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Ab initio study of the atomic level structure of the rutile TiO_2 (110) – titanium nitride (TiN) interface

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ABSTRACT

Titanium nitride (TiN) is widely used in industry as a protective coating due to its hardness and resistance to corrosion and can spontaneously form a thin oxide layer when it is exposed to air, which could modify the properties of the coating. With limited understanding of the $TiO_2 - TiN$ interfacial system at present, this work aims to describe the structural and electronic properties of oxidized TiN based on a density functional theory (DFT) study of the rutile $TiO_2 (110) - TiN (100)$ interface model system, also including Hubbard +U correction on Ti 3d states. The small lattice mismatch gives a good stability to the $TiO_2 - TiN$ interface after depositing the oxide onto TiN through the formation of interfacial Ti – O bonds. Our DFT+U study shows the presence of Ti^{3+} cations in the TiO_2 region, which are preferentially located next to the interface region as well as the rotation of the rutile TiO_2 octahedra in the interface structure. The DFT+U TiO₂ Electronic Density of States (EDOS) shows localised Ti^{3+} defect states forming in the mid-gap between the top edge of the valence and the bottom

of the conduction band. We increase the complexity of our models by the introduction of non-stoichiometric compositions. Although the vacancy formation energies for Ti in TiN $(E_{vac} (Ti) \ge 4.03 \text{ eV})$ or O in the oxide $(E_{vac} (O) \ge 3.40 \text{ eV})$ are quite high relative to perfect $TiO_2 - TiN$, defects are known to form during the oxide growth and can therefore be present after TiO_2 formation. Our results show that a structure with exchanged O and N can lie 0.82 eV higher in energy than the perfect system, suggesting the stability of structures with interdiffused O and N anions at ambient conditions. The presence of N in TiO_2 introduces N 2p states localized between the top edge of the O 2p valence states and the mid-gap Ti^{3+} 3d states, thus reducing the bandgap in the TiO_2 region for the exchanged O/N interface EDOS. The outcomes of these simulations give us a most comprehensive insight on the atomic level structure and the electronic properties of oxidised TiN surfaces.

Keywords: TiO₂, TiN, interface, defects, biofouling

1. INTRODUCTION

Titanium nitride (TiN) is a ceramic material widely used in industry as a protective coating due to its hardness (H ~ 19-22 GPa)¹ and resistance to corrosion². TiN combines good electrical and thermal conductivity, high melting point (T_{melt} = 3222 K) and biocompatibility²⁻⁵. The combination of these properties explains the widespread use of TiN coatings in multiple fields and applications such as medical devices, cutting tools, automotive parts, aerospace components, jewellery or sporting goods^{2, 4, 6-7}. TiN also displays significant plasmonic performance⁸ while it is a promising coating for microelectronic devices, acting both as a diffusion barrier and as an anti-biofouling protection for detectors that are designed to work in aggressive environments⁹⁻¹¹. TiN is compatible with most standard microelectronics fabrication methods and can be deposited using a number of techniques such as magnetron sputtering, ion-beam sputtering, physical vapour deposition (PVD), chemical vapour deposition (CVD) or atomic layer deposition (ALD)¹²⁻¹⁵. It forms a uniform film with stoichiometric oxygen-free composition when deposited on Si (100) at high temperature while the (200) orientation has been identified on the polycrystalline structured surface, with no voids are observed at the TiN – Si interface^{16-19.}

The TiN surface is easily oxidised, thus the oxidation of TiN coating surfaces²⁰⁻²³ or TiN powder²⁴⁻²⁵ has been extensively investigated for many years. TiN spontaneously forms a Tibased oxide layer when it is exposed to air, even at ambient conditions^{21-23, 26-28}. The formation of TiO_x may reduce the adherence of the coating and decrease the wear protection, deteriorating the resistivity, mechanical properties and anti-corrosion features of TiN²⁸⁻³⁰. On the other hand, TiO₂ can be specifically sputtered on TiN, and this interfacial system is interesting for applications such heat mirrors and photocatalysis³¹⁻³³. When O₂ is adsorbed atop Ti on a TiN (100) surface, it can spontaneously dissociate or bind to a surface Ti site to form TiO₂, similar to the oxidation of other metal surfaces³⁴. The oxide layer will then grow

 on the TiN surface following various pathways, showing features that may vary between a thermodynamically stable (minimum energy) non-defective interface and a kinetically driven interfacial structure with the possible formation of metastable intermediate non-stoichiometric structures. Zimmermann et al.³⁵ used ab initio molecular dynamics simulations to show that at high temperatures, an ordered oxide structure can grow on the surface, preventing further oxidation of the substrate due to the high energy needed to adsorb more incoming O₂. On the other hand, when the temperature is very low, vacancies and defects are prone to remain trapped inside the structure³⁵. Most recently, Moatti et al.²⁶ analysed the epitaxial growth of rutile (110) TiO₂ on TiN/Si film and observed by SuperX Energy Dispersive Spectrometry (SuperX EDS) the presence of a oxynitride (TiN_xO_y) transition layer, which is proposed to be associated to the diffusion of oxygen atoms into the TiO₂ – TiN interface.

Nevertheless, despite the wide-spread use of TiN and the significant studies carried out in recent years, the existence of theoretical studies aiming to gain physico-chemical insights into the oxide – nitride interface are still rather scarce. Therefore, with limited knowledge of the atomic level structure of oxidised TiN currently available, we aim to improve our understanding of the $TiO_2 - TiN$ system by a comprehensive simulation study aiming to identify the structural and electronic characteristics of the $TiO_2 - TiN$ interface.

We apply first principles Density Functional Theory (DFT) simulations using the General Gradient Approximation (GGA) to the exchange correlation functionals, which have been proven to describe structural parameters of TiN with excellent agreement compared to experimental values³⁶. Rutile TiO₂ (110) and rock-salt TiN (100) surfaces have the lowest surface energy for their respective compositions³⁶⁻³⁷, therefore in this work we build an atomic level rutile TiO₂ (110) – TiN (100) interface structure as a model system for an oxidised TiN surface. This interface also shows a reasonable lattice match between TiO₂ and

TiN, reducing stress in the TiO_2 layer when interfaced with a TiN (100) surface. Our simulations involve the study of the ideal stoichiometric interface structure and the introduction of defects that could be present in this interface such Ti vacancies in the TiN substrate, O vacancies in the oxide and the formation of structures in which oxygen from TiO_2 and nitrogen from TiN exchange sites. We also use DFT+U (DFT corrected for on-site Coulomb interactions) to consistently describe partial reduction of Ti atoms in TiO_2 in the interface that arise from charge transfer between TiN and the oxide. The simulations carried out provide a comprehensive insight into the atomistic description of oxidised TiN surfaces.

2. COMPUTATIONAL DETAILS

In this work we use first principles calculations within the framework of the Vienna Ab Initio Simulation Package $(VASP)^{38}$. This package performs Density Functional Theory (DFT) simulations on periodic solids. We use projector augmented-wave (PAW) potentials³⁹⁻⁴⁰ to describe the core-valence interaction, where the valence electrons (Ti 4s² and 3d² electrons, N 2s² and 2p² electrons, and O 2s² and 2p² electrons) are described by periodic plane waves whereas the remaining electrons are considered as core states. The cut-off energy for the plane wave expansion is 400 eV. The generalized gradient approximation in the form given by Perdew and Wang (GGA-PW91)⁴¹ was employed for the exchange correlation functional. The ionic relaxation is converged when all the forces are less than 0.02 eV/Å, while self-consistency in the energy is achieved when successive energy differences are less than 10^{-4} eV.

We calculated the equilibrium lattice for the bulk TiN (a = 4.26 Å) and rutile TiO₂ (a = 4.64 Å; c = 2.97) using a Monkhorst-Pack sampling grid of (14x14x14) k-points and (4x4x4) k-points respectively. Upon cleaving from the bulk, the 5-layer thick (10.66 Å) rock-salt TiN (100) surface is composed of neutral planes with TiN stoichiometry and the 4 O – Ti – O tri-

layer (11.10 Å) TiO₂ slab exhibits the well-known rutile (110) surface structure. To assure that there is no interaction between the opposite surfaces through the 3-D periodic boundary conditions, a vacuum thickness of at least 15 Å was introduced between the interface slabs. The rutile TiO₂ (110) supercell presents a = 8.92 Å; b = 13.12 Å dimensions in the in-plane and contains 144 atoms. The TiN (100) slab size is a = 8.51 Å; b = 12.77 Å for the supercell composed of 120 atoms. We use a (4x4x1) Monkhorst-Pack sampling grid for the TiO₂ and TiN isolated free-standing surface simulations. While Γ -point calculations (1x1x1 k-point) were sufficient to reach energy convergence for our interface supercell models, containing up to 264 atoms, we relaxed the energetically most favourable structures with a (4x4x1) Monkhorst-Pack sampling grid to obtain a better defined Electronic Density of States (EDOS). We integrate the Brillouin Zone using the Methfessel-Paxton smearing function with $\sigma = 0.1$ eV. The EDOS around the Fermi level are normalized per atom so that their contribution to the total EDOS depends on the relative weight of each species in the structure. The Fermi level is set to 0 eV and all calculations were spin-polarized to account for the possible presence of unpaired electrons.

We perform DFT+U calculations²⁵ (DFT corrected for on-site Coulomb interactions) to describe potentially reduced Ti³⁺ species in TiO₂ that may result from the TiN – TiO₂ interface. The DFT+U approach can effectively localize electrons and correct the inaccurate description of the electron self-interaction in partially occupied 3d states found with standard DFT calculations⁴², while adding little in the computational cost compared to a conventional DFT-GGA functional. A number of previous works have found that U = 4.5 eV can correctly describe the charge localisation in defective TiO₂⁴³⁻⁴⁵. Therefore the Hubbard +U parameter, which describes the on-site Coulomb repulsion, was applied to the Ti 3d states in TiO₂ and we set U = 4.5 eV. We did not apply DFT+U corrections to TiN or O. Bader charge analysis was then carried out with the software developed by Henkelman's group⁴⁶.

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Aiming to simulate more realistic systems, we probed the possible presence of point defects that can be expected in the interface such as O vacancies in the oxide, Ti vacancies in the alloy surface or the exchange of O and N atoms within the interface. To calculate vacancy formation energies with respect to the stoichiometric surfaces, we perform Γ -point calculation for an isolated gas-phase O₂ molecule as well as a bulk Ti hexagonal closed-packaged (hcp) structure with Monkhorst–Pack grid of (20x20x20) k-points. We used the same energy cut-off and convergence criteria as the slabs. The reference energies for defect formation are set as $E_O = -4.68$ eV, corresponding to one half of the energy of an O₂ gas molecule; and $E_{Ti} = -7.74$ eV is the energy of a single Ti atom within the bulk hcp equilibrium structure.

The formation vacancy energy (E_{vac}) of an O or Ti vacancy in the interface was then computed with the following expression:

$$E_{vac} = E[TiO_2 - TiN]_{non-stoich} - E[TiO_2 - TiN] + E_{O/Ti}$$

Where $E[TiO_2 - TiN]_{non-stoich}$ and $E[TiO_2 - TiN]$ are the energy of the non-stoichiometric and the ideal interface model systems respectively, while $E_{O/Ti}$ corresponds to the energy of a single oxygen (E_O) or Ti (E_{Ti}) atom. The PW91 functional overestimates the binding energy of an O₂ molecule which results in an overstabilisation of the oxygen vacancy formation. However, given that this error is *ca.* 0.7 eV⁴⁷⁻⁴⁹, we will see below that including this error makes no change to the key features of the oxygen vacancy formation process. The relative energy of the O and N exchanged structures are determined with reference to the ideal interface structure.

The relevant input and output files from our DFT simulations, including the ideal $TiO_2 - TiN$ interface and the energetically favoured non-stoichiometric structures are available via the Nomad repository (DOI to be added at proof stage).

3. RESULTS AND DISCUSSION

3.1 TiO₂ surface and TiN surface

We started the present work with the calculation of the equilibrium lattice for the bulk TiN and rutile TiO₂ as a first step to build the rutile TiO₂ (110) – TiN (100) interface structure. Rutile tetragonal TiO₂ has P4₂/mnm symmetry and presents equilibrium lattice parameters of a = b = 4.64 Å and c = 2.97 Å, close to the experimentally measured lattice parameters of a = 4.593 Å and c = 2.958 Å⁵⁰. TiN crystallizes in the B1 rock-salt (NaCl) structure, with space group number 225 and Fm $\overline{3}$ m symmetry. We found a TiN equilibrium lattice parameter of a = 4.26 Å for the bulk, which is also in good agreement compared with the experimental lattice of a = 4.24 Å⁵¹. The bulk were then used to cleave the surface structures. Rutile (110) TiO₂ and rock-salt TiN (100) are the most stable low index crystal faces for rutile TiO₂⁵² and TiN ^{19, 53} and have been studied in previous theoretical works^{36, 42}. We include these surfaces as a reference for comparison with our interface models, where we will analyse the interaction between these two surfaces.

The Electronic Density of States (EDOS) of rutile TiO₂ (100) and TiN (100) are also shown in Figure 1. The EDOS reflects the semiconductor character of TiO₂, with a computed energy gap between the valence and conduction bands of around 1.80 eV, underestimated compared to the experimental value around 3 eV⁵⁴. Nevertheless errors in the reproduction of the band gap are generally observed in DFT calculations either with local density approximation (LDA) or generalized gradient approximation (GGA)⁵⁵ and do not affect the key findings of this work. While hybrid DFT gives a better description of the band gap, such calculations within a plane wave basis set are too expensive for our interfacial system with 264 atoms⁵⁶. The O 2p states dominate a broad band between -5.4 eV and the Fermi level (E_F) with some Ti 3d contribution. The well-known O 2p peaks are found between -2.7 eV and E_F while Ti



Figure 1. Surface structures and Electronic Density of States (EDOS) of (a) rutile TiO₂ (110) and (b) rock-salt TiN (100) surfaces models. In the structure figure Ti atoms are grey, N atoms are blue and O atoms are red. From top to bottom, the TiO₂ atomic layers are labelled as L4 - L1; the TiN layers are labelled in the reverse order, being L1 the top and L5 the bottom layer. In the EDOS figure the Ti 3d electrons are represented with black lines, the O 2p electrons in red and the N 2p electrons in blue. The EDOS values are normalized per atom. The top and bottom values of the EDOS correspond to -2 states/eV and 2 states/eV respectively while the 0 eV energy stands for the Fermi level.

3d states dominate the states at the bottom of the conduction band. The distribution of the TiN EDOS reflects the metallic character of this solid. The EDOS shows strong Ti – N hybridization for the states located under -2.5 eV relative to E_F while Ti 3d contribution is more important for the states near the Fermi level.

3.2 Structural and electronic properties of the TiO₂ – TiN interface

In building an interface model between TiO₂ and TiN, we selected the rutile TiO₂ (110) surface due to its reasonable lattice match compared to TiN (100). The TiO₂ (110) unit cell was placed on the equilibrium TiN (100) surface and adjusted along the interfacial plane to fit the substrate's lattice parameters. To build our unit cell, a rutile (110) 3x2 supercell expansion (a = 8.91 Å; b = 13.12 Å) was compressed 2.7% along $[1 \overline{1} 0]$ and 4.6% in the [001] direction with respect to the equilibrium lattice, and thereafter placed on a TiN (100) 2x3 supercell (a = 8.51 Å; b = 12.77 Å). This approach was chosen considering that the oxide grows on the alloy surface, thus the rutile TiO₂ must fit the TiN equilibrium lattice. Other rutile and anatase surfaces have significantly larger lattice mismatches, e.g. up to 9 % for rutile (100) or 10% for anatase (001). The small lattice mismatch gives a good stability to the rutile TiO₂ (110) – TiN interface after depositing the compressed oxide slab onto TiN through the formation of Ti – O bonds, as shown in Figure 2 (a).

Unfortunately, DFT simulations of metal oxides often fail to describe localised d and f electrons. Such inaccuracy, common in simulations of strongly correlated materials due to the incomplete cancellation of the exchange term in LDA or GGA exchange-correlation functionals, typically results in an inconsistent delocalisation of electrons over the system and leads to an inaccurate description of the structural and electronic properties of the system. To overcome this drawback, the so-called LDA+U (or DFT+U) method defines a screened on-site Coulomb interaction which affects only the electrons on the same atom helping to localize the d and f-electrons in partially filled states⁵⁷. The Hubbard "+U" parameter gives



Figure 2. Equilibrium structure of rutile TiO_2 (110) - TiN (100) (a) DFT and (b) DFT+U interface models. The perspective, front and side views are shown in the figure. The Ti^{3+} atoms in TiO_2 are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red.

 the strength for the on-site Coulomb repulsion, thus the effective potential will be the difference between U and the on-site exchange terms. In this work, we perform DFT+U calculations to account for the potential reduction of Ti atoms in the interface, where the metal may transfer electrons to the oxide upon interface formation, as occurs in other oxide – metal interfaces such CeO₂–Cu⁵⁸, CeO₂–Pt⁵⁹ or TiO₂–NiTi⁶⁰. Therefore, we use the Hubbard model for the Ti 3d electrons in TiO₂, while the rest of Ti valence electrons, all Ti states in TiN, O and N electrons are defined with standard DFT formulation. The value of U applied on Ti 3d states in the oxide is 4.5 eV, a widely used value in the literature to describe charge localization in defective TiO₂⁴²⁻⁴⁵.

Figure 2 shows the (a) DFT and (b) DFT+U equilibrium structures for the rutile (110) TiO_2 – rock salt TiN (100) interface model. The rutile TiO_2 surface binds to the substrate through the bottom O_{2f} atoms. The bridging O atoms slightly alter their initial position and bind with the topmost Ti_{5f} on TiN. The adhesion between both surfaces is quite strong, with a DFT adhesion energy of -2.69 eV and DFT+U adhesion energy of -5.27 eV for the four Ti – O bonded adsorption sites (-1.32 eV per site).

As mentioned before, the GGA description delocalises electrons over all Ti sites in TiO₂ which may result in an inaccurate description of the structural and electronic properties of the system. The DFT+U corrected structure for the TiO₂ – TiN interface model is shown in Figure 2 (b). We use Bader charge analysis to identify the oxidation states of the different Ti ions in our system. The DFT computed Bader charges are between 1.35 and 1.51 electrons, indicating delocalisation of Ti³⁺ species. Whereas in the +U corrected system, the Ti⁴⁺ atoms (grey spheres) in TiO₂ exhibit Bader charges between 1.24 and 1.32 electrons and the five Ti³⁺ (light green spheres) present Bader charges between 1.65 and 1.73 electrons as well as spin magnetizations which absolute values range between 0.86 and 0.92 μ_B . In analogy with Figure 1, we will refer to the Ti plane in TiO₂ that is closer to the interface as L1 while the

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successive planes towards the surface of the interface will be defined as L2, L3 and L4. Our relaxed structure shows a configuration in which the Ti³⁺ atoms are preferentially located in the rutile layer next to the interface region (denoted as L1), while their large ionic radius compared to Ti⁴⁺ force them to be uniformly distributed around the oxide, avoiding the Ti³⁺ neighbouring sites. In fact, the next Ti³⁺ cations are two layers above L1 (in L3), due to the proximity between L1 and L2 that does not leave enough space for Ti³⁺ to be found on this plane. The exact location of the reduced cations is not expected to affect our results. Even for the case of two electrons produced by formation of one O vacancy in metal oxides such as TiO₂ or CeO₂, a large number of solutions in an energy range of up to 0.3 eV can be found, being such a spread is very small compared to the magnitude of the cost of vacancy formation⁶¹⁻⁶³. The electron localization in the +U approximation, perhaps also influenced by compression of 2.7% imposed along the TiO₂ $[1\overline{1}0]$ axis to compensate the lattice mismatch between TiO₂ and TiN, leads to a rotation of the rutile TiO₂ octahedra, similar to the distortion observed in perovskites⁶⁴. The rotation, that can be easily observed in the front view shown in Figure 2 (b), takes place perpendicular to the [001] axis and involve all the O atoms in the system.

The TiO₂ slabs shown in Figure 2 are strongly affected by the influence of the TiN substrate. We observe an enlargement of the distances in the L2 – L3 inter-layer region, where the absence of Ti – O bonds denotes the larger separation between layers, against the shortened L1 – L2 and L3 – L4 distances. All bonds between the in-layer Ti rows in L3 under Ti_{5f} (L4) and the O beneath those are broken as a result of the L2 – L3 inter-layer enlargement (bonds are set to be plotted for distances lower than 2.25 Å), becoming the O_{3f} bridging atoms in the TiO₂ slab into O_{2f} in the interfaced system.

In the interface region, Ti atoms in the TiN (100) surface migrate from their initial positions to bind with the bottom O_{2f} in TiO₂. The displacement is most pronounced for the

 interfacial Ti that binds to oxygen in TiO₂. The four-fold coordinated Ti, which has two Ti – O and two Ti – N bonds, migrates 0.92 Å (DFT) or 0.89 Å (DFT+U) with respect to its initial position in the TiN surface. The TiN surface Ti_{6f} migrate towards the oxide in a range between 0.42 Å and 0.58 Å (DFT), and between 0.40 Å and 0.56 Å (DFT+U), calculated with reference to a bulk terminated TiN (100) surface. These findings suggest, in line with previous studies $^{26, 35}$, that the progressive oxidation of TiN may facilitate the creation of Ti vacancies on the TiN surface. We do not observe distortion on the atoms under the TiN surface (TiN bulk-like region) either in the DFT or DFT+U relaxed structures.

Figure 3 shows the EDOS projected onto the Ti 3d and N 2p states from TiN as well as the Ti 3d and O 2p states from TiO₂ for the DFT+U relaxed structure. The EDOS from standard DFT calculations is shown in Figure S1. We divide our supercell into three regions to give a more detailed description for the contribution of each species to the EDOS depending on its location in the interface structure. The regions defined in Figure 3 are, from top to bottom: TiO₂ bulk (brown dashed squares), interface region (purple dashed squares) and TiN bulk (light blue dashed squares). The interface region contains the TiO₂ bottom layer (L1) in-plane atoms, the topmost TiN layer and the TiN – TiO₂ interfacial bridging oxygen atoms. The TiO₂ and TiN bulk domains include the atoms above and below the interface region respectively.

Variations in the interface EDOS, in comparison with the surface models in Figure 1, are particularly strong in the metal oxide region. From DFT (Figure S1(a)), previously unoccupied Ti 3d states in TiO₂ cross the Fermi level and become occupied upon relaxation of the interface structure. The inaccurate description of d-electrons in standard DFT-GGA calculations leads to the delocalization of Ti 3d states that occupy the bottom of the conduction band giving metallic features to the TiO₂ EDOS in our system.



Figure 3. Graphical representation of TiO_2 bulk, $TiO_2 - TiN$ interface and bulk TiN regions along with the EDOS of DFT+U relaxed rutile TiO_2 (110) - TiN (100) interface. The colour code is used to identify the different regions, where the figures within the brown dashed squares represent the TiO_2 bulk region, the purple dashed squares stand for the interface region and the light blue dashed squares stand for the TiN bulk region. In the interface structure the Ti^{3+} atoms in TiO_2 are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red. In the EDOS figure the Ti 3d electrons are represented with black lines, the O 2p electrons in red and the N 2p electrons in blue. The EDOS values are normalized per atom. The top and bottom values of the EDOS correspond to -2 states/eV and 2 states/eV respectively while the 0 eV energy stands for the Fermi level.

The inconsistent electron delocalization is corrected by the DFT+U method. The resulting Ti^{3+} defect states are separated from the conduction band states and lie in the mid-gap

between the valence and the conduction bands when the +U correction is applied. The Ti^{3+} defect states in bulk TiO_2 are centered at -0.90 eV with respect to E_F and start 0.80 eV above the valence band edge; while the Ti^{3+} peak in the interface region, located at around -1.25 eV from E_F , starts at -0.50 eV and is centered at -0.90 eV, both relative to the top edge of valence band. We should note that since the states between the valence and conduction bands have their origin in the presence of Ti^{3+} electrons; these are more visible in the interface region, where the Ti^{3+} contribution has a more weight in the average DOS (3 out of a total of 12 Ti atoms) compared to the bulk region.

In the TiN EDOS, Ti 3d and N 2p occupy the states under -2 eV relative to E_F while the Ti 3d contribution is more important around the Fermi level. The p-d hybridizations introduce a strong peak at around -5eV in the bulk and at -4 eV in the interface region. The small interface Ti EDOS at E_F indicates the stability of the TiN distorted rock-salt structure within this region⁶⁵. The metallic character of TiN is still present in the interface structure model due to the contribution of the Ti 3d electrons to the total EDOS.

3.3 Vacancies and defects in the TiO₂ – TiN interface

Whereas the previous section considers the ideal $TiO_2 - TiN$ interfaces, in this section we increase the complexity in our models with the aim to simulate more realistic structures by the introduction of non-stoichiometry. Defects can arise during growth and processing of TiN and may have a critical impact on interface properties. We probe the possible presence of point defects that can be expected starting from a perfect rutile TiO_2 (110) – TiN (100) interface. These defects are (I) O vacancies in the TiO_2 interface region, (II) Ti vacancies in the TiN surface and (III) the exchange of N and O in the interface region. We chose these defects based on recent studies that suggested the presence of vacancies and formation of oxynitrides in metal – oxide interfaces, for example Ti vacancies could form due to surface Ti

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migration on the TiN surface when this is in contact with atmospheric O_2^{17} . The formation of O vacancies is a common defect in TiO₂ and can take place under thermal annealing⁴¹. In addition, experimental studies have suggested that the TiO₂ growth on TiN is preceded by the formation of an TiO_xN_y intermediate structure¹⁸. Therefore, we perform relaxations on different model structures to find the energetically favoured defects among a number of possible atomic conformations, with the atoms involved indicated in Figure 4. Table 1 shows the energy cost for the formation of the most stable Ti and O vacancies and the relative energy of the O/N exchanged composition. As explained in the methodology, the formation vacancy energy (E_{vac}) is given by the difference between the energy of a single O or Ti atom. The relative energy of the O/N exchanged structures were calculated with respect to the ideal interface structure. The Hubbard-corrected DFT+U equilibrium structure and the energy costs were calculated for the most favourable cases.



Figure 4. Different point defects evaluated in the TiO_2 (110) - TiN (100) interface region. The 1-3 labels stand for Ti vacancies in TiN while the 1'-5' stand for the O vacancies in TiO_2 . The N atoms labelled as N4 and N5 are exchanged with O2' and O3' respectively to form of exchanged O/N structures within the interface.

Ti vacancy		O vacancy		Exchanged O/N formation	
Site	E (eV)	Site	E (eV)	Site	E (eV)
1	3.84	1'	3.89	2' - 4	0.72
1 (4x4x1)	3.41	1' (4x4x1)	3.83	2' - 4 (4x4x1)	0.58
1 (+U)	4.03	1' (+U)	3.40	2' - 4 (+U)	0.82
2	4.11	2'	3.94	3' - 5	0.92
3	4.63	3'	4.36		
		4'	4.46		
		5'	5.47		

Table 1. Formation energy for different non-stoichiometric structures evaluated on the rutile TiO_2 (110) - TiN (100) interface region. The energy values for standard DFT calculations on Γ -point, 4x4x1 k-points sampling grid (for the most stable configuration) and DFT+U (with 4x4x1 k-points sampling grid) are given. The atom sites within the interface structure are shown in Figure 4.

3.3.1 Ti vacancy formation in the TiO₂ – TiN interface

The most favourable Ti vacancy in TiN, which corresponds to Ti1 in Figure 4, exhibits very high vacancy formation energy of 3.84 eV (DFT, Γ -point), 3.41 eV (DFT, 4x4x1 k-points sampling grid) or 4.03 eV (DFT+U). The Ti1 vacancy is more stable by 0.27 eV compared to Ti2 and by 0.79 eV compared to Ti3 vacancy. Ti1 is a surface five-fold under-coordinated atom that is not bound to oxygen in TiO₂; Ti2 is a six-fold coordinated (Ti_{6f}) due to the Ti – O bonds that forms with O1' and O2' in the interface plus the four bonds formed with its first-order nearest-neighbours on the TiN surface; and Ti3 binds to a bridging O_{2f} in TiO₂ so that these are Ti_{6f} and O_{3f} respectively. Although the tested Ti_{6f} atoms migrated by 0.90 Å towards TiO₂ for Ti2 and 0.44 Å Ti3 (DFT+U) with respect to their initial position in the free-standing TiN surface, the under-coordinated Ti1 is the most energetically favourable Ti vacancy.



Figure 5. Equilibrium structure for the most stable Ti-vacancy rutile TiO₂ (110) - TiN (100) DFT+U interface model. The yellow sphere represents the vacancy site, Ti^{3+} atoms in TiO₂ are green, Ti^{4+} atoms in TiO₂ and all Ti in TiN are grey, N atoms are blue and O atoms are red.

Figure 5 (DFT+U) and Figure S2 (DFT) illustrate the interface structure for the Til vacancy system. The site from which the Ti was atom was removed to form the vacancy is represented by a yellow sphere. The Ti vacancy on the TiN surface does not produce significant changes in the symmetry of the structure. Figure 5 shows a distribution of Ti^{3+} modified from the ideal case, with one reduced oxide's Ti located on the rutile (110) surface. In the modified structure, 3 out of the 5 Ti^{3+} are contained in L1, with each atom located in a different Ti row along the [001] direction. The charges on the N near the vacancy site are lower in comparison with the N in the bulk, with computed Bader charges of 6.81 – 6.89 electrons (compared to 7 electrons in the TiN surface, which indicates hole formation on neighbouring N sites as a result of removing a neutral Ti atom.

3.3.2.a O vacancy formation in the $TiO_2 - TiN$ interface

The interfacial three-fold coordinated O1' vacancy site (denoted in Figure 4) is the most stable O vacancy with $E_{vac} = 3.89 \text{ eV}$ (DFT, Γ -point), 3.83 eV (DFT, 4x4x1 k-points sampling grid) or 3.40 eV (DFT+U). The magnitude of these formation energies is significantly larger than the error in the O₂ binding energy. We can consider O1' and O2' (Figure 4) as equally stable, since the DFT vacancy energy of O2' is only 0.05 eV higher than O1'. The O1' and O2' atoms in TiO₂ bridge the oxide to TiN through a surface Ti atom. The two Ti – O bonds combined with two Ti – N bonds leads Ti2 to a four-fold coordination (Ti_{4t}) in the DFT+U ideal interface. When O2' is absent (Figure 6 (a)), Ti2 migrates 0.32 Å towards the TiN surface, with respect to its position in the ideal interface structure (Figure 2 (b)). After the migration, Ti2 changes from four-fold coordinated in the ideal system (with two Ti – O and two Ti – N bonds) into five-fold coordinated (with one Ti – O and five Ti – N bonds) when the O1' vacancy is introduced, leading the system to the most stable O vacancy configuration in our work.

Our calculated O minimum vacancy energy is slightly higher than the vacancy energy of rutile (110) surface $(E_{vac} = 3.66 \text{ eV})^{42}$ but smaller than the O vacancy formation in the bulk rutile TiO₂ structure $(E_{vac} = 4.4 \text{ eV})^{66}$. The O vacancy introduces 2 extra electrons that result in the presence of 7 Ti³⁺ atoms within the oxide (Figure 6 (a)). The distribution of Ti³⁺ shows that 5 out of the 7 Ti³⁺ in the oxide region are located in L1, near to the interface region.

The O1' vacancy site is 0.47 eV more stable than O3', 0.57 eV more stable than O4' and 1.58 eV more stable than O5'. The interfacial three-fold coordinated O5' is the most strongly attached oxygen ($E_{vac} = 5.47 \text{ eV}$) due to its three-fold coordination in the rutile TiO₂ structure. The short distance that separates O4' (O_{2f}) from the closest Ti on TiN (2.65 Å) makes this oxygen more prone to bind with the surface Ti and become three-fold coordinated,

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leading this system to a higher stability. In fact, the O4' vacancy formation energy is only 0.10 eV higher compared to O3' (O_{3f}). We should note that despite of the high cost for the vacancies formation (E_{vac} (Ti) \geq 4.03 eV; E_{vac} (O) \geq 3.40 eV) relative to a perfect interface, such vacancies could arise during the oxide growth and can therefore be present after TiO₂ formation. For O vacancy, adding electrons to an already reduced system can also increase the energy cost to form vacancy.

3.3.2.b Highly non-stoichiometric O vacancy formation in the TiO₂ – TiN interface

In the previous section, we analyzed the formation of one O vacancy starting from a perfect $TiO_2 - TiN$ interface. Nevertheless, a significantly greater number of Ti-anion bonds could be formed within the interface if multiple oxygen were removed from the (110) TiO₂. Thus, in addition the one O vacancy system, we also consider the formation of highly non-stoichiometric interfaces, in which one half and all of the bridging O are removed from the interface region.

Figure 6 (b) shows a TiN – TiO₂ interface structure in which one half (O1', O3' and O4' in Figure 3) of the bridging oxygen atoms are removed. The total formation energy for the introduction of three O vacancies in the ideal interface, relative to $\frac{3}{2}O_2$ molecules, is 5.36 eV (1.79 eV/atom). The O vacancy formation energy normalized per atom is 67% smaller than the formation of one single O vacancy in the ideal interface (E_{Ovac} = 3.40 eV). The binding energy between the non-stoichiometric oxide slab and the TiN surface is -4.77 eV, which leads to a quite strong adsorption of -1.59 eV/site for the three Ti-O bonds created in this system. The total binding energy is 0.50 eV higher than the formation of the stoichiometric rutile (110) – TiN interface, while the adsorption per site is 0.27 eV stronger. Upon interface formation, Ti atoms in the TiN (100) surface migrate between 0.28 Å and 0.36 Å from their initial position on the TiN surface. The Ti³⁺ formed exhibit Bader charges between 1.66 and

1.80 electrons, compared to charges around 1.3 electrons for the Ti^{4+} . Six out of the nine reduced Ti are located in the bottom TiO_2 layer, perhaps originated by the three O vacancies introduced in the system. Their larger size compared with Ti^{4+} introduces a distortion in the rutile structure.

TiN – TiO₂ interface structure in which all the O bridging atoms were removed. Created from the ideal interface, this structure presents a formation energy of 7.80 eV referred to $3O_2$ molecules, that corresponds to 1.30 eV/atom. The O vacancy formation energy per atom is 62% smaller than the formation of one single O vacancy in the ideal interface ($E_{Ovac} = 3.40$ eV) and 27% smaller than the formation energy normalized per O vacancy in the 3xO vacancies system ($E_{Ovac} = 1.79 \text{ eV}$). These values suggest that despite the high energy needed for the formation of the first O vacancy in the perfect interface system, the introduction of O vacancies in a non-stoichiometric system progressively becomes more favourable. In the interface, the surface Ti on TiN bind with the oxide's three-fold coordinated oxygen. We do not observe significant migration in the surface Ti that bind with the O, while the slight distortion on the TiN interface region could be attributed to the typical surface rumpling. The calculated binding energy between the non-stoichiometric oxide slab and the TiN surface is -4.39 eV, which result in an adsorption of -0.88 eV per adsorption site for the five Ti-O bonds created within the interface. The total formation energy is 0.88 eV higher compared to the formation of the stoichiometric interface and 0.33 eV higher than the formation to the 3xO vacancy interface, whereas the Ti - O bonds formed in the interface are 0.44 eV weaker than in the perfect interface. We observe 12 reduced Ti cations, originated by the extra electrons introduced in the system after the creation of O vacancies. The high concentration of Ti³⁺, with larger atomic radii compared to Ti⁴⁺, distorts the TiO₂ rutile structure leading to amorphous-like domains within the interface region.



Figure 6. Equilibrium structure of DFT+U relaxed rutile TiO_2 (110) - TiN (100) interface models with (a) one bridging O vacancies, (b) three bridging O vacancies and (c) six bridging O vacancies in the interface. The yellow sphere represents the vacancy sites in (a) and (b), Ti^{3+} atoms in TiO_2 are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red.

The EDOS of the interfaces with 3 and 6 O vacancies (Figure S4 and Figure S5 respectively) show similar features compared to the one O vacancy (Figure 3), where the Ti^{3+} states are localized in the mid-gap between the valence and the conduction bands while TiN conserves its metallic character.

3.3.3 Exchange of O and N in the TiO₂ – TiN interface

We have considered two different cases for the stability of interface models in which one N atom from the substrate and an O from the oxide exchange their positions in an otherwise perfect structure. To explore the differences between vacancy sites we analyse two atomic conformations, denoted as O2' \leftrightarrow N4 and O3' \leftrightarrow N5 (Figure 4). In both cases, we chose to substitute a two-fold under-coordinated bridging oxygen in the TiO₂ – TiN interface region

 $(O_{2f} under L1 in the TiO_2 free-standing model)$, which correspond to the energetically most stable O vacancy site defect in TiO₂.

 In the O2' \leftrightarrow N4 configuration, we exchange the positions between N4 and its neighbour O, which exhibit the lowest vacancy formation energy. N4 is located beneath an O_{2f} row along [001] and between two Ti atoms that bridge the interface system through the Ti – O bonds formation. In the O3' \leftrightarrow N5 configuration, we chose one N placed between the two O_{2f} rows along [001] in our supercell which has only one bridging Ti as first neighbour. The exchanged O/N structure in which we substituted O2' \leftrightarrow N4 is only 0.72 eV higher in energy (0.58 eV for the DFT and 0.82 eV for the DFT+U, both using a 4x4x1 k-points sampling grid) than the perfect system (Figure 2) while the corresponding O3' \leftrightarrow N5 exchange is 0.92 eV higher.

Although our DFT results do not show a spontaneous formation of an exchanged O/N structure in the interface region, the low energy values suggest the stability of structures with interdiffused O and N at ambient conditions, as proposed in previous experimental works ^{21, 26}. Figure 7 shows the DFT+U interface structure along with the EDOS for the most favoured O/N exchanged atomic conformation O2' \leftrightarrow N4. We observe that the bridging Ti2 migrates 0.94 Å along the vertical axis with reference to a bulk terminated (100) to produce N – Ti – O features in the O/N exchanged structure, 0.14 Å larger than the migration of the same Ti atom in the ideal interface. The Ti2 binds then to three atoms: a surface N, with Ti – N distance equal to 2.11 Å, the exchanged N4 at 1.94 Å and the bridging O2' at 2.01 Å. The O introduces an extra electron in the TiN, and the N introduces a hole in the TiO₂ region so that balance between these two effects results in the same number of Ti³⁺ in our O/N exchanged structure (Figure 7) compared to the perfect interface (Figure 2 (b)). The Ti³⁺ exhibit a similar distribution compared with the ideal and Ti-vacancy structures; nonetheless we do not observe any Ti³⁺ near the region where the O and N are exchanged.

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The EDOS in the TiN and TiO₂ bulk regions are close to the EDOS of the ideal interface model shown in Figure 3. However, the N contribution in the TiO₂ region and the O contribution to TiN introduce interesting features within the interface region EDOS. In particular, the presence of N in the TiO₂ interface region introduce N 2p states between the top edge of the O 2p valence states and the 3d Ti³⁺ peak. The N 2p states exhibit a high peak centred at around -2 eV under E_F , with N 2p states present in the gap between the valence band top edge and the Ti³⁺ states. Thus, the presence of N 2p electrons reduce the band gap in the TiO₂ region by introducing localized states between the top of the valence band and the mid-gap Ti³⁺ peak, as happens in N-doped TiO₂⁶⁷. Whereas the presence of O in TiN introduces O 2p states that make their main contribution between -5 eV and -7 eV with respect to the Fermi level. The O 2p may lead to a more stable structure within this region by the introduction of low energy states in the EDOS.

Summarizing, the energy costs for the formation of defects like Ti vacancies in the substrate $(E_{vac} (Ti1) = 4.03 \text{ eV})$ or O vacancies in the oxide $(E_{vac} (O1') = 3.40 \text{ eV})$ are quite high relative to perfect $TiO_2 - TiN$, even in the interface region, suggesting a defect free interface and an abrupt transition from the TiN crystalline rock-salt structure to the rutile TiO_2 . Nevertheless, it is important to note than the presence of defects will depend on the kinetics of the growth and such defects can form during the processing of TiN, and therefore influence the structural and electronic properties of the system. The exchange of O and N in the interface region is more favourable, lying 0.82 eV higher relative to the perfect interface. This results suggest the stability of an TiO_xN_y transition layer in the region between the TiN and TiO_2 bulk-like domains, in line with previous experimental results^{21, 26}.



Figure 7. DFT+U relaxed structure for the most stable rutile TiO_2 (110) - TiN (100) interface model with exchanged O and N. The colour code is used to identify the different regions, where the figures within the brown dashed squares represent the TiO_2 bulk region, the purple dashed squares stand for the interface region and the light blue dashed squares stand for the TiN bulk region. In the interface structure figure the Ti^{3+} atoms in TiO_2 are green, Ti^{4+} atoms in TiO_2 and all Ti in TiN are grey, N atoms are blue and O atoms are red. In the EDOS figure the Ti 3d electrons are represented with black lines, the O 2p electrons in red and the N 2p electrons in blue. The EDOS values are normalized per atom. The top and bottom values of the EDOS correspond to -2 states/eV and 2 states/eV respectively while the 0 eV energy stands for the Fermi level.

4. CONCLUSIONS

 We carried out a comprehensive Density Functional Theory (DFT) study aiming to describe the structural and electronic properties of the $TiO_2 - TiN$ interface. The small lattice

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mismatch between the rutile TiO_2 (110) and the TiN (100) supercells together with the formation of Ti - O bonds give a good stability to our interface model. Upon formation of the interface, the TiO_2 inter-layer distances are distorted while surface Ti atoms in the outermost TiN surface layer migrate from their initial positions to bind with two-fold coordinated O atoms in TiO₂.

DFT+U calculations, to account for the potential reduction of Ti atoms in the oxide, show that there is charge transfer to rutile (110) to form reduced Ti^{3+} cations and the localisation of the excess charge leads to a rotation of the TiO_2 octahedra perpendicular to the [001] axis. The TiO_2 electronic density of states show the formation of occupied Ti 3d states in the band gap upon relaxation of the interface structure.

We have also evaluated the stability of different non-stoichiometric, defective structures, starting from a perfect rutile TiO₂ (110) – TiN (100) interface. The calculated vacancy formation energies for Ti vacancy in TiN (E_{vac} (Ti) ≥ 4.03 eV) or O vacancies in the oxide (E_{vac} (O) ≥ 3.40 eV) relative to perfect TiO₂ – TiN are quite high. Nevertheless, despite the high vacancy formation energies, such defects usually arise during oxide growth and can be present after TiO₂ formation, and can subsequently influence the properties of the system²⁸⁻³⁰. The most stable Ti vacancy configuration shows a distribution of Ti³⁺ uniformly distributed around the oxide, with hole formation on the neighbouring N sites. We observe that each O vacancy introduces two extra electrons within the oxide, thus creating two extra Ti³⁺ atoms in TiO₂ with respect to the stoichiometric system. The Ti³⁺ cations, formed upon interface formation or originated in the non-stoichiometric systems from the creation of O vacancies, are preferentially localized near the interface region.

The formation of an exchanged O/N structure in the interface region is only 0.82 eV higher in energy than the perfect system, suggesting the likely stability of this structure at room conditions ^{21, 26}. In the exchanged O/N structure, the extra electron introduced by O in the

TiN compensates the hole created by the exchanged N in TiO_2 , leading to the same number of Ti^{3+} in the non-stoichiometric system compared to the ideal interface. The substitution of N on an oxygen site introduces N 2p states localized between the top edge of the O 2p valence states and the mid-gap Ti^{3+} 3d peak, thus reducing the bandgap in the interface region of the TiO_2 EDOS.

These DFT+U simulations of the rutile TiO_2 (110) – TiN (100) interface give the most comprehensive insight to date on the properties of oxidised TiN and provide a basis upon which to study further the properties of this materials system in different applications such as anti-biofouling⁹⁻¹¹.

SUPPORTING INFORMATION

Bonds and inter-layer distances in the $TiO_2 - TiN$ interface structure; $TiO_2 - TiN$ interface DFT EDOS; structure of Ti-vacancy, O-vacancy and O/N exchanged TiO_2 - TiN interface models relaxed with standard DFT; EDOS of DFT+U relaxed TiO_2 - TiN interface models with 3xO and 6xO vacancies in the interface.

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