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Density Functional Theory Study of First-Layer Adsorption of ZrO_2 and HfO_2 on Ge(100)

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Abstract

Density functional theory was used to model the adsorbate bonding configurations of two transition metal oxide (MO_2 = ZrO_2, HfO_2) on the Ge(100)-4×2 surface. Surface bonding geometries of metal-down (O-M-Ge) and oxygen-down (M-O-Ge) types were compared, as well as both adsorbate and displacement geometries of M-O-Ge. Calculated enthalpies of adsorption reveal that bonding geometries with metal-Ge bonds (O-M-Ge) are nearly degenerate with oxygen-Ge bonding (M-O-Ge). Calculated electronic structures indicate that adsorbate surface bonding geometries of the form O-M-Ge tend to create metallic interfaces, while M-O-Ge geometries produce more favorable electronic structures. Hydrogen passivation of both oxygen and metal atoms was used to eliminate the density of states contributions from dangling bonds, thereby mimicking a thicker oxide structure. The hydrogen passivation improved the electronic structure of both types of MO_2 adsorbate systems and produced proper semiconducting band gaps for the adsorbate-type M-O-Ge geometries. Shifts observed in the DOS minima for both O-M-Ge and M-O-Ge adsorbate geometries are consistent with surface band bending induced by the adsorbate films.

Introduction

The most studied, and probably most successful, gate dielectric materials for use in Ge-based MOSFET devices are the transition metal dioxides ZrO_2 and HfO_2 (denoted here as MO_2), usually grown by atomic layer deposition (ALD). Typically, these oxides are amorphous, though high-resolution TEM imaging indicates the some oxide/Ge interfaces may be ordered. HR-TEM imaging reveals that ZrO_2 tends to form more abrupt interfaces, while HfO_2 has been shown to be more likely to form interfacial interlayers (but thinner than seen on Si).[1]

Ge-based MOSFET (and MOSCap) device quality is found to vary greatly in MO_2/Ge(100) gate stacks, with the electronic properties being closely correlated to the quality and composition of the oxide-semiconductor interface.[2] However, the published experimental data is not sufficient to develop an atomic model of the oxide/Ge interface, so detailed conclusions about the exact causes of electronic defects at these interface are problematic.

We have performed a survey of potential ordered oxide/semiconductor interface structures between stoichiometric molecular ZrO_2/HfO_2 and Ge(100) varying both surface coverage and surface binding configuration (O-metal-Ge bonding vs. metal-O-Ge bonding) using density functional theory (DFT) modeling. This work is by no means intended to be an exhaustive set of structures, but merely an attempt to provide some insight into the MO_2/Ge interfacial system. Additionally, these structures will serve as precursors for computational studies of thick amorphous MO_2 layers on Ge(100).

Methods

All DFT calculations presented here were performed using the Vienna Ab-Initio Simulation Package (VASP)[3,4] using the PBE exchange-correlation functional, with projector augmented wave (PAW) potentials.[5] The system studied consisted of a Ge(100) slab supercell with a (4×2) surface dimer reconstruction. Stoichiometric MO_2 molecules were adsorbed to the surface of the Ge(100) slab in both metal-down and oxygen-down configurations, and analyzed for enthalpies of adsorption and electronic structure; a summary of geometries considered is given in Table 1.

TABLE 1. Summary of MO_2/Ge adsorbate geometries and calculated enthalpies of adsorption.

Identification	Geometry	$\Delta H_{ads}(ZrO_2)^a$	$\Delta H_{ads}(HfO_2)^a$
Half-Coverage O-M-Ge Adsorption		-3.16 eV	-3.63 eV
Full-Coverage O-M-Ge Adsorption		-2.78 eV	-3.29 eV
Half-Coverage M-O-Ge Displacement		-1.62 eV	-2.13 eV
Half-Coverage M-O-Ge Adsorption		-2.97 eV	-3.67 eV

a: Calculated adsorption energies, ΔH_{ads}, are given with respect to the clean Ge(100)-4×2 surface and single SiO molecules. Displacement sites are calculated with respect to the creation of Ge ad-dimers.

Discussion

The calculated enthalpies for MO_2 on Ge(100)-4×2, given in Table 1, indicate that ZrO_2 and HfO_2 adsorb strongly to Ge, with HfO_z bonding more strongly than ZrO_2, but the displacement-type reaction (where O atoms displace Ge atoms on the surface) is considerably less stable. Therefore, it is unlikely that the displacement bonding geometry will exist in any significant concentration at the oxide/Ge interface. The metal-down (O-M-Ge) and oxygen-down (M-O-Ge) configurations show nearly degenerate adsorption enthalpies, indicating that a mixture of the two geometries is likely to exist at the oxide/Ge interface.

To understand the differences between the various nearly degenerate bonding geometries, the electronic structure of each configuration was calculated. To simulate

a metal-Ge interface at the first layer of MO_2 on the Ge(100) surface, molecular ZrO_2 and HfO_2 were adsorbed in an O-M-Ge geometry. The metal-Ge interface models atomic layer deposition (ALD) growth in which the metal atoms are deposited first onto the clean surface. In this geometry, the metal atom binds directly to the Ge dangling bonds, with half the oxygen atoms pointing upward (away from the surface) and half sideways, bonding with the next metal atom over.

Figures 1 and 2 present the results of the half-coverage and full-coverage O-M-Ge adsorption geometries. The upper O atoms were H-passivated to eliminate near-E_F density of states (DOS) contributions due to the half-filled dangling bonds and to mimic the effect of bonding within a thicker oxide layer. The calculated Fermi levels for the O-M-Ge systems are indicated by E_F' in Figs. 1 and 2; in both half- and full-coverage cases the MO_2/Ge Fermi level is relatively unchanged from the clean Ge(100) level (located at 0.0 eV). At half coverage, this geometry induces a large shift in the DOS minima consistent with surface band bending. At full coverage, this geometry induces an increase a semi-metallic DOS in the near-E_F region, presumably due to metallic M-Ge bonding.

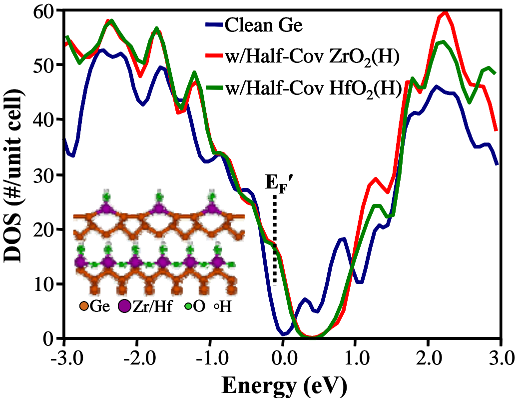

FIGURE 1. Calculated DOS for half-coverage O-M-Ge.

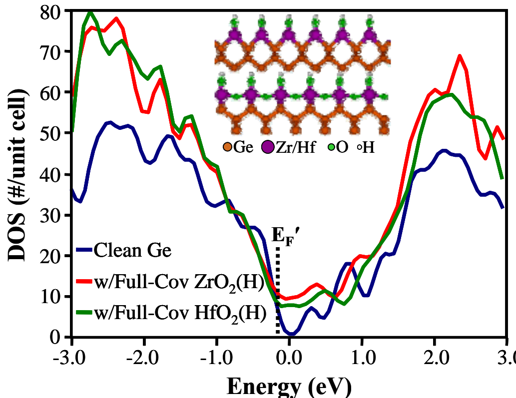

FIGURE 2. Calculated DOS for full-coverage O-M-Ge.

Figure 3 presents the results of the half-coverage M-O-Ge adsorption geometry, with the dangling bonds on the Zr and Hf atoms passivated with H atoms. In this case we find that band gaps have been produced, with proper calculated intrinsic mid-gap Fermi level positions (E_F' and E_F'' for ZrO_2 and HfO_2, respectively; see Fig. 3), indicating a significant passivation effect by the M-O-Ge type interface. The HfO_2/Ge gap width is considerably narrower than that of ZrO_2/Ge; the reason for this is still under investigation.

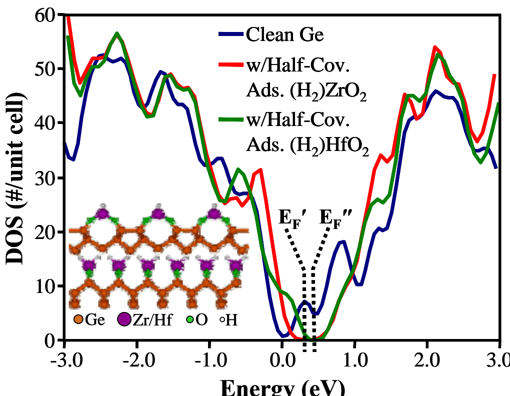

FIGURE 3. Calculated DOS for half-coverage M-O-Ge.

Conclusions

We have performed a survey of various transition metal dioxide (ZrO_2 and HfO_2) ordered adsorbate bonding configurations on the Ge(100) surface to provide insight into the high-κ/Ge interface. The calculated enthalpies of adsorption show that bonding geometries with metal-Ge bonds (O-M-Ge) are as thermodynamically favorable as ones with oxygen-Ge bonds (M-O-Ge); therefore, careful processing may be needed to control the bonding at the interface. The calculated electronic structure results indicate that O-M-Ge adsorbate surface bonding geometries tend to create semi-metallic (large near-E_F DOS) interfaces at high coverage due to the metallic nature of the metal-Ge bonds. Adsorbate surface bonding geometries of the M-O-Ge sort produce more favorable electronic structures, including the formation of proper semiconducting band gaps for the H-passivated systems.

References

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