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First-principles investigation of the WC/HfO2 interface properties

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The thermodynamic and electronic properties of tungsten carbide surfaces and interfaces with monoclinic hafnia (WC/m-HfO2) are investigated through first-principles calculations. We show that oxidation of the WC surface and of the WC/m-HfO2 interface is energetically favorable. An oxygen monolayer on the W-terminated WC(0001) surface gives rise to a larger vacuum work function than that for the C-terminated WC(0001) surface, while the opposite result is obtained for the WC(0001) effective work function on hafnia: a carbon intermediate layer results in larger work function than an oxygen intermediate layer. This result is explained by the atomic structure of the intermediate layers neighboring the interface which differ if the interface is O or C rich. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189209]

I. INTRODUCTION

To continue the historical trend of transistor performance enhancement the necessary miniaturization of device dimensions involves, among other things, thinner gate oxides, reduced channel length, and reduced junction depths.1 In particular, the thinning of the SiO2 layer has resulted in considerable power loss through leakage current in the device, a problem that will become severe as the current scaling trend continues. To allow for further reduction of the equivalent gate oxide thickness (EOT) the replacement of SiO2 by a high-k material such as ZrO2 or HfO2 (or corresponding silicates and nitrides), La2O3 (or corresponding aluminates), or more complex oxide alloys must be considered.2 The depletion length in the current polycrystalline silicon (polySi) gate technology also imposes a lower boundary on EOT, incompatible with future generations of complementary metal-oxide-semiconductor (CMOS) technology.1 Moreover, it was recognized that new high-k materials can react with the polySi gate causing undesirable electrical property changes, such as Fermi level pinning at the interface which results in large threshold voltages.3 All these problems may be overcome by the adoption of a high-k gate dielectric to replace SiO2 and suitable metal gates to replace polySi.

The use of metal gates in a p-type metal-oxide-semiconductor (PMOS) [n-type metal-oxide-semiconductor (NMOS)] transistor requires a close alignment of the metal Fermi level with the silicon valence (conduction) band edge in the substrate. For bulk metal-oxide-semiconductor field-effect transistor (MOSFET) devices the optimal metal work functions (WFs) should be within ±0.1 eV of both the Si valence-band edge for PMOS and the conduction-band edge for NMOS.4 While it is relatively easy to control the Fermi level of polySi through appropriate doping, the Fermi levels of metals are not so readily manipulated. Thus, a significant challenge for the adoption of metal gates is the identification of metals with suitable WFs that are also compatible with conventional CMOS processing conditions.

The nitrides and carbides of transition metals are promising candidates for metal gates since they possess excellent mechanical and chemical stability,5 and adjustable electronic properties.6 For example, tungsten carbide in addition to having a high melting point and high hardness has unique structural and electronic properties.7 For this reason tungsten carbide films have attracted a lot of attention in the microelectronics industry as diffusion barriers and as potential metal gates.8,9

A number of experimental works have explored the growth of WC films using different deposition techniques.8–14 In Ref. 8 tungsten carbon layers with a stoichiometric composition of W:C=1:1 were deposited on Si forming a single polycrystalline phase by dc magnetron sputtering. It was shown that both W- and C-terminated surfaces (denoted by WC-W and WC-C, respectively) can be obtained during deposition. Theoretical studies of WC surfaces were performed in Refs. 15 and 16. It was found that W termination has the lowest surface energy and a vacuum WF of 5.2–5.3 eV, which meets the requirements for PMOS transistor devices.

However, it is well known that the WF of a metal on an oxide (the so-called effective WF, or WFeff) can differ significantly from its vacuum WF due to the change of the chemical composition at the interface and formation of interface dipoles. For example, it was found17 that interaction of oxygen with the WC(0001) surface leads to removal of carbon atoms from the (sub)surface layers. Similar modifications can proceed at a WC/oxide interface. Predicting
through atomistic simulations possible $W_{\text{eff}}$ values for this interface for a variety of interface stoichiometries may offer important clues to the relation between different deposition techniques and deposition conditions, and the resulting electrical characteristics. Therefore, the goal of this study is to investigate the thermodynamic stability and electronic properties of the WC/HfO$_2$ interface using first-principles calculations.

This paper is organized as follows: in Sec. II we describe the computational method and the atomic structure of the model WC/m-HfO$_2$ interfaces simulated. In Sec. III we present and discuss our results for the surface and interface calculations. Finally, the conclusions of this work are summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

The bulk and surface structural and electrical properties of WC and $m$-HfO$_2$, and of WC/$m$-HfO$_2$ interfaces were investigated using the local density approximation (LDA) and the generalized gradient approximation (GGA) of density-functional theory (DFT), with core electrons replaced by pseudopotentials (PP), and valence states described by a plane wave (PW) basis set as implemented in the VASP code. Ultrasonic nonlocal PPs (Ref. 22) were used for all atomic species. Relativistic PPs for Hf and W were generated for the neutral atomic configurations $5d^56s^1$ and $5d^66s^1$, respectively. The PW basis was expanded up to a cutoff energy of 497 eV and sampling of $k$ space was done using an $11\times11\times11$ $k$-point Monkhorst-Pack grid for the WC hexagonal bulk phase and a $5\times5\times1$ grid for interface calculations. The structures of all slabs were fully optimized until the maximum residual force was less than 0.07 eV/Å.

Our calculated bulk lattice constants for hexagonal WC are $a = 2.880$ Å and $c = 2.802$ Å, in good agreement with the experimental values of 2.91 and 2.84 Å, respectively. The calculated WC formation energy with respect to W(bcc) and C(diamond) is $-0.48$ eV, which is also in good agreement with the experimental value of $-0.42$ eV. The calculated unit cell parameters of the $m$-HfO$_2$ phase $a = 5.035$, $b = 5.106$, $c = 5.20$ Å, and $\beta = 99.52^\circ$ are within typical DFT/LDA error of the experimental data [Ref. 25]. The calculated $m$-HfO$_2$ total density of states (DOS) (Fig. 1) shows a clean band gap of about 3.7 eV, which is in agreement with other DFT studies of this dielectric.

To test our computational approach we calculated the vacuum WF of the W(110), WC(001), and WC(1120) surfaces (see Table I). For the WC(0001) surface, both WC–C and WC–W were considered. In addition, the C-depleted surface, obtained by removing the closest to the surface C layer from the W-terminated slab, was also considered [denoted by WC(0001)-WW]. In all cases, both slab surfaces were modified identically resulting in symmetric and nonstoichiometric structures. The thickness of all slabs was $\sim 20$ Å (15 layers for WC and nine layers for W). The calculated WFs for the WC(0001) surface are in reasonable agreement with previous theoretical results. Table I also shows that C depletion near the WC(0001) surface increases the WF slightly as expected from the larger value of the W(110) WF with respect to the WC(0001)-W surface.

The surface energies of the nonstoichiometric WC(0001) surfaces were calculated using a generalized definition of the surface free energy,

$$\sigma = \frac{1}{2A} [E_{\text{slab}} - N_w \mu_{\text{WC}}(\text{bulk}) + (N_w - N_C) \mu_C],$$

where $E_{\text{slab}}$ is the calculated slab total energy, $\mu_{\text{WC}}(\text{bulk})$ is the chemical potential of bulk tungsten carbide, $\mu_C$ is the chemical potential of carbon in the diamond phase, and $N_w$ and $N_C$ are the numbers of W and C atoms in the slab. The calculated surface energies of WC–W and WC–C are plotted as a function of the carbon chemical potential in Fig. 2. The figure indicates that the WC(0001)-W surface has a lower surface energy than the C-terminated surface over the entire range of carbon chemical potentials in which WC is stable. The surface energy of WC(0001)-W is smaller than the surface energy of the stoichiometric WC(1120) surface (4.17 J/m$^2$). Our results for the surface energy of the WC(0001) surface are in good agreement with the literature.

Models of the WC(0001)/$m$-HfO$_2$(001) interface were constructed using a $(2 \times \sqrt{3})$ super cell on the WC(0001) surface. Since the lattice parameters for $m$-HfO$_2$ ($a = 5.117$ Å, $b = 5.1754$ Å) and WC [($a = 5.033$ Å, $b = 5.812$ Å for the $(2 \times \sqrt{3})$ cell] are significantly different, the WC structure was expanded along $a$ by 1.7% and contracted.

![Fig. 1. Calculated density of states (DOS) for monoclinic HfO$_2$.](image)

**TABLE I.** Calculated work functions of tungsten and tungsten carbide compared with previous calculations and experimental data (in eV).

<table>
<thead>
<tr>
<th></th>
<th>Exp</th>
<th>VASP</th>
<th>VASP</th>
<th>VASP</th>
<th>VASP</th>
<th>LDA</th>
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</thead>
<tbody>
<tr>
<td>W(110)</td>
<td>5.25</td>
<td>4.94</td>
<td>4.99</td>
<td>4.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC(0001)-C</td>
<td>6.36</td>
<td>6.52</td>
<td>6.2</td>
<td>6.4</td>
<td>5.3</td>
<td>5.2</td>
</tr>
<tr>
<td>WC(0001)-W</td>
<td>4.97</td>
<td>5.20</td>
<td>5.8</td>
<td></td>
<td>5.0</td>
<td>4.94</td>
</tr>
<tr>
<td>WC(1120) WW</td>
<td>5.04</td>
<td>5.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 15.

$^b$Reference 16.

$^c$Reference 28.
along $b$ by 11%. Despite the considerable artificial deformation introduced by our lattice matching procedure, test calculations for the contracted structure of WC demonstrated that its calculated WF is rather insensitive to this deformation (the WF of the contracted slab is only 0.2 eV smaller than that of the noncontracted slab). In order to model possible interfaces, we used slabs-containing HfO$_2$ and WC layers without any vacuum gap. The slabs contain six W layers of WC and six layers of HfO$_2$ and involve two identical HfO$_2$/WC interfaces. Figure 3 shows the five WC(0001)/m-HfO$_2$ model interfaces created for this study: (a) full monolayer (ML) of oxygen at the interface; (b) full ML of C at the interface; (c) half ML of O at the interface; (d) half ML of C at the interface; and (e) only direct W–Hf bonds at the interface.

Two methods were used for the calculation of band alignment: the projected density-of-states (PDOS) technique$^{30}$ and the planar averaged potential (PAP) method of van de Walle and Martin,$^{30}$ in which the electrostatic potential across the slab is calculated in conjunction with an additional bulk calculation for each material to obtain the valence-band offset (VBO).

### III. RESULTS AND DISCUSSION

Using the optimized structures of the slabs shown in Fig. 3, we investigated the thermodynamic stability of the WC/HfO$_2$ interface with respect to oxidation and carbidization reactions. The same analysis was applied to the WC(0001) surface. The following reactions were considered:

$$M\text{-}C + O_2(g) \rightarrow M\text{-}O + CO(g),$$

(1)

$$M\text{-}O + 2C(co) \rightarrow M\text{-}C + CO(g),$$

(2)

where $M\text{-}C$ stands for the WC/HfO$_2$ interface with the WC slab terminated by a C interfacial layer or the WC(0001) surface terminated by a C surface layer. Similarly, $M\text{-}O$ stands for the equivalent interface/surface with an O layer at the interface/surface. C(co) stands for condensed carbon taken in the diamond phase. The energy of an O$_2$ gas molecule was obtained using the calculated energy of an O atom and the experimental dissociation energy of O$_2$ molecule. To check the accuracy of this approach we calculated the bulk heat of reaction: WC+(1/2)O$_2$(g) → W+CO(g). The calculated value, −0.70 eV, is in good agreement with the experimental value, −0.72 eV.$^{31}$

The calculated energetics of the various surface and interface reactions are given in Table II [the M1 structure corresponds to the case with direct W–Hf bonding at the interface shown in Fig. 3(e)]. It is seen that oxidation of carbon on the surface or at the interface (reactions 1 and 3 in Table II) is strongly exothermic, while carbidization of the oxygen-terminated surface or interface (reactions 2 and 4 in Table II) is strongly endothermic. However, carbidization of the oxygen-terminated surface by gas phase C atoms is exothermic. Oxidation of the interface with direct W–Hf bonds (reaction 5 in Table II) is also strongly exothermic, while carbidization of this interface is slightly endothermic.

The relative stabilities of the various interfaces with respect to the fully oxidized interface (four O atoms per surface unit cell) are presented in Table III. It is seen that reduction of the fully oxidized interface by solid carbon is strongly endothermic. The same is valid for oxygen desorp-
tion from the interface: the energy required to remove one O₂ molecule from the fully oxidized interface to the gas phase is 11.2 eV. Notice that this value is significantly larger than the SiO₂ formation energy (about 9 eV), thus indicating that a fully oxidized HfO₂/WC interface should be stable with respect to oxidation of the Si substrate.

In addition in Table III we present the calculated VBO’s for all of the investigated interfaces. To verify that the VBO values reported in Table III were fully converged with respect to the slab thickness, we performed additional calculations using the van de Walle method in which we changed the WC/HfO₂ slab thickness (a) from six Hf layers down to four Hf layers and (b) from six W layers up to nine W layers. We found that for both cases the calculated VBO was within 0.1 eV of that of the original oxide and metal slab thicknesses. This means that the plane-averaged electrostatic potential is bulklike in the middle of the slabs. Moreover, it is seen from Table III that the results calculated using the van de Walle method and the PDOS analysis are in close agreement with each other.

The calculated VBO for a full C ML at the interface (2.3 eV) is smaller than the value obtained for the model slab with a full O ML at the interface (2.6 eV). The WC WFₐₐₐ on hafnia can be estimated using the simple formula $WF_{eff} = BG_d + EA_d - VBO$, where $BG_d$ and $EA_d$ are the dielectric’s band gap and electron affinity, respectively. Because the LDA and GGA exchange-correlation approximations used in DFT to describe quantum many-body effects result in underestimation of the band gap, it is necessary to use instead the measured band gap in the formula above. Here we employ $BG_d$=5.65 eV (Ref. 32) and $EA_d$=2.9 eV (Ref. 33), yielding $WF_{eff}$=5.95 (6.25) eV for a full O (C) ML at the interface. These $WF_{eff}$ values are larger than experimental data which place the WC vacuum and effective (on HfO₂) work functions in the range of 4.5–5.0 eV.⁴¹ Similar to the band-gap problem, calculated VBO values can be also underestimated as discussed previously for the Mo/ZrO₂ interface.⁴² If that happens then $WF_{eff}$ is overestimated as our results above indicate. Studies of VBOs using GW, which offers a more exact approximation to the many-body problem albeit at a considerable computational cost, seem to indicate that indeed calculated VBO’s are not accurate within the LDA/GGA approximations.⁴³ A possible way to empirically correct the $WF_{eff}$ value is to scale the VBO by the experimental/theoretical band-gap ratio.⁴⁴ Proceeding in this way we obtain $WF_{eff}$=4.58 (5.04) eV for a full O (C) ML at the interface, results that are more in line with the experimental data.

For the WC/HfO₂ interface with a half O ML at the interface, the calculated VBO is 3.0–3.1 eV (see Table III). This value is about 0.5 eV larger than the VBO for the interface with a full O ML. For the WC/HfO₂ interface with a half C ML at the interface, the calculated VBO is 0.3 eV higher than for the case of a full carbon ML. This dependence of the VBO on the stoichiometry of the interface is similar to what we found previously for the Mo/ZrO₂ case⁴⁵ and result from the smaller interface dipoles obtained for the O/C half-filled interfaces.

For the WC/HfO₂ interface with direct metal-metal bonds the calculated VBO is 3.2 eV, which is significantly larger than those with full O- and C-intermediate layers at the interface (2.3–2.6 eV). The large value of the VBO for this case is expected due to the relatively small amount of charge transfer across the interface compared to the cases of O- and C-intermediate layers at the interface. This is a consequence of the electronegativity difference between W and Hf atoms, which is a lot smaller than between O (C) and W atoms.

A C ML at the WC/HfO₂ interface gives rise to a 0.3 eV larger $WF_{eff}$ than an O ML at the interface (see Table III). This is unexpected since oxygen is more electronegative than carbon which should result in a larger interface dipole in the case of oxygen, and therefore a larger $WF_{eff}$. To understand the difference in VBO values for C- and O-interfacial MLs we calculated the vacuum WF of O-terminated WC(0001) (surface carbon layer replaced with O atoms). The resulting WF was 7.38 eV, which is about 0.9 eV larger than that for C-terminated WC(0001) (6.52 eV). Thus the calculated WC $WF_{eff}$’s on HfO₂ cannot be directly correlated to its vacuum WF’s. Instead, structural differences at the interface explain this behavior. As shown in Fig. 4, while the relaxed interfacial oxygen ML has a structure similar to the topmost layer of m-HfO₂ (that is, it is split into two sublayers with different heights from the tungsten layer), the relaxed interfacial carbon ML has a structure similar to the C-terminated WC slab (that is, all the interfacial C atoms are practically at the same height from tungsten layer). In a separate calculation we found that swapping interfacial C with O in each of these two structures (WC-O/HfO₂ and WC-C/HfO₂) results in higher energy configurations in both cases. This deceptively minor difference between the two structures significantly impacts the electrical properties. For example, the calculated VBO with an interfacial C layer and a structure similar to the topmost oxygen layer of m-HfO₂ phase is 2.6 eV, which is higher than the value 2.3 eV obtained for the original (WC-like) structure, and is close to the VBO of the structure with

<table>
<thead>
<tr>
<th>Interface</th>
<th>Relative stability (eV/surface unit cell)</th>
<th>VBO (WM) (eV)</th>
<th>VBO (PDOS) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O full</td>
<td>0</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>C full</td>
<td>30.3</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>O half filled</td>
<td>11.2</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>C half filled</td>
<td>25.4</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Empty (W-Hf)</td>
<td>24.5</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4. Optimized structures of the WC/HfO₂ interfaces with (a) one ML O and (b) one ML C interfacial layers. Large light gray: W; large dark gray: Hf; small medium gray: O; small dark gray: C.
an interfacial O layer. Moreover, we made a direct integration of the electron density in the WC slab (between the two outermost W planes) on HfO₂ and found that the total number of electrons in the metal region for the case of interfacial C is smaller than for the case of interfacial O, indicating a larger charge transfer between the metal and the oxide for interfacial C, and confirming our VBO results.

IV. CONCLUSIONS

We performed a first-principles investigation of the thermodynamic and electronic properties of tungsten carbide surfaces and of several interfaces with monoclinic hafnia (WC/m-HfO₂) having different stoichiometries. We have shown that oxidation of the WC surface and of the WC/m-HfO₂ interface is energetically favorable. We also found that depletion of carbon from the first subsurface layer does not have a strong influence on the WC(0001) vacuum work function. The W-terminated WC(0001) surface with an adsorbed oxygen ML has a larger vacuum work function than the C-terminated WC surface, while the opposite result was obtained for the WC(0001) effective work function on hafnia (i.e., the carbon interfacial layer results in a larger effective work function than the oxygen interfacial layer). This counterintuitive trend can be explained by differences in the relaxed atomic arrangement of the C- and O-rich interfacial layers.

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