

Comparison of $\text{ZrO}_2/\text{Ge}(100)$ and $\text{HfO}_2/\text{Ge}(100)$ Bonding and Electronic Structure

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One of the most successful dielectric materials for $\text{Ge}(100)$ MOSFETs is ZrO_2 .^{1,2} HfO_2 gate oxide has also been used, but the results have been less favorable, especially without oxynitride passivation³. In order to better understand these oxide/Ge interfaces, a systematic density functional theory (DFT) study of the $\text{ZrO}_2/\text{Ge}(100)$, $\text{HfO}_2/\text{Ge}(100)$, and Ge_xO_y interfaces has been performed. Multiple initial first-layer bonding configurations of ZrO_2 , HfO_2 , and Ge_xO_y on $\text{Ge}(100)-2\times1/4\times2$ have been simulated to determine the most stable bonding structures. The sites were also modeled for electronic structure in order to help provide an understanding of the requirements for passive oxide/Ge interfaces. We note that these calculations have currently been performed with only standard DFT and, therefore, do not exhibit a proper band gap. Work is in progress to correct this issue.

DFT simulations of 4 different oxygen binding sites on $\text{Ge}(100)$ show that oxygen does not induce formation of mid-gap states, even when it displaces Ge atoms from the surface (Fig. 1). This is consistent with oxygen inserting into Ge-Ge bonds or creating Ge-O-Ge bonds by displacement without creating any new dangling bonds on the surface. Therefore, formation of Ge-O bonds does not inherently pin the Fermi level.

Figure 1. (left) Density of states (DOS) for clean $\text{Ge}(100)$ vs. $\text{Ge}(100)$ with an oxygen atom inserted into a Ge-Ge backbond; (right) DOS for clean $\text{Ge}(100)$ vs. $\text{Ge}(100)$ with two oxygen atoms replacing the surface Ge-Ge dimer.

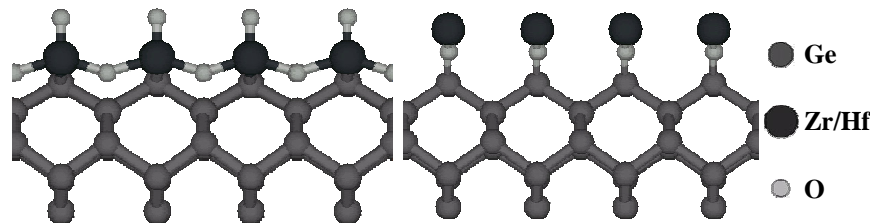
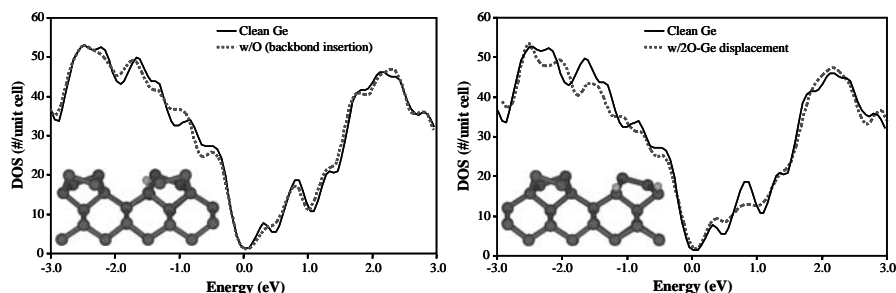


Figure 2. (left) ZrO_2 bonding for the oxygen down geometry, with Ge-O-Zr bonds formation; (right) ZrO_2 bonding for the metal down geometry, with Ge-Zr-O bond formation.

It has been found that ZrO_2 bonds to the $\text{Ge}(100)$ surface very strongly in both Zr- and O-end down configurations (Fig. 2), with the Zr-end down geometry being the strongest. DFT calculations also indicate that the Ge-Zr bonds are covalent rather than metallic, and neither Zr- nor O-end down bonding configuration results in an increase in near-Fermi level density of states (DOS) (Fig. 3). DFT simulation of H-passivation of dangling bonds on the distal Zr and O atoms, which simulates further oxide growth, yields a further reduction in the near-Fermi level DOS (Fig. 4), but only the passivation of the O atoms is thermodynamically stable at elevated temperature.

Figure 3. (left) DOS for ZrO_2 bonding with oxygen down (Ge-O-Zr) vs. clean $\text{Ge}(100)$; (right) DOS for ZrO_2 bonding with Zr down (Ge-Zr-O) vs. clean $\text{Ge}(100)$.

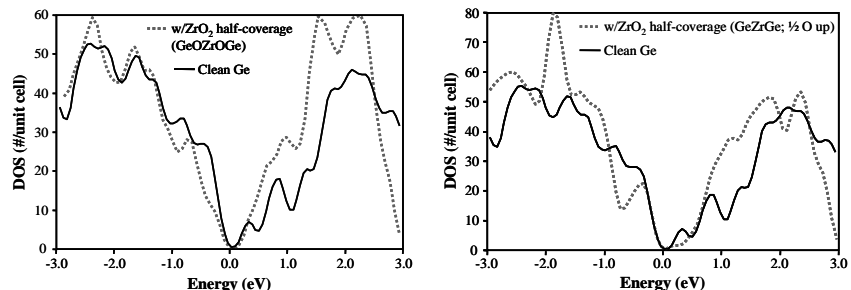
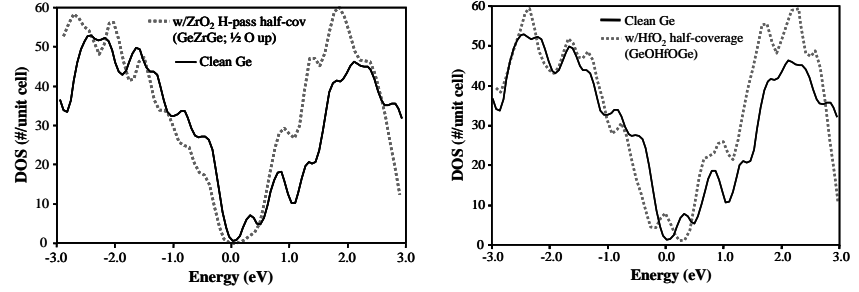


Figure 4. (left) DOS for hydrogen-passivated ZrO_2 bonding with oxygen down (Ge-O-Zr) vs. clean Ge(100); (right) DOS for HfO_2 bonding with O down (Ge-O-Hf) vs. clean Ge(100).



The DFT oxide/semiconductor calculations were repeated for $\text{HfO}_2/\text{Ge}(100)$. For the oxygen down sites (Ge-O-Hf), the DFT simulations indicate probable formation of states in the band gap region (Fig. 4). This is particularly strange because Zr and Hf are isoelectronic and neither is making a direct bond to Ge. The projected density of states shows the mid-gap (i.e. near- E_F) states localized to the Hf atoms, consistent with a subtle difference in the Zr and Hf being responsible for the new state formation. This result may help explain why direct deposition of HfO_2 on Ge generally results in inferior C-V characteristics in MOS capacitors, while an interfacial layer has been demonstrated to rectify this problem.³⁻⁵ Along the same lines, the DFT results are also consistent with the experimental data (Fig. 5) showing that there is a large decrease in gate leakage for $\text{HfO}_2/\text{Ge}(100)$ with an interfacial control layer (IL) compared to $\text{HfO}_2/\text{Ge}(100)$ without an interfacial control layer because states at the oxide/semiconductor interface increase gate leakage. Conversely, $\text{ZrO}_2/\text{Ge}(100)$ does not require an interfacial control layer for low gate leakage, because of the lack of such near- E_F states.

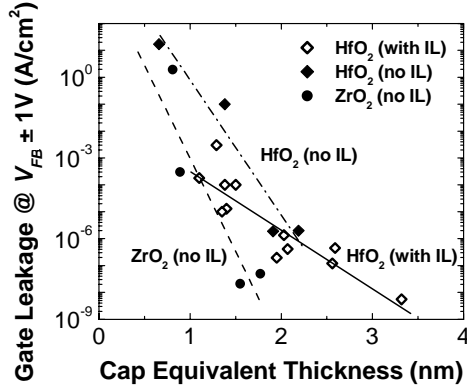


Figure 5. Metal-gated Ge MOS capacitor gate leakage benchmarked from the literature.⁴ The gate leakage of $\text{HfO}_2/\text{Ge}(100)$ is greater than the gate leakage of $\text{ZrO}_2/\text{Ge}(100)$ in the absence of an interfacial control layer (IL) of GeON. The Interfacial control layer greatly reduces the gate leakage for $\text{HfO}_2/\text{Ge}(100)$.

In summation, although zirconium and hafnium are isoelectronic, the electronic structure of monolayers of ZrO_2 and HfO_2 on Ge(100) are distinct. The differences in electronic structure may be responsible for the varying requirement for interfacial control layers when fabricating Ge MOSFETs.

¹ C. O. Chui *et al.*, *IEEE IEDM Tech. Dig.*, p. 437, 2002.

² Y. Kamata *et al.*, *IEEE IEDM Tech. Dig.*, p. 441, 2005.

³ W. Bai *et al.*, *VLSI Symp. Tech. Dig.*, p. 121, 2003.

⁴ C. O. Chui *et al.*, *IEEE Trans. Electron Dev.*, vol 53, p.1509, 2006.

⁵ Whang *et al.*, *IEEE IEDM Tech. Dig.*, p. 307, 2004.