the

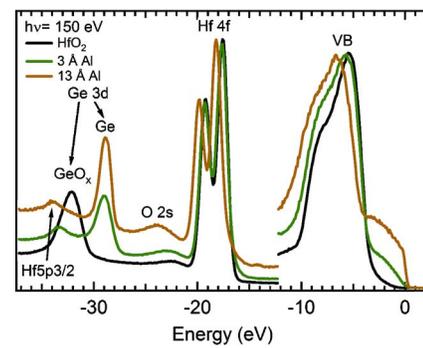


FIG. 2. (Color online) Ge 3d, Hf 4f core levels, and valence band evolution upon Al deposition. For a better estimation of the core level shift, the core levels side of the graph is normalized to the Hf 4f core level while the valence band is normalized to its maximum.

Fermi level, indicating a downward band bending of 0.2 eV at the Ge/HfO₂ interface. While the VBO determined here in is good agreement with previous photoemission measurements VBO=2.70.15 eV,⁵ it is about 0.3 eV smaller than that determined by internal photoemission VBO=3.00.1 eV and CBO=2.00.1 eV.⁶ The band gap determined here is the same as the one obtained by internal photoemission.⁶

In addition to the valence band features, the spectra of Fig. 2 show several shallow core levels for the clean and Al-covered HfO₂/Ge sample. For the clean surface, the highest binding energy peak at -32.2 eV is from the 3d core levels of oxidized Ge (primarily Ge⁴⁺).⁹ Owing to the short mean free path of the photoelectrons at this kinetic energy (~ 115 eV) no 3d peak from bulk Ge is observed. Previous medium energy ion scattering measurements⁸ of this sample have indicated the presence of an interfacial germanium oxide between the Ge substrate and the HfO₂ film. A small O 2s feature is observed at -23.8 eV. The two prominent features at binding energies of -19.3 and -17.6 eV are associated with the Hf 4f_{3/2} and Hf 4f_{5/2} core levels, respectively, of HfO₂.¹⁰

As seen in the green and yellow spectra of Fig. 2, upon deposition of 3 Å of aluminum, spectral density appears near the Fermi level. More importantly, strong changes occur in the Ge 3d core level region. Upon initial Al deposition, the Ge oxide peak at -32.2 eV is replaced by a Ge 3d peak at -28.9 eV, close to the energy expected for bulk Ge. The absence of the 0.6 eV spin-orbit splitting of the Ge 3d levels in this spectrum suggests that the reduced Ge atoms at the HfO₂ interface are not all in equivalent sites, and that a small amount of Ge suboxide may be present. Upon initial Al deposition, a weak Hf 5p_{3/2} at -33.3 eV also appears, but the Hf 4f peaks do not show any significant change. For an accumulated deposition of 13 Å of Al, additional changes occur. The Hf 4f core levels, the weak O 2s level, the Hf 5p_{3/2} feature, and the O 2p portion of the valence band are all shifted by 0.7 eV away from the Fermi level. Thus, all HfO₂ related features are rigidly shifted deeper in binding energy. For this thickness of Al, emission is clearly visible at the Fermi level, suggesting the presence of metallic Al. In addition, the Ge 3d peak does not exhibit an energy shift, but is more narrow, indicating possible further reduction of the germanium. Note that an identical rigid shift of the density of states is found in the VB and CB spectra for the metallized surfaces shown in Fig. 1.

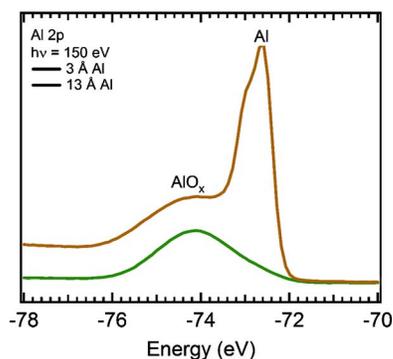


FIG. 3. (Color online) Al 2*p* evolution during sequential Al deposition on HfO₂ on Ge(001).

To further explore the nature of the Al overlayer, the Al 2*p* core level spectrum for the two Al depositions is shown in Fig. 3. For the 3 Å exposure, a broad peak centered at a binding energy of -74.3 eV is observed indicating an oxidized Al layer. For a 13 Å exposure however, the Al 2*p* doublet ($2p_{1/2}$ at -73 eV and $2p_{3/2}$ at -72.6 eV), characteristic of the metallic Al, appears. This is accompanied by a shift of the oxide feature to higher binding energy. This latter observation is consistent with the shifts upon metallization seen in Figs. 1 and 2. To ensure that the Al oxidation is not the result of reaction with the residual gasses in the chamber, Al was deposited under the same conditions on a clean silicon surface and no oxidation was observed.

From the results in Figs. 2 and 3, we observe that the oxidation of the Al and reduction in Ge interface oxide simultaneously occur. Moreover, as the Hf 4*f* core levels offer no evidence for HfO₂ reduction, it appears that the aluminum effectively draws oxygen from the thermodynamically unstable interfacial GeO_x through the HfO₂ layer.¹¹ This may occur by direct transport of oxygen through the HfO₂ film, or it may be a cascade effect where Al reacts with oxygen from the HfO₂ which is subsequently replenished by oxygen drawn from deeper in the film and ultimately from the high- κ /Ge interface. It is remarkable, however, that this reaction occurs at room temperature. There are reports of GeO behaving as a volatile product that migrates through HfO₂, but this has only been observed at temperatures higher than 400 °C for a HfO₂/Ge structure covered by a metal gate.¹

Our results indicate that, upon Al deposition, a minimum thickness of Al oxide must form before metallic Al is stable. Furthermore, this oxide formation does not induce a shift in the energy levels of the underlying structure. In contrast, the energy levels of the oxide shift by -0.7 eV once metallic Al is present, and that shift does not change when more metallic Al is added. The magnitude of this shift is in very poor

agreement with what would be expected for the Al/HfO₂ system as predicted by the modified metal induced gap state model.¹² However, a similar -0.7 eV shift of the underlying energy levels has been observed upon Al deposition on an Al₂O₃/Si(100) structure.¹³ In that case, the magnitude of this shift is in accordance with what the modified metal induced gap states model predicts.¹² This suggests that even for the small amount of Al₂O₃ that forms in the Al/Al₂O₃/HfO₂/Ge system studied here, the energy level alignment of the outer interface is dictated by Al/Al₂O₃ properties, alignment at the inner interface is dictated by the HfO₂/Ge properties, and a voltage drop occurs across the high- κ layer to accommodate the difference in these respective band alignments.

Another important observation is that Al deposition on HfO₂/Ge may allow a sharp interface formation between the substrate and the high- κ material without losing the high permittivity between the substrate and the metal gate. More detailed studies should follow in order to better characterize the Ge/HfO₂ interface after Al deposition, in particular for the presence Ge suboxides and dangling bond creation upon Ge oxide reduction.

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