A first-principles study of ultrathin nanofilms of MgO-supported TiN

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As a first step towards a microscopic understanding of supported ultrathin nanofilms of TiN, we present state-of-the-art density-functional theory (DFT) calculations to investigate the interfacial properties of the TiN/MgO system as a function of film thickness. Optimized atomic geometries, energetics, and analysis of the electronic structure of the TiN/MgO systems are reported. In particular, we find that the work function of 1 ML of TiN(100) on MgO(100) exhibits a significant decrease, rationalized by the large surface dipole moment formation due to the changes in charge densities at the interface of this system. This decrease in the work function of TiN/MgO systems (as compared to pristine MgO(100) surface) could well benefit their application in metal-oxide-semiconductor devices as an ideal gate-stack material.

Introduction

Titanium nitride (TiN) is commonly considered as one of the classical refractory nitrides. This material has a considerably high melting point as well as a high degree of chemical stability, lending it numerous important industrial and technological applications. In particular, TiN thin films are of great interest to the scientific community and are among the most extensively studied refractory nitrides.1 Traditionally, these films have been used as a durable coating material for cemented carbide cutting tools,2 and have also found recent applications in multifunctional biocoatings,3 as well as attracting much interest due to their novel superinsulating properties.4 To study the surface and coating properties of supported TiN thin films, magnesium oxide (MgO) is commonly chosen as the substrate material because both TiN and MgO share the same lattice type, with only a small misfit of 0.6% with no structural relaxation, no dislocation5 and no mosaic disorder.6 Notably, the quality of TiN thin films on MgO substrates has been greatly improved. Recently, it has been successfully demonstrated that thin layers of TiN can be grown epitaxially on inert support materials like MgO by various methods.7–10 Magnus et al. reported that as the growth temperature is increased from room temperature to 600 °C, the film thickness becomes continuous from 5.5 to 0.7 nm.11 It is thought that TiN could be a potential gate metal in metal-oxide-semiconductor devices with high-k gate dielectrics, while MgO is considered an interesting high-k gate oxide candidate.10,12 In this respect, the TiN/MgO system is postulated to be an ideal gate stack for many potential optoelectronic applications.8,9,11,13 From high-resolution electron diffraction images, it is shown that the interface of the TiN/MgO system is coherent.1 It is also found that with increasing growth temperature, the stoichiometry of the TiN film is further improved with increasing grain size.11 Though these studies focused on characterizing the microstructure of the TiN/MgO interface, a detailed picture of both the atomic and electronic structure is lacking.

As a first step towards an atomic understanding of these MgO-supported ultrathin nanofilms of TiN, we present state-of-the-art density-functional theory (DFT) calculations to investigate the interfacial properties of the TiN/MgO system as a function of the TiN film thickness. In particular, we investigate and highlight the effects of supported ultrathin (1 to 4 atomic layers thick) TiN films on our system, in contrast to pristine TiN films. The thickness of TiN film is believed to strongly affect the atomic and electronic structures of the TiN/MgO interface.7,10 Consequently, this study will provide a platform for future investigations to tailor ultrathin nanofilms of TiN for multifunctional devices in emerging technologies.

Computational method

All calculations are performed using DFT as implemented in the all-electron DMol3 code,14,15 where we employ the generalized gradient approximation (GGA) due to Perdew et al.16 for the exchange-correlation functional. The TiN/MgO atomic ultrathin layers are modeled using a supercell slab approach, where we use five or seven-layer MgO(100) slabs as a substrate for the ultra-thin layers of TiN, with a vacuum region of 25 Å.

TiN layers are set on both surfaces of the MgO substrate in the supercell slab, preserving inversion symmetry, with varied thickness. The constituent atoms of the TiN layers and the MgO layers are allowed to atomically relax, except for those of...
the mid-three layers of the MgO substrate. The element-dependent localization cutoff radius is set to range from 7 to 12 Bohr. The convergence criteria for the total energy, force on the atoms, and displacements are set to within $1 \times 10^{-6}$ Ha (2.7 $\times$ 10$^{-5}$ eV), $3 \times 10^{-4}$ Ha Bohr$^{-1}$ (1.5 $\times$ 10$^{-5}$ eV Å$^{-1}$) and $3 \times 10^{-4}$ Bohr (1.6 $\times$ 10$^{-5}$ Å), respectively. The Brillouin zone integrations are performed using a (12 $\times$ 12 $\times$ 1) Monkhorst-Pack $k$-point grid for the (1 x 1) surface unit cell, yielding 21 special $k$-points in the irreducible surface Brillouin zone.

To understand the stability of TiN(100)/MgO(100) structures, we define the atomic binding energy $E_{\text{bind}}$ as follows:17

$$ E_{\text{bind}} = \frac{E_{\text{sys}} - n_{\text{Ti}}E_{\text{Ti}} - n_{\text{N}}E_{\text{N}} - E_{\text{MgO}}}{n_{\text{Ti}} + n_{\text{N}}}, $$

where $E_{\text{sys}}$ is the total energy of the supercell slab system, and $n_{\text{Ti}}$, $n_{\text{N}}$ are the number of titanium atoms and of nitrogen atoms in the surface unit cell, and $E_{\text{Ti}}$, $E_{\text{N}}$, $E_{\text{MgO}}$ are the total energies of a free titanium atom and of a free nitrogen atom, and $E_{\text{MgO}}$ is the total energy of the MgO substrate slab set in the same supercell, respectively. The atomic binding energy is defined as the energy that titanium and nitrogen atoms gain as they form the atomic layers on the MgO substrate. If it takes on a positive value, it indicates that the TiN thin film is unstable with respect to free Ti and N atoms. However, if it is calculated to be a negative value, then the TiN thin film is more stable than free Ti and N atoms and its formation reaction is exothermic.

The surface energy can be obtained from the following expression:18

$$ \sigma = \frac{E_{\text{sys}} - n_{\text{i}}E_{\text{bulk}}}{2S}, $$

where $n_{\text{i}}$ is the number of atoms for the component $i$, $E_{\text{bulk}}$ is the corresponding energy of the bulk for component $i$, and $S$ is the surface area of the supercell slab.

The interfacial energy of a supercell slab system, $\gamma_{\text{inf}}$, is defined as:18

$$ \gamma_{\text{inf}} = \frac{E_{\text{sys}} - E_{\text{TiN}} - E_{\text{MgO}} - 2\sigma_{\text{TiN}}S}{2S}, $$

where $\sigma_{\text{TiN}}$ is the surface energy of the TiN(100) surface. As a basic quantity for an interface, the work of adhesion $W_{\text{ad}}$, which is defined as the reversible work needed to separate an interface into two free surfaces, is widely used to predict the mechanical and thermodynamic properties. $W_{\text{ad}}$ of the TiN/MgO interface can be easily determined by the following definition:18

$$ W_{\text{ad}} = \sigma_{\text{TiN}} + \sigma_{\text{MgO}} - \gamma_{\text{inf}}. $$

The work function $\Phi$ is determined as an energy difference between a vacuum level $E_{\text{vac}}$ and the Fermi energy $E_{\text{F}}$, which can be expressed as19

$$ \Phi = E_{\text{vac}} - E_{\text{F}}. $$

The electronic structure of the system is investigated by analysis of the projected density-of-states (PDOS), as well as the differences in the charge density $\Delta\rho(r)$ due to growth of the TiN films. The latter can be derived by considering:

$$ \Delta\rho(r) = \rho(r)^{\text{sys}} - \rho(r)^{\text{MgO}} - \rho(r)^{\text{TiN}}, $$

where $\rho(r)^{\text{sys}}$, $\rho(r)^{\text{MgO}}$ and $\rho(r)^{\text{TiN}}$ are the electron charge densities of the supercell TiN/MgO slab system, the pure MgO slab and the pure TiN films respectively. In calculation of the latter two quantities, the atomic positions are fixed as those they have in the TiN/MgO system.

The bulk lattice constant and the bulk modulus of MgO and TiN are calculated to be 4.246 Å, 152.6 GPa and 4.210 Å, 275.5 GPa respectively. Our calculated results are consistent with the corresponding experimental values, which are 4.210 Å, 160 GPa and 4.240 Å, 288 GPa respectively.8,20 In addition, the surface energy $\sigma$ of the TiN(100) and MgO(100) surfaces is 0.077 and 0.061 eV Å$^{-2}$, respectively, which is consistent with other calculated ab initio results.21,22

### Results and discussion

Fig. 1 shows the results of atomic binding energy, $E_{\text{bind}}$, as a function of the number of TiN(100) monolayers, $n$, with a different number (5 or 7) of MgO(100) support layers. It can be seen from Fig. 1 that the values of atomic binding energies are negative, which means that it is more favorable for N and Ti atoms to form TiN films on the MgO substrates with respect to the free Ti and N atoms, i.e. that formation of these films is exothermic when compared to the atomic sources. In addition, we have also considered the nanofilm formation energy (with respect to the relevant elemental ground state, i.e. N$_2$ molecule and bulk Ti). We find that in all cases, they are all exothermic, clearly demonstrating that the formation of nanofilms from their elemental states is also thermodynamically favorable. Thus, from now, we will focus on discussing only with respect to their atomic binding energy. The value of $E_{\text{bind}}$ decreases (becomes more stable) for increasing $n$, and shows a convergence at around –6.94 eV as $n$ increases to 4. Increasing the number of MgO(100) support layers from 5 to 7 did not result in a noticeable difference in the atomic binding energy. It appears that five MgO layers are sufficient to describe the structure and energetics of these interface systems.

The estimates of the interface energy should be of help in understanding the mechanism of the growth of TiN ultrathin films on the MgO substrate. The interface energy of TiN/MgO systems, $\gamma_{\text{inf}}$, decreases when $n$ increases from 1 to 3, as shown in Fig. 2.
behavior,\textsuperscript{21,22} where the anions tend to relax away from the interface energy and the work of adhesion. Layers from 5 to 7 did not result in a noticeable difference in the binding energy, increasing the number of MgO(100) support substrate, indicating poorer adhesion properties. However, increasing the number of TiN monolayers improves the adhesion performance of the TiN/MgO systems. Similarly to the atomic binding energy, increasing the number of MgO(100) support layers from 5 to 7 did not result in a noticeable difference in the interface energy and the work of adhesion.

It is well known that B1-structured (100) surfaces (e.g. TiN(100) and MgO(100)) exhibit a rumpling relaxation behavior,\textsuperscript{21,22} where the anions tend to relax away from the surface and the cations are pulled inwards towards the bulk. The outermost layer for the pristine (100) surface of TiN and MgO shows a tendency towards inward relaxation, with a larger surface relaxation for the case of TiN(100) as compared to MgO(100). The surface and interface structures of the TiN/MgO system can be characterized by two parameters: surface relaxation describing the changes in the interlayer distances with respect to the bulk value, and the rumpling effect describing a relative arrangement of cations and anions in the monolayer.\textsuperscript{22} For the clean TiN(100) and MgO(100) surfaces, the rumpling effects (with respect to the bulk-interlayer spacing) are 8.1% and 2.0%, respectively, which are consistent with other calculated results of 8.4% and 2.3%.\textsuperscript{21,22} For the TiN/MgO system, the surface relaxation is shown in Fig. 3, and the rumpling effects are listed in Table 1. Generally, for the supported films, TiN(100) layers undergo about a 1% inward relaxation (exception for 1 ML). Relaxation of the supporting MgO(100) layers shows negligible atomic relaxations. As shown in Fig. 3, the TiN plane at the interface relaxes away from the interface and it becomes almost constant when the number of TiN monolayers increases from 2 to 4, which is around 4.5%. We also find the rumpling effect of the TiN plane at the interface to be larger than that of the MgO plane at the interface, as shown in Table 1. For the 1ML-TiN/MgO system, the rumpling of the MgO plane at the interface is 1.5%, which is close to that of the pure MgO surface of 2.0%, while the rumpling of the TiN plane is 2.4%, which is much smaller than that of the pure TiN surface of 8.4%. When the number of TiN monolayers is increased from 1 to 2, the rumpling effect of the TiN surface is 7.5%, which is approaching that of the pure TiN surface of 8.4%. For the rumpling effect at the interface region, with the exception of the 1ML-TiN/MgO system, they all yield similar results, which explains the significant differences in results of the atomic binding energy, the interface energy, the work of adhesion and the work function for the 1ML-TiN/MgO system when compared with the thicker films.

Now, turning to the electronic structure of these supported ultrathin films, Fig. 4 shows the variation of work function

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{nML-TiN/MgO-5L} & \textbf{Surface} & \textbf{Interface TiN} & \textbf{Interface MgO} & \textbf{nML-TiN/MgO-7L} & \textbf{Surface} & \textbf{Interface TiN} & \textbf{Interface MgO} \\
\hline
1 & -2.4 & 2.4 & 1.5 & -2.5 & 2.5 & 1.5 \\
2 & -7.5 & 3.9 & 0.6 & -7.5 & 3.9 & 0.6 \\
3 & -9.0 & 6.1 & 0.2 & -9.0 & 6.1 & 0.2 \\
4 & -7.6 & 3.2 & 0.5 & -7.7 & 4.8 & 0.5 \\
\hline
\end{tabular}
\caption{The rumpling of the TiN surfaces and TiN/MgO interfaces for the nML-TiN/MgO-5L and nML-TiN/MgO-7L systems with respect to the bulk-interlayer spacing (in %). For TiN surfaces, negative values denote that N atoms shift further towards vacuum than Ti atoms. In the interfaces, positive values denote that N atoms shift further towards the side of MgO than Ti atoms, while Mg atoms shift further towards the side of TiN than O atoms.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{The atomic interlayer distances and corresponding deviation from the bulk interlayer distance for the nML-TiN/MgO-5L systems.}
\end{figure}
The work function, \( \Phi \), of a material is defined as the energy required to remove an electron from the surface of the material to infinity. It is given by the difference between the Fermi level and the vacuum level, \( \Phi = E_F - E_{\text{vac}} \), where \( E_F \) is the Fermi energy and \( E_{\text{vac}} \) is the energy of the vacuum level.

The work function of a material can be significantly altered by the presence of adsorbates or surface modifications. For instance, the work function of TiN on MgO can be varied by changing the number of TiN monolayers. The work function, \( \Phi \), of the system can be calculated using the expression:

\[
\Phi = \Phi_{\text{TiN}} - \Phi_{\text{MgO}},
\]

where \( \Phi_{\text{TiN}} \) and \( \Phi_{\text{MgO}} \) are the work functions of TiN and MgO, respectively.

### Figure 4

This figure shows the variation of the work function relative to that of the MgO(100) surface for increasing number, \( n \), of TiN(100) monolayers, supported on 5 and 7 MgO(100) layer slabs. The work function is calculated as:

\[
\Delta \Phi = \Phi_n - \Phi_{\text{MgO}},
\]

where \( \Phi_n \) is the work function of the system with \( n \) TiN monolayers. The work function decreases with increasing number of TiN monolayers, indicating that the surface dipole moment increases.

### Figure 5

This figure shows the side view of differences in charge density, \( \Delta \rho(\tilde{r}) \), for the 1ML-TiN/MgO-5L and 4ML-TiN/MgO-5L systems. Red shows regions of charge accumulation, and blue shows charge depletion, clearly demonstrating the charge redistribution across the interface.

The Ti (N) atoms loose (gain) more electron density than Mg (O) atoms, resulting in a larger charge density difference in the TiN plane than that in the MgO plane. This difference in the electronic structure would then account for the larger variation of atomic structure in the TiN plane compared to the MgO plane in the interface region, as mentioned above. For both systems, a large increase in the work function is observed for 1ML-TiN/MgO as compared to that of 4ML-TiN/MgO. This larger surface dipole moment then aids electrons to escape from the surface, which results in the larger decrease of work function of 1ML-TiN/MgO, compared with 4ML-TiN/MgO, as highlighted in Fig. 4. This phenomenon of electron transfer was also found in the similar VN/MgO system. We note that similar but reversed interfaces (e.g. ultrathin MgO films deposited on metal surfaces) have been studied and shown that the substantial change in the work function is also due to an electrostatic charge compressive effect, rather than solely due to the transfer of charges across the interface.

Furthermore, the PDOS of bulk TiN and MgO have been calculated (not shown here). MgO is clearly an insulator (calculated band gap of \( E_{\text{gap}} = 9.82 \text{ eV} \) while the experimental value is \( E_{\text{gap}} = 7.83 \text{ eV} \)), while TiN is a metal (0.85 states eV\(^{-1}\) at the Fermi level). For bulk MgO, the conduction band comprises mainly empty Mg 3s and p states, while the valence band has strong O 2p character. For bulk TiN, largely dispersive unoccupied bands are composed of Ti 3d states, while the occupied bands show a strong hybridization of N 2p and Ti 3d states, consistent with earlier studies. Taking the 4ML-TiN/MgO system as an example, Fig. 6 displays the PDOS of each different layer decomposed into N 2p, O 2p,
Most dramatic decrease, rationalized by the large surface dipole moment formation due to the changes in charge densities at the interface of this system. In addition, from analysis of the PDOS of the TiN/MgO interface systems, it is found that their metallic character is largely due to the Ti 3d states at the interface. It is expected that modulation of Ti 3d states could offer a route to tune the electronic properties of the system to satisfy the need of a particular application.

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