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

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Physical Chemistry Chemical Physics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>CP-ART-11-2011-023534.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>n/a</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Zhang, Renqin; Yonsei University, Kim, Chang Eun; Yonsei University, Materials Science and Engineering Delley, Bernard; Paul Scherrer Institut; Stampfl, Catherine; The University of Sydney, Soon, Aloysius; Yonsei University, Materials Science and Engineering</td>
</tr>
</tbody>
</table>
PCCP’s high standards

August 2011: Physical Chemistry Chemical Physics (PCCP) is a high quality journal with a large international readership from many communities

Only very important, insightful and high-quality work should be recommended for publication in PCCP.

To merit acceptance in PCCP - a manuscript must report:

- Very high quality, reproducible new work
- Important new physical insights of significant general interest
- A novel, stand-alone contribution

Routine or incremental work should not be recommended for publication. Purely synthetic work is not suitable for PCCP.

If you rate the article as ‘routine’ yet recommend acceptance, please give specific reasons in your report.

Less than 50% of articles sent for peer review are recommended for publication in PCCP. The current PCCP Impact Factor 3.45.

PCCP is proud to be a leading journal. We thank you very much for your help in evaluating this manuscript. Your advice as a referee is greatly appreciated.

With our best wishes,

Philip Earis (pccp@rsc.org)
Editor, Physical Chemistry Chemical Physics

Pekka Pyykko
Chair, Editorial Board

General Guidance (For further details, see the RSC’s Refereeing Procedure and Policy)

Referees have the responsibility to treat the manuscript as confidential. Please be aware of our Ethical Guidelines which contain full information on the responsibilities of referees and authors.

When preparing your report, please:
- Comment on the originality, importance, impact and scientific reliability of the work;
- State clearly whether you would like to see the paper accepted or rejected and give detailed comments (with references, as appropriate) that will both help the Editor to make a decision on the paper and the authors to improve it;

Please inform the Editor if:
- There is a conflict of interest;
- There is a significant part of the work which you cannot referee with confidence;
- If the work, or a significant part of the work, has previously been published, including online publication, or if the work represents part of an unduly fragmented investigation.

When submitting your report, please:
- Provide your report rapidly and within the specified deadline, or inform the Editor immediately if you cannot do so.
- We welcome suggestions of alternative referees.
A first-principles study of ultrathin nanofilms of MgO-supported TiN

Ren-Qin Zhang¹, Chang-Eun Kim¹, Bernard Delley², Catherine Stampfl³ and Aloysius Soon¹*

¹ Department of Materials Science and Engineering, Yonsei University, Seoul, Korea
² Paul-Scherrer-Institut, Villigen, Switzerland
³ School of Physics, The University of Sydney, Sydney 2006, Australia

Abstract. 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 of the work function of TiN/MgO systems (as compared to pristine MgO(100) surface) could well benefit its 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 to 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 its 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

*Corresponding author. E-mail: aloysius.soon@yonsei.ac.kr
both TiN and MgO share the same lattice type, with only a small misfit of 0.6% with no structural relaxation, no dislocation formation and no mosaic disorder. 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 grow epitaxially on inert support materials like MgO by various methods. 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. 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. In this respect, the TiN/MgO system is postulated to be an ideal gate stack for many potential optoelectronic applications. From high-resolution electron diffraction images, it is shown that the interface of the TiN/MgO system is coherent. It is also found that with increasing growth temperature, the stoichiometry of the TiN film is further improved with increasing grain size. 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 for 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. 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 DMol\(^3\) code, where we employ the generalized gradient approximation (GGA) due to Perdew et al. 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 (1.5
Ultrathin Nanofilms of MgO-supported TiN

$10^{-2}$ eV/Å and $3 \times 10^{-4}$ Bohr (1.6 x $10^{-2}$ Å), respectively. The Brillouin zone integrations are performed using a (12 x 12 x 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 $E_{\text{bind}}^{\text{atom}}$ as follows:

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

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 $E_{\text{Ti}}^{\text{atom}}$, $E_{\text{N}}^{\text{atom}}$ are the total energies of a free titanium atom and of a free nitrogen atom, and $E_{\text{MgO}}^{\text{slab}}$ 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 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:

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

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

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

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

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:

$$W_{\text{ad}} = \gamma_{\text{inf}}.$$
The work function $\Phi$ is determined as an energy difference between a vacuum level $E_{\text{vac}}$ and the Fermi energy $E_F$, which can be expressed as:

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

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 $\Delta\rho(\vec{r})$ due to growth of the TiN films. The latter can be derived by considering:

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

where $\rho(\vec{r})_{\text{sys}}$, $\rho(\vec{r})_{\text{MgO}}$ and $\rho(\vec{r})_{\text{TiN}}$ 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. In addition, the surface energy $\sigma$ of the TiN (100) and MgO (100) surfaces are 0.077 and 0.061 eV/Å² respectively, which is consistent with other calculated ab initio results.

**Results and discussion**

Figure 1 shows the results of atomic binding energy, $E_{\text{bind}}^{\text{atom}}$, as 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 its atomic binding energy. The value of $E_{\text{bind}}^{\text{atom}}$ decreases (becomes more stable) for increasing $n$, and shows a convergence at around −6.94 eV as $n$ increases to 4. Increasing
the 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 energetic 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, \( \gamma^{inf} \), decreases when \( n \) increases from 1 to 3, as shown in Fig. 2. When 4 TiN monolayers are deposited on the MgO substrate, \( \gamma^{inf} \) exhibits a small fluctuation. We believe that further increase of TiN monolayers may not change \( \gamma^{inf} \) very much. The small value of \( \gamma^{inf} \) suggests that the interface is both coherent and stable. In addition, the work of adhesion \( W_{ad} \) is related to adhesion properties of the considered interface. Our results, also presented in Fig. 2, indicate that 1 TiN monolayer supported on the MgO substrate is only weakly attached to its 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,\(^{21,22}\) 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.\(^{22}\)

For the clean TiN(100) and MgO(100) surfaces, the rumpling effect (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%.\(^{21,22}\) 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 1ML). Relaxation of the supporting MgO(100) layers show 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 TiN monolayer 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 in 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 TiN monolayer is increased from 1 to 2, the rumpling effect of the TiN surface is 7.5%, which is approaching to 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 compared with that of the MgO(100) surface with increasing the number, \( n \), of TiN monolayers. It can be seen that for 1 ML of TiN, the work function of the system is decreased significantly when compared to the bare MgO substrate. Namely, it has decreased by 1.63 eV (compared to the calculated \( \Phi_{\text{MgO}} = 3.89 \) eV for the pristine MgO(100) substrate). With increasing number of TiN layers to 2 and 3, the work function of the system starts to show an increase. It then exhibits a very slight decrease when \( n = 4 \). We can expect that as the thickness increases, the work function will converge to around \(-2.80\) eV, which is approaching the value of the clean surface of TiN(100) calculated to be \( \Phi_{\text{TiN}} = 2.90 \) eV.

Again increasing the number of MgO(100) support layers from 5 to 7 did not show a noticeable difference in the variation of the work function. These results correlate well with the corresponding decrease in the interface energy and the atomic binding energy. To understand the large decrease in the work function of 1ML-TiN/MgO relative to bare MgO(100), we firstly investigate the surface dipole moment \( \mu \) (in Debye) of this system. It can be calculated by considering \( \mu = \frac{S \Delta \Phi}{12\pi \Theta} \), where \( \Theta \) is defined to be the number of TiN monolayers.\(^{17}\) It is found that for 1ML-TiN/MgO, \( \mu = -0.779 \) Debye, while that of 4ML-TiN/MgO is \(-0.122\) Debye. The negative value denotes that the dipole moment is pointing inwards, i.e. from TiN to MgO. This yields a large change of 0.657 Debye, accounting for the dramatic dip in the work function as described above.\(^{23,24}\) Furthermore, according to the definition of the work function, the variation of the Fermi level (relative to the potential at the vacuum) then determines the change in the work function. Taking \( n \)ML-TiN/MgO-5L systems as an example, the Fermi level decreases by \(-3.30\), \(-4.28\), \(-4.71\) and \(-4.88\) eV respectively when \( n \) is 1, 2, 3 and 4, resulting in the lowest work function observed for the 1ML-TiN/MgO-5L system. Moving from \( n = 3 \) to \( n = 4 \), we also find that the minimal change in the Fermi level, as reflected in the work function change mentioned above.

To further aid our understanding, we discuss this difference via the plots of charge density differences, as shown in Fig. 5 for the 1ML-TiN/MgO and 4ML-TiN/MgO systems. The charge redistribution is mainly among the interface area. Taking their respective electronegativities into account, we rationalize that Ti (N) atoms loose (gain) more electron density than Mg (O) atoms, resulting in a larger charge density difference in TiN plane than that in 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, we find a rather large enhancement "under" the N atoms (i.e. in the direction of the N-Mg interfacial bond) and a corresponding depletion at the Ti atoms. This effect is found to be more extreme for 1ML-TiN/MgO, as compared to 4ML-TiN/MgO. Noting these differences, the net depletion thus generates a larger surface dipole moment at the interface of 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 also was found in the similar system of VN/MgO system.\textsuperscript{25} 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.\textsuperscript{23,24,26} This lowering of the work function motivates the consideration of using ultrathin MgO-supported TiN films as a potential gate metal in metal-oxide-semiconductor field effect transistors.\textsuperscript{12}

Furthermore, the PDOS of bulk TiN and MgO have been calculated (not shown here). MgO is clearly an insulator (calculated band gap of $E_{\text{gap}} = 4.82$ eV while the experimental value is $E_{\text{gap}} = 7.83$ eV\textsuperscript{27}), while TiN is a metal (0.85 states/eV at the Fermi level). For bulk MgO, the conduction band comprises mainly of empty Mg 3$s$ and $p$ states, while the valence band has strong O 2$p$ character. For bulk TiN, largely dispersive unoccupied bands are composed of Ti 3$d$ states, while the occupied bands show a strong hybridization of N 2$p$ and Ti 3$d$ states, consistent with earlier studies.\textsuperscript{28} Taking the 4ML-TiN/MgO system as an example, Fig. 6 displays the PDOS of each different layer decomposed into N 2$p$, O 2$p$, Ti 3$d$ and 4$s$, Mg 3$s$ and 3$p$ states, as well as its total density-of-states. Although pristine MgO(100) has a large band gap, the TiN/MgO interface presents a metallic character due to the partially occupied states at the Fermi level. Ultrathin nanofilms of TiN(100) retain their metallic character when supported on MgO(100). The Ti 3$d$ states of the interface layer (i.e. TiN layer 4), mainly accounts for the metallic character of the system as they dominate at the Fermi level. This indicates that if the electronic properties of these interfacial systems need further to be modified, one possible strategy would be to alter the character of the Ti 3$d$ states by, for example, considering intrinsic point defects or extrinsic dopants at the interface.

As a whole, we find that the atomic binding energy, the interface energy, the work of adhesion and the work function exhibit a similar variation with increasing number of TiN monolayers. In particular, the 1ML-TiN/MgO system is found to be most interesting—having extreme values of the various physical/chemical properties mentioned above. Increasing the TiN monolayers beyond 1 brings about bulk-like characteristics, only showing that these properties of the interface have a weak-dependence on the thickness of TiN layers, with the exception for the 1ML-TiN/MgO system.
Conclusions

In summary, the properties of TiN/MgO interface systems, including the interface energy, the work of adhesion, the work function and the atomic and electronic structures, are investigated by first-principles calculations based on DFT. The large negative atomic binding energy demonstrates the stability of the TiN/MgO interface systems with respect to their atomic sources. With increasing number of TiN monolayers, these properties are found to quickly become bulk-like beyond 1 ML of TiN. The work function of TiN/MgO systems compared to pure MgO(100) surface decreases with decreasing number of TiN monolayers. In particular, that of 1ML-TiN/MgO shows the 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.

Acknowledgment

The authors gratefully acknowledge support from the Korean Ministry of Education, Science, and Technology (MEST) through an institutional research program of the Korea Institute of Science and Technology (KIST) (Contract No. 2E22121) and the Australian Research Council (ARC). Computational resources have been provided by the Australian National Computational Infrastructure (NCI). RQZ acknowledges the Second Stage of Brain Korea 21 Project (Division of Humantronics Information Materials) for funding.

Keywords: interface · nanofilm · titanium nitride · magnesium oxide · work function

References

Ultrathin Nanofilms of MgO-supported TiN

Fig. 1. The atomic binding energy, $E_{\text{atom}}^{\text{bind}}$, as function of the number, $n$, of TiN(100) monolayers supported on 5 and 7 MgO(100) layers, which are denoted as $n$ML-TiN/MgO-5L and $n$ML-TiN/MgO-7L, respectively.
Fig. 2. The interface energy and work of adhesion as function of the number $n$ of TiN(100) monolayer supported on 5 and 7 MgO(100) layers.
Fig. 3. The atomic interlayer distances and corresponding deviation from the bulk interlayer distance for the $n$ML-TiN/MgO-5L systems.
Fig. 4. 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. $\Delta\Phi = \Phi_{\text{sys}} - \Phi_{\text{MgO}}$, where $\Phi_{\text{sys}}$ and $\Phi_{\text{MgO}}$ are the work function of the TiN/MgO interface system and MgO, respectively.
Fig. 5. Side view of differences in charge density, $\Delta \rho(r)$, for the 1ML-TiN/MgO-5L and 4ML-TiN/MgO-5L systems. Red shows regions of charge accumulation, and blue charge depletion, clearly demonstrating the charge redistribution across the interface.
Fig. 6. Projected density of states (PDOS) for each monolayer for the 4ML-TiN/MgO-5L system, as well as the total density of states. The vertical dashed line indicates the Fermi level.
Table 1. The rumpling of the TiN surfaces and TiN/MgO interfaces for the \( n \)ML-TiN/MgO-5L and \( n \)ML-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.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( n )ML-TiN/MgO-5L</th>
<th>( n )ML-TiN/MgO-7L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>surface TiN</td>
<td>interface TiN</td>
</tr>
<tr>
<td>1</td>
<td>-2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>-7.5</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>-9.0</td>
<td>6.1</td>
</tr>
<tr>
<td>4</td>
<td>-7.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Top of Content: Dramatic decrease in the work function of MgO-supported ultrathin TiN nanofilms is rationalized by large charge transfer at the heterointerface.