Interaction of oxygen with $\mathrm{TiN}(001) : \mathrm{N} \leftrightarrow \mathrm{O}$ exchange and oxidation process

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Interaction of oxygen with TiN(001):N↔O exchange and oxidation process

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This work presents a detailed experimental and theoretical study of the oxidation of TiN(001) using a combination of synchrotron-based photoemission and density functional theory (DFT). Experimentally, the adsorption of O_2 on TiN(001) was investigated at temperatures between 250 and 450 K. At the lowest temperature, there was chemisorption of oxygen ($O_{2,gas} \rightarrow 2O_{ads}$) without significant surface oxidation. In contrast, at 450 K the amount of O_2 adsorbed increased continuously, there was no evidence for an oxygen saturation coverage, a clear signal in the Ti $2p$ core level spectra denoted the presence of TiO_x species, and desorption of both N_2 and NO was detected. The DFT calculations show that the adsorption/dissociation of O_2 is highly exothermic on a TiN(001) substrate and is carried out mainly by the Ti centers. A high oxygen coverage (larger than 0.5 ML) may induce some structural reconstructions of the surface. The exchange of a surface N atom by an O adatom is a highly endothermic process ($\Delta E = 2.84$ eV). However, the overall oxidation of the surface layer is thermodynamically favored due to the energy released by the dissociative adsorption of O_2 and the formation of N_2 or NO. Both experimental and theoretical results lead to conclude that a $TiN + mO_2 \rightarrow TiO_x + NO$ reaction is an important exit channel for nitrogen in the oxidation process. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2743418]

I. INTRODUCTION

Early transition metal nitrides are commonly referred to as refractory hard metals because they exhibit an unusual combination of properties.[1,2] They have brittleness and high electrical and thermal conductivities like metals, ultrahardness and high melting point like covalent compounds, and a rocksalt structure like ionic solids. Such an unusual combination of properties makes these materials good candidates for technological applications in many areas. For example, TiN is used in silicon microelectronic circuits because of its excellent properties as a Cu diffusion barrier, as well as its thermal, mechanical, and a very effective adhesion/glue layer performance.[3,4] Because of their hardness, metal nitrides are used as hard wear resistant coatings on cutting tools,[5,6] and to enhance the surface resistance of surgery tools and implants, especially in the field of dental surgery.[7] Finally, they have also attracted considerable interest as potential sensors and catalysts.[8,9]

Many theoretical[10–21] and experimental studies[22–30] have been published on the relationship between the electronic structure and the bulk and surface properties of metal nitrides. In general, these materials have a valence band with a strong mixed *p-d* character—as expected for a covalent compound—and a conduction band with mainly *d* character—as expected for a metallic compound.[28–30] Oxidation of the metal nitrides may dramatically change their properties and therefore a number of papers have addressed this process mainly from an experimental point of view and using films as working samples.[31–35] From a theoretical point of view only one work has been devoted to the oxidation of TiN, using Car-Parrinello *first principles* molecular dynamics simulations.[7] However, the microscopic and atomic details of the oxidation process are not fully understood and the initial steps of the oxidation process are unclear. What is the role of the metal and N in the dissociation of O_2? Are the N atoms simple spectators? How difficult is the N↔O exchange process in the surface? How viable are NO and N_2 as reaction products? Are metal oxynitride (MeO_xN_y) phases stable intermediates? Two recent works examining the interaction of oxygen with the (001) surface of a closely related family of compounds, early transition monocarbides, have shown complex trends in the reactivity of the metal and carbon sites depending on the electronic properties of the carbide and the filling of its valence band.[36,37]

In this work, we present a detailed experimental and theoretical study of the oxidation of TiN(001) using a combination of synchrotron-based photoemission and density functional theory (DFT). To the best of our knowledge, this is the first experimental work examining the adsorption of O_2 on a well-defined metal nitride surface. On the basis of DFT static calculations, we investigate in detail the adsorption and dissociation of molecular oxygen on the TiN(001) surface as well as the energetics of the N↔O exchange. The paper is arranged as follows. In Sec. II the experimental procedures and theoretical models are described. Section III starts de-

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scribing the experimental results moving next to the theoretical analysis. Finally, the conclusions are reported in Sec. IV.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Photoemission and XPS experiments

The adsorption and dissociation of O_2 on TiN(001) were investigated using photoemission and x-ray photoelectron spectroscopy (XPS). The photoemission data were collected at the U7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). This beamline is equipped with an ultrahigh-vacuum chamber (UHV, base pressure of 3×10^{-10} Torr) that contains a hemispherical electron energy analyzer with multichannel detection, instrumentation for low-energy electron diffraction (LEED), and a quadrupole mass spectrometer.[36,37] The photoemission spectra were recorded using a photon energy of 625 eV for the O(1s), Ti(2p) and N(1s) core levels. At this photon energy the excited electrons had kinetic energies in the range of 85–230 eV and, therefore, photoemission probed only the first two to three layers of the sample. The overall instrumental resolution in the photoemission experiments was ~0.3 eV. The binding energy scale in the photoemission spectra was calibrated by the position of the Fermi edge in the valence region.

Additional experiments of XPS and thermal-desorption mass spectroscopy were carried out at the Tokyo Institute of Technology (TIT) using an UHV chamber (base pressure ~2×10^{-10} Torr) that has capabilities for these techniques (Al $K\alpha$ x-ray source, hemispherical electron energy analyzer, quadrupole mass spectrometer) plus LEED and Auger electron spectroscopy.[36,37]

The TiN(001) surface was prepared at the TIT starting with procedures described in the literature.[36,37] These led to a N/Ti ratio of 0.83–0.86, according to quantitative XPS, and a (1×1) LEED pattern.[38,39] Subsequent exposure to hydrazine (N_2H_4) or ammonia (NH_3) at 600–750 K, 5×10^{-8} Torr for 5 min,[40,41] increased the N/Ti ratio to 0.94–0.97. On this type of system, we performed the experiments for the adsorption of molecular oxygen. The sample was mounted on manipulators capable of resistive heating to 1500 K and e-beam heating to 2200 K. Surface impurities were removed by ion sputtering and the nitrogen/titanium ratio was kept close to 1 by exposing the sputtered surface to N_2H_4 or NH_3 at 600–750 K. At these high temperatures, the nitrogen from the NH_x groups is incorporated into the lattice of the metal nitride and the hydrogen evolves into gas phase.[40,41] The cleaning procedure led to a clear 1×1 pattern in LEED and no surface impurities in photoemission or XPS. Molecular oxygen (99.995% purity) was dosed to the TiN(001) surface at 250–450 K using dosing tubes with apertures located ~5 mm away from the sample.[36,37] These dosing systems provided a large enhancement factor (>10 times) in the mass adsorbed with respect to dosing by backfilling the UHV chambers with O_2. The reported exposures of O_2 are based on the direct ion gauge readings (i.e., no correction for the enhancement factors of the dosers).
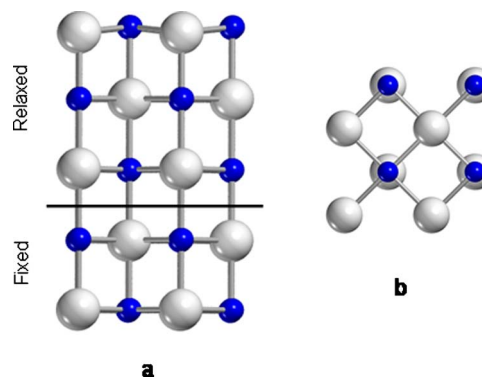

FIG. 1. (Color online) Schematic side (a) and top (b) views of the surface slab model. Atom colors: blue N and gray Ti.

B. Models and computational details

In order to model the extended nature of these surfaces, periodic three-dimensional DFT calculations were carried out using the VASP 4.6 code[42,43] with the projector augmented wave method.[44] In these calculations, the energy was obtained using the generalized gradient approximation implementation of DFT proposed by Perdew *et al.*[45] and the electronic states were expanded using plane waves as a basis set with a cutoff of 400 eV. In the case of Ti atoms, the semicore $3s3p$ states were also included. Thermal smearing of one-electron states ($k_B T = 0.05$ eV) was used together with the Methfessel-Paxton scheme of order one. The energy was sampled on a $4 \times 4 \times 1$ grid generated using the Monkhorst-Pack method. The number of k points was selected in order to get TS corrections to the energy lesser than 0.001 eV/atom together with negligible changes in the optimized cell parameters (<0.01 Å).

Forces on the ions were calculated through the Hellmann-Feyman theorem as the partial derivatives of free energy with respect to the atomic position, including the Harris-Foulkes[46] correction to forces. This calculation of the forces allows a geometry optimization using the conjugate-gradient scheme. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 0.001 eV. With this criterion, forces on the atoms generally were less than 0.1 eV/Å.

The surfaces were modeled by means of a slab of TiN five layer thick, three of which were allowed to relax while the other two layers were fixed. This supercell with 40 atoms included a vacuum space that kept a separation of 20 Å between slabs (see Fig. 1). The relaxation of the TiN (001) surface was exhaustively studied in a previous work[47] and it was shown that the {2 fixed/3 free}-layer slab was enough to properly describe the properties of this surface. Nevertheless, preliminary test calculations were carried out in the present work, and we found out that the error in the adsorption energies of molecular oxygen using this {2 fixed/3 free}-layer slab was smaller than 0.01 eV in comparison with a fully relaxed nine layer slab. Moreover, as we previously showed, an equivalent setup used for bulk calculations led to a cell parameter of 4.245 Å,[47] in very good agreement with the experimental value (4.238 Å).[48]
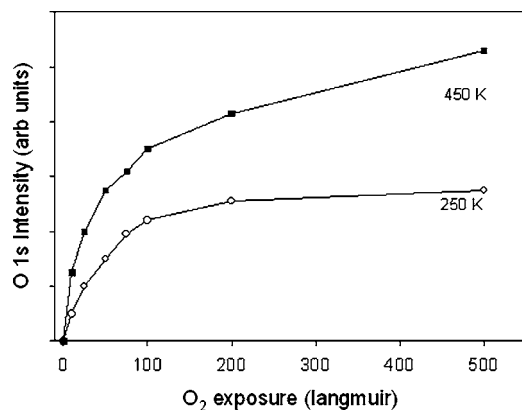
FIG. 2. Uptake of oxygen for the adsorption of O_2 on TiN(001) at 250 and 450 K. The coverage of oxygen was monitored using the intensity of the O 1s peak in XPS.

III. RESULTS AND DISCUSSION

A. Photoemission and XPS studies

The adsorption of O_2 on TiN(001) was investigated at temperatures between 250 and 450 K. In our studies, the O 1s spectra showed a broad single peak with the maximum at binding energies of 530.4–531.2 eV, typical for chemisorbed oxygen atoms ($O_{2,gas} \rightarrow 2O_{ads}$) on metals[49] or TiO_x species.[50] Figure 2 shows the uptake of oxygen for TiN(001) at 250 and 450 K. At the lower temperature, there is a saturation in the amount of oxygen adsorbed. Under these conditions the system does not have enough energy to overcome the kinetic barriers associated with an oxidation process (see below). At 450 K the amount of O_2 adsorbed is always larger than at 250 K, and we did not see evidence for an oxygen saturation coverage. The titanium nitride was being oxidized into TiO_x.

Ti 2p core level spectra ($h\nu$=625 eV) acquired before and after dosing O_2 to TiN(001) at 450 K are displayed in Fig. 3. The spectrum for clean TiN is complex.[33,51] In addition to the main $2p_{3/2}$ peak at 455.1 eV, there is a shake-up satellite at 457.7 eV (labeled S in the figure). Exposure of the sample to 10 L of oxygen leads to significant changes in the line shape of the Ti 2p features (spectrum "b"). After subtraction of the spectrum for clean TiN, a clear signal is seen around 456 eV that denotes the presence of TiO_x in the sample.[52,53] This signal grows upon an additional dose of 50 L of O_2 (spectrum "c"). After a large dose of 500 L of O_2 at 450 K (spectrum not shown), TiO_x was the dominant species seen in the sample region (first two to three layers) probed by photoemission. No evidence was found for the formation of TiO_2. In another set of experiments, the adsorption of O_2 was performed at 250 K and no significant features for any titanium oxide appeared in the Ti 2p region indicating a lack of a TiN$\rightarrow$TiO$_x$ transformation.

Figure 4 displays N 1s core level spectra ($h\nu$=625 eV) collected after dosing 50 L of O_2 to TiN(001) at 250, 350, and 450 K. At 250 K, two peaks are observed that match well the positions expected for TiN (Ref. 33) and NO or a NO-like species.[54] The small peak at ~400.5 eV could be due to O atoms bonded to N sites or a consequence of the formation of some NO on the surface (see DFT calculations
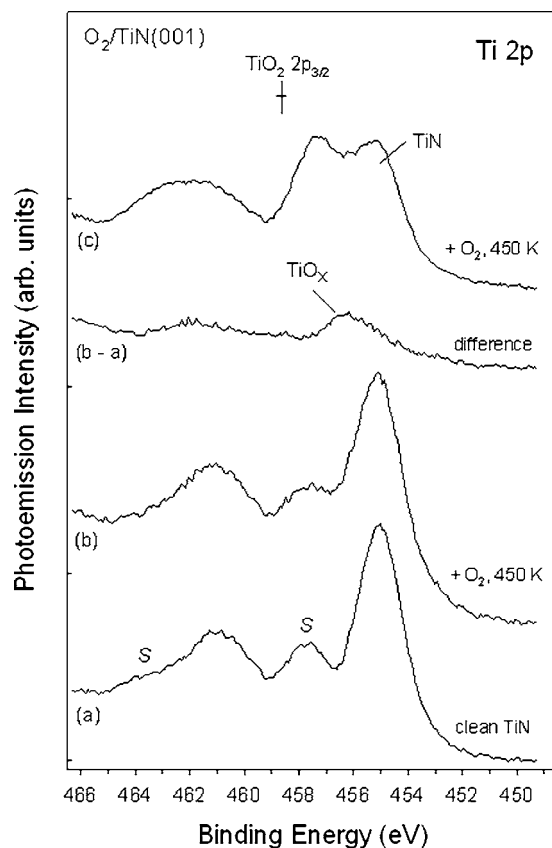

FIG. 3. Ti 2p core level spectra for the adsorption of O_2 on TiN(001) at 450 K. The surface was exposed to 10 and 50 L of O_2. For comparison we are including at the top of the figure the Ti $2p_{3/2}$ binding energy of TiO_2. A photon energy of 625 eV was used to acquire the spectra.

below). The intensity of the peak indicates a coverage of 0.1–0.2 ML for the adsorbed species. This peak disappeared when the sample was heated to 300 K and there was a minor evolution of NO into gas phase. The N 1s spectra acquired after dosing O_2 to TiN(001) at 350 and 450 K show only the peak for TiN with a reduction in its intensity. No features are seen at the binding energies expected for species such as NO, NO_2, or NO_3.[51]

The photoemission data in Figs. 3 and 4 point to a TiN+$O_2$$\rightarrow$TiO$_x$/TiN transformation. However, it is not clear how the N is being removed from the surface. Possible products such as NO_x or N_2 may have a low adsorption energy and not being detected in O 1s and N 1s spectra. Experiments were carried out in which the sample was set in front of a mass spectrometer and exposed to an incident beam of O_2 molecules at 250, 350, or 450 K. Figure 5 shows the corresponding results for a temperature of 450 K. At t=30 s, the dosing of O_2 (5×10^{-7} Torr pressure) started and it was stopped at t=120 s. During the dosing of O_2 only signals for N_2 (m/e=28) and NO (m/e=30) were detected. No signal for NO_2 (m/e=46) or N_2O (m/e=44) was seen. In Fig. 5, the signal for N_2 starts strong and decays with time. It can be attributed to a TiN+$nO_2$$\rightarrow$TiO$_x$+$N_2$ reaction whose rate decreases as the concentration of N in the surface decreases. The signal for NO in Fig. 5 does not decay with time as much as the signal for N_2, and it appears that the main channel for the removal of nitrogen at 450 K is TiN+mO_2
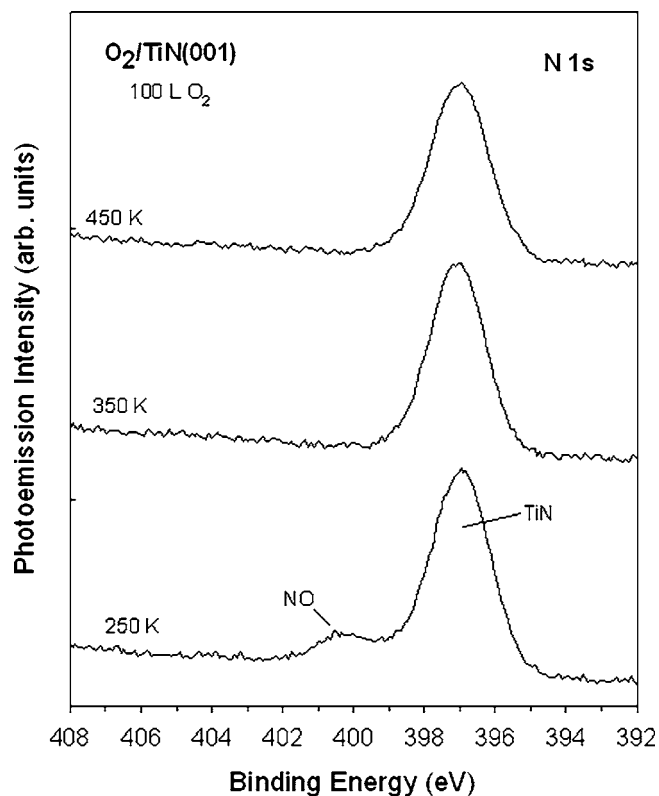
FIG. 4. N 1*s* core level spectra recorded after dosing 50 L of O_2 to TiN(001) at 250, 350, and 450 K. A photon energy of 625 eV was used to collect the spectra.

$\rightarrow TiO_x + NO$. Similar experiments done at a temperature of 250 K showed no desorption of N_2 or NO_x species, consistent with the idea that there is no significant oxidation of the surface at this low temperature.
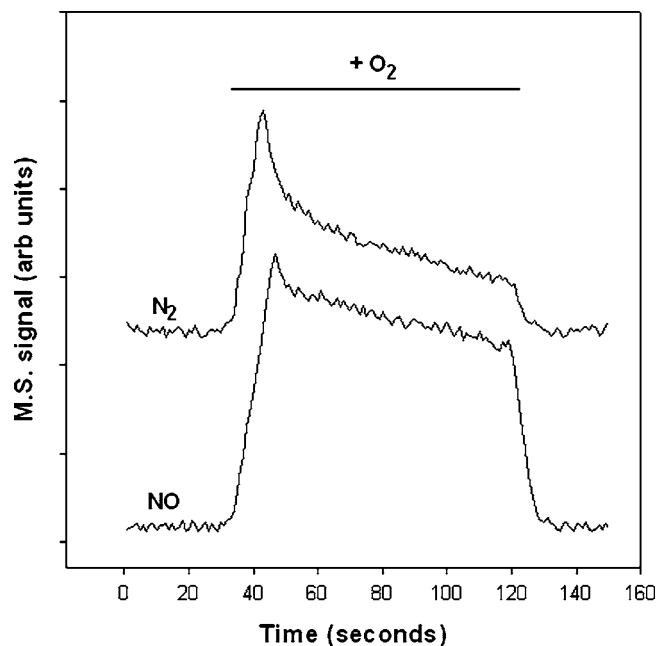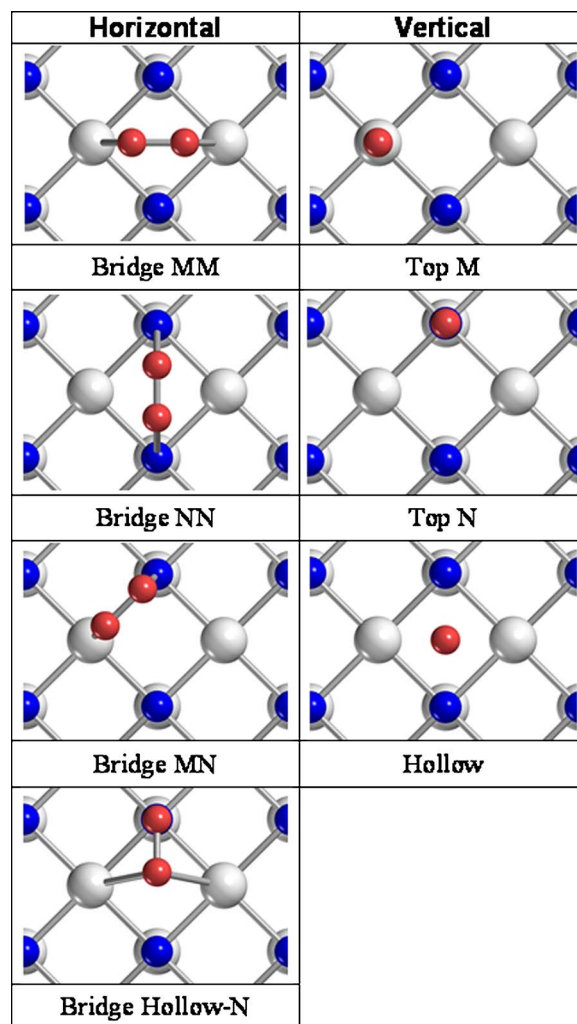

FIG. 6. (Color online) Sites for horizontal and vertical adsorptions of molecular oxygen on the TiN (001) surface.

In the next section we will examine the energetics associated with the oxidation process of TiN (dissociation of O_2, $N \leftrightarrow O$ exchange, formation of N_2 or NO) using first principles DFT calculations.

B. Theoretical studies

1. Adsorption and dissociation of O_2

For the adsorption of the oxygen molecule on the nitride surface, two different orientations have been considered: vertical, with the O–O axis perpendicular to the surface, and horizontal, with the O–O axis parallel to the surface. Also, two different spin states have been computed: that with paired spins, and therefore there is no magnetic moment, and that coming from a spin-polarized calculation, which formally corresponds to a triplet and hence correlates with the ground state of molecular oxygen. For the vertical approach of O_2 to the surface, there are three possibilities: on top of nitrogen atoms, on top of metal atoms, and at hollow site corresponding to the center of the surface squares (see Fig. 6). When the O_2 molecule adsorbs parallel to the surface we found that the oxygen atoms can interact either with two metal atoms or with two nitrogen atoms. Also, molecular oxygen can simultaneously interact with a Ti–N pair directly

FIG. 5. Variation in the gas concentration of N_2 ($m/e=28$) and NO ($m/e=30$) after exposing a TiN(001) surface to O_2 (5×10^{-7} Torr) at 450 K. The molecular oxygen was leaked into the UHV chamber from $t=30$ s to $t=120$ s.

TABLE I. Adsorption energies (ΔE_{ad}/eV) and oxygen-to-surface distance (R/Å) for molecular and atomic oxygen on the TiN (001) surface. See Fig. 6 for a description of the sites.

Site	Molecular O_2		Atomic O	
	Singlet	Triplet	ΔE_{ad}	R (O-surf)
Top (Ti)	−1.50	−1.42	−2.80	1.65
Top (N)	0.14	0.21	−0.19	1.19
Hollow	−0.51	−0.60	−1.80	1.36
(Ti–Ti)	−2.89	−2.86		
(N–N)		a		
(Ti–N)	−1.41	−1.33	−0.69	1.73
(Hollow-N)	−1.06	−1.02		

^aNo stationary point. It leads to the hollow-N position.

bound, and a fourth possibility is when it binds a N atom and two Ti atoms at a hollow site. These four cases will be labeled as (Ti–Ti), (N–N), (Ti–N) and (hollow-N), respectively.

The adsorption energies of molecular oxygen on these sites are reported in Table I. Such energies are estimated with respect to the ground state of free molecular oxygen: $E_{ads} = E(O_2/surf) - E(surf) - E(O_2)$. According to this, negative values mean bound states while if positive the states are unstable with respect to desorption. As can be seen, adsorption on top of N atoms is not favorable, the preferred sites being the on top of metal atoms for vertical interaction and at the Ti–Ti position when O_2 approaches the surface in a horizontal way. The singlet always appears to be only slightly lower than the triplet except for the vertical-hollow position, although it should be noticed that these structures are only stationary points and not real minima on the potential energy hypersurface (i.e., when the symmetry is broken down, the system readily evolves to geometries where the oxygen molecule lies parallel to the surface). The adsorption energies for parallel interaction are found to be almost twice that for a vertical approach.

Taking the most stable optimized structure of O_2 adsorbed on TiN as a starting point, the O–O bond was then smoothly stretched until we reached molecular dissociation. This process involves a small barrier of 0.2 eV and leads to two oxygen atoms on top of Ti surface atoms with a Ti–O bond distance of 1.63 Å. The reaction is highly exothermic with an energy release of −4.75 eV (with respect to free molecular oxygen). However, this was not the most stable structure as we found that diffusion of an oxygen atom to a nearby surface Ti atom lowers the repulsion between oxygen atoms releasing an extra energy of −0.66 eV (Fig. 7). In order to asses whether or not the structure obtained in the dissociation reaction is the most favorable one on the surface, we performed a systematic exploration of the possible
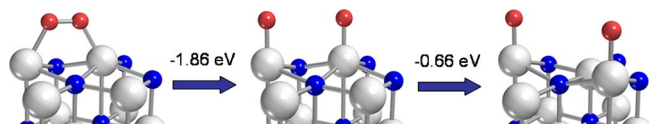

FIG. 7. (Color online) Dissociation of adsorbed O_2 on the TiN (001) surface.
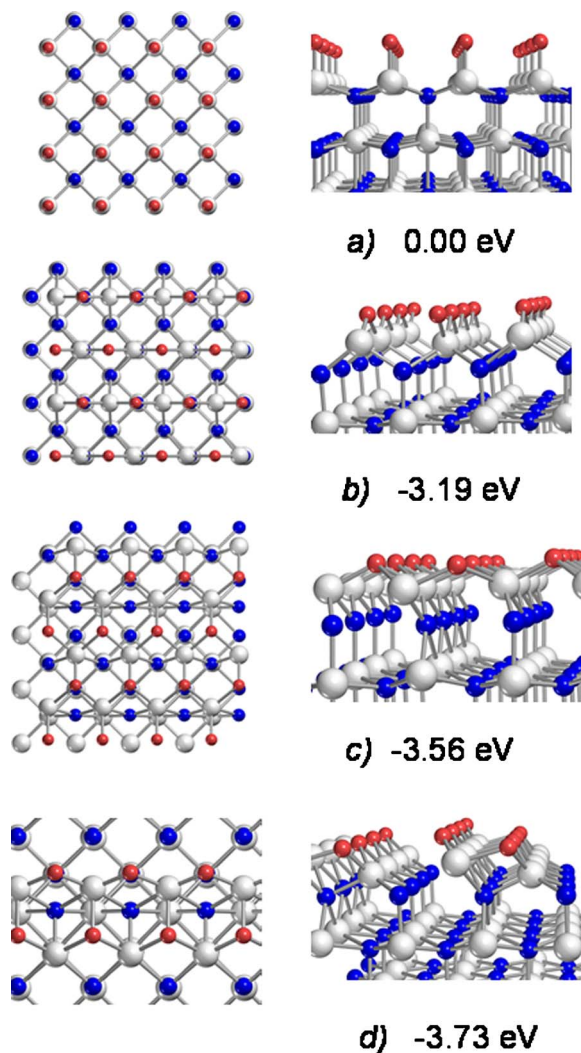

FIG. 8. (Color online) Different structures of TiN (001) surface fully covered by oxygen viewed from the top (left) and from the side (right). The initial structure showing the inverse rippling relaxation is depicted in (a) and taken as the energy reference.

sites for atomic oxygen adsorption. The results of these calculations are also reported in Table I taking again as reference the energy of free molecular oxygen, $\Delta E_{ad} = E(O\text{-surf}) - E(surf) - 1/2 E(O_2)$. As expected, adsorption of atomic oxygen atop of Ti atoms appears to be clearly preferred (−2.80 eV), strongly suggesting that the dissociation process takes place easily and smoothly. The energies release for the other possibilities fall far apart, in particular, the interaction with nitrogen atoms is clearly weaker. Nevertheless, during the O_2 dissociation process at low temperatures, some O atoms could be trapped on top of N sites (see N $1s$ spectrum at the bottom of Fig. 4) in metaestable states associated with step edges or imperfections of the surface.

To end with this section, it must be said that we also investigated the surface reconstructions mentioned in a previous theoretical study.[7] When the O coverage was below 0.5 ML, we did not find evidence of a surface reconstruction in the range of temperatures explored. For a system with 0.5 ML of O in which the O atoms are aligned on a row, our molecular dynamics (MD) calculations gave a reconstruction in which the O atoms move in a concerted way to hollow
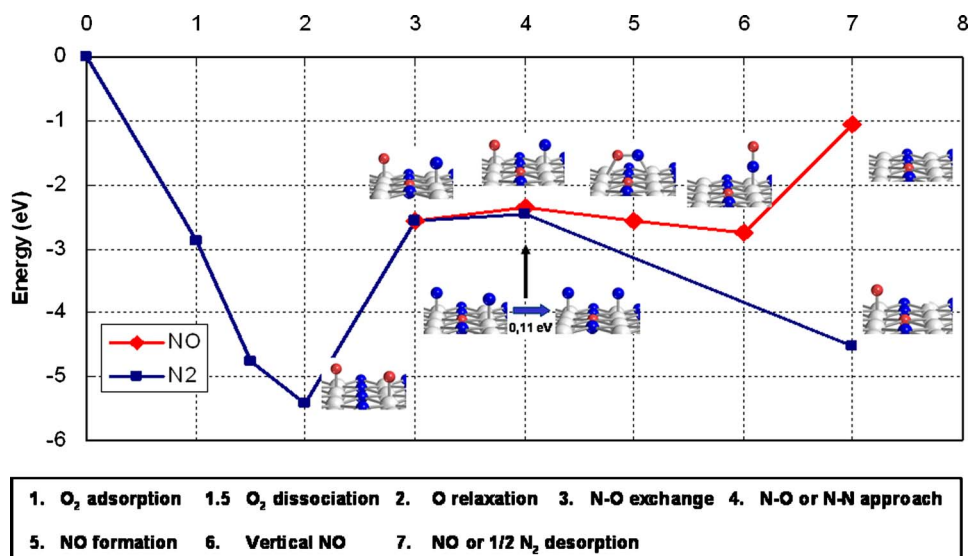
FIG. 9. (Color online) Schematic view of the energetics of the adsorption and dissociation of O_2, as well as the exchange and recombination processes that take place on the TiN (001) surface.

1. O_2 adsorption	1.5 O_2 dissociation	2. O relaxation	3. N-O exchange	4. N-O or N-N approach
5. NO formation	6. Vertical NO	7. NO or 1/2 N_2 desorption		

positions and pull Ti atoms away from the surface leading to a configuration akin to that reported in Ref. 7. Although this process is downhill by -1.69 eV, it should be noticed that it starts from an O configuration that is not the most stable for a coverage of 0.5 ML. Actually, if this O/TiN(001) interface initially adopts its most stable configuration, with the O atoms in zigzag, there is no reconstruction. Finally, at an O coverage of 1 ML the adsorption energy of oxygen (-2.70 eV) is much lower than at 0.5 ML (-4.75 eV), due to a strong repulsion between the negatively charged adatoms, and after geometry optimization the system exhibits the geometry displayed in Fig. 8, where an inversion of the rippling relaxation in the surface layer is observed, the Ti atoms being now above the N atoms. Their shift upward (~ 0.7 Å) essentially breaks the Ti–N bonds. This structure is metastable and gets disordered when heated even at 200 K. Low temperature MD simulations of this system leaded to three main patterns that were later frozen and whose optimized structures are shown in Fig. 8. As can be seen, there is a significant stabilization with an energy release of up to -3.73 eV for the most favorable case.

In the following sections, we will study the first steps in the oxidation process of TiN(001). These steps occur at O coverages that are well below 1 ML. We will assume that adsorption of O_2 has already occurred and the adatoms are dispersed on the nitride substrate.

2. Nitrogen↔oxygen *exchange*

For the oxidation process to proceed after adsorption of oxygen on the surface, some elementary steps involving oxygen penetration into the lattice should take place. We first estimated the energy associated with a nitrogen↔oxygen exchange step in which one of the O adatoms replaces a N surface atom. Our calculations showed this process to be highly endothermic (2.84 eV) indicating that a nondefective (001) surface of TiN has no tendency to oxidize at low coverages of O atoms. The oxidation reaction could progress to some extension on surface steps and other defects with low coordination Ti atoms, but our theoretical estimates in general show no tendency of O atoms to be located inside of the

fcc lattice of TiN. For instance, to exchange a surface oxygen atom by a subsurface nitrogen atom takes 0.55 eV extra energy (3.39 eV in total). This tendency agrees with the fact that the stable structure of fcc-type packed TiO actually is monoclinic and features a significant number of O vacancies.[55]

3. Formation and desorption of NO *and* N_2

Although energetically unfavorable, it is conceivable that a N↔O exchange could take place on the surface, since -5.41 eV are liberated during the adsorption/dissociation of O_2. Therefore, it seems relevant to analyze the energetics of processes which involve recombination of N and O adatoms. A $N_{ads} + O_{ads} \rightarrow NO_{ads}$ reaction yields a molecule bridging a couple of Ti atoms (see Fig. 9 for a full description of the process). Such a recombination is exothermic by -0.23 eV, and when NO is bound vertically on top of a Ti atom, through a Ti–N bond, there is an extra energy release of -0.17 eV (the possibility of NO attached to Ti atoms through the oxygen corresponds to an unbound state). To end the process, the NO molecule should desorb and this costs 1.69 eV. This highly endothermic desorption energy for an NO molecule could explain the peak observed at ~ 400.5 eV in the N $1s$ core level spectra collected after dosing O_2 to TiN(001) at 250 K and its disappearance at higher temperatures (Fig. 4). In spite of this endothermic step, the whole process (adsorption and dissociation of O_2, N↔O exchange, formation and desorption of NO) is exothermic (-1.05 eV, path "a" in Fig. 9). The fact that it was only observed at high temperatures in the experiments of photoemission is probably due to activation barriers associated with the N↔O exchange and NO desorption.
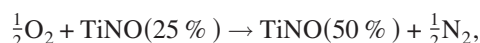
Next, on the basis of the data in Fig. 5, we must consider the reaction of two N adatoms to give N_2. The likelihood for this process is high only when the N/O ratio is large due to a relatively low O coverage. Starting from an almost noninteracting initial structure consisting of two separated adsorbed N atoms, there is an initial barrier (0.11 eV) to surmount which allows them to sit on top of contiguous Ti atoms. Once at this position, they readily combine and des-

orb releasing −2.08 eV per N atom. This pathway is schematically shown in Fig. 9, path b. From a thermodynamic viewpoint, it should be the preferred reaction pathway for the removal of N from the system when the O coverage is not large and the formation of NO has a low probability.
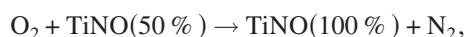
Above, we have studied the process of replacing 25% of the N atoms in the first layer of TiN(001) by O atoms. In order to complete our analysis of the oxidation process, we must establish if a full N↔O exchange is thermodynamically possible in the first layer of TiN(001) and the energetics associated with the migration of O from the surface to the bulk of the nitride. For the N↔O exchange in the first layer, the DFT calculations predict exothermic reactions independently of the amount of N replaced:

$$\tfrac{1}{2}O_2 + TiN \rightarrow TiNO(25\%) + \tfrac{1}{2}N_2,$$

$$\Delta E = -2.04 \text{ eV},$$

$$\tfrac{1}{2}O_2 + TiNO(25\%) \rightarrow TiNO(50\%) + \tfrac{1}{2}N_2,$$

$$\Delta E = -2.02 \text{ eV},$$

$$O_2 + TiNO(50\%) \rightarrow TiNO(100\%) + N_2,$$
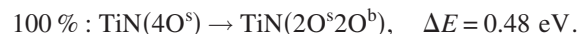
$$\Delta E = -3.25 \text{ eV}.$$

To investigate the energetics of O migration into the bulk, we moved O atoms from the first layer (O^s in our notation) to the second layer (O^b in our notation) in the TiNO systems and calculated the corresponding ΔE:

$$25\% : TiN(O^s) \rightarrow TiN(O^b), \quad \Delta E = 0.55 \text{ eV},$$

$$50\% : TiN(2O^s) \rightarrow TiN(O^sO^b), \quad \Delta E = 0.53 \text{ eV},$$

$$50\% : TiN(O^sO^b) \rightarrow TiN(2O^b), \quad \Delta E = 0.69 \text{ eV},$$

$$50\% : TiN(2O^s) \rightarrow TiN(2O^b), \quad \Delta E = 1.22 \text{ eV},$$

$$100\% : TiN(4O^s) \rightarrow TiN(2O^s2O^b), \quad \Delta E = 0.48 \text{ eV}.$$

Thus, the diffusion of O from the surface to the bulk is always endothermic if the system maintains a rocksalt structure. In addition, one could expect also kinetic barriers for the diffusion process. It can be concluded that the bulk oxidation of titanium nitride must occur at elevated temperatures. Furthermore, once all the N atoms of the surface have been replaced with O, the additional oxygen would prefer the formation of TiO_{1+x} instead of migrating into the bulk of the sample to form $TiN_{1-x}O_x$ phases with a cubic structure. This agrees with results of time-resolved x-ray diffraction for the oxidation of TiN,[56] which show TiO_2 and TiN with a negligible amount of $TiN_{1-x}O_x$.

IV. CONCLUSIONS

The first steps in the oxidation process of the TiN(001) surface have been analyzed by means of both experimental and theoretical studies. The photoemission data show that at low temperature (250 K) molecular oxygen chemisorbs on the surface giving rise to O atoms bound to Ti surface atoms. There is saturation in the adsorption indicating that in this regime of temperature the oxidation does not make progress into the bulk and that it is likely limited to the first layer. At variance, when the temperature is raised to 450 K no saturation is observed and the signal due to TiO_x species consistently increases, suggesting that in order the oxidation to go further, some barriers need to be overcome. The theoretical analysis performed nicely allows us to interpret these results. Indeed, the adsorption/dissociation of molecular oxygen on the surface is found to be exothermic, yet the necessary N–O surface exchange is a highly endothermic step (2.84 eV) that can take place only at high temperature. Moreover, the analysis shows that further N–O substitution involving inner TiN layers is always endothermic as far as the cubic rocksalt structure is preserved. These findings indicate that a hypothetical rocksalt structure for TiO_xN_y is highly unlikely and strongly suggest that oxidation of TiN involves a simultaneous loss of the initial structure.

The experimental data show that oxidation at 450 K involves formation of both N_2 and NO at the first stages of the reaction. The N_2 signal, due to N recombination at the surface, starts strong but rapidly decays with time. In its turn, a steady signal of NO is observed indicating that the main channel of the reaction is $TiN + mO_2 \rightarrow TiN_{1-x}O_x + NO$. The theoretical calculations predict that both N recombination and NO formation processes are exothermic, although it seems obvious that the former may only take place at very low oxygen coverage.

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