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Ab initio study of Ti$_{0.5}$Al$_{0.5}$N(001)—residual and environmental gas interactions

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Abstract. We have explored surface processes on Ti$_{0.5}$Al$_{0.5}$N(001) interacting with residual and environmental gases, namely O$_2$, H$_2$O and CO$_2$, using ab initio molecular dynamics. Dissociative adsorption of O$_2$ occurs on Ti sites, which are unusual sites, as Al$_2$O$_3$ is more stable than TiO$_2$. This may be understood based on the electronic structure. We suggest that an increased Ti–O bond strength relative to Al–O surface bond strength is the electronic origin for the early stages of TiO$_2$ formation on Ti$_{0.5}$Al$_{0.5}$N(001). Another unexpected atomic mechanism, identified as O covers the surface: Ti escapes from the Ti$_{0.5}$Al$_{0.5}$N(001)/O interface layer, generating vacancies, and hence enables mobility at the interface. In the case of H$_2$O and CO$_2$, the dominating physical mechanism is dissociative adsorption, where O–H and N–H as well as C–O and Ti–O dipoles are formed, respectively. These fundamental surface processes are relevant for initial stages of oxidation, surface diffusion and nucleation of reaction layers upon exposure to residual and environmental gases.

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1. Introduction

A predictive modelling in solid-state physics requires a detailed knowledge of all underlying fundamental mechanisms on the nanoscale. For instance, surfaces should be considered when solids interact with another medium. However, very often these surface models are idealized, as surface structure and energetics are usually described in vacuum [1–3]. An important benchmark system in surface protection of tools is cubic metastable Ti$_{1-x}$Al$_x$N (space group $Fm\overline{3}m$, prototype NaCl), which exhibits considerable improvements of physical and chemical properties with respect to its binary counterparts, cubic TiN and hexagonal AlN [4–6]. The metastable solubility limit of AlN in TiN, forming cubic rather than thermodynamically stable hexagonal Ti$_{1-x}$Al$_x$N, was experimentally determined to be in the range $x = 0.5$–0.9 [7–13]. Furthermore, Ti$_{1-x}$Al$_x$N has extensively been studied by ab initio calculations, probing its bonding, phase stability, structure and elastic properties [14–20]. It was suggested that the phase stability of Ti$_{1-x}$Al$_x$N does depend not only on the Al content but also on the Al distribution on the metallic sublattice [16, 21].

Synthesis of metastable Ti$_{1-x}$Al$_x$N can only be facilitated under non-equilibrium conditions, which is readily available in physical vapour deposition techniques such as sputtering and cathodic arc [7–13]. These non-equilibrium synthesis methods are governed by an interplay of thermodynamics and kinetics [22]. Fundamental understanding of elementary growth processes, such as surface diffusion and ion–surface interactions, is crucial for obtaining the required combination of physical and chemical properties for a particular application [22]. Interaction of Ti$_{1-x}$Al$_x$N with residual gas during synthesis as well as post-exposure has not been considered using ab initio methods. Recently, potential energy maps for Ti and Al adatoms on ordered and disordered Ti$_{0.5}$Al$_{0.5}$N(001) surfaces were calculated using ab initio methods and it was suggested that the surface disorder reduces Ti adatom mobility [23]. Furthermore, surface energetics is relevant for various processes, ranging from initial stages of oxidation to preferred crystallographic orientation [24–28]. Based on ab initio molecular dynamics (MD) data, it was argued that the oxidation of TiN(001) is facilitated by dissociative adsorption of O$_2$ and consequent formation of crystalline TiO$_2$ at 900 K [25]. No such data are available for Ti$_{1-x}$Al$_x$N. It is, however, known from annealing experiments that TiO$_2$ preferably forms upon oxidation of Ti$_{1-x}$Al$_x$N [29, 30]. It was suggested that Ti outward diffusion is responsible for these observations [29, 30], but no understanding on the atomic and electronic structure levels is available. Generally, other residual and environmental gases, such as H$_2$O, may also be relevant for synthesis, namely impurity incorporation, nucleation and surface diffusion, as well as for many physical properties such as ferroelectric, elastic and tribological [31–34]. Based on
Ab initio calculations, it was reported that molecular H\textsubscript{2}O adsorption occurs on TiN(001) and TiN(111) surfaces, while dissociative H\textsubscript{2}O adsorption is observed for TiN(110) \cite{35}. As soon as AlN is incorporated into cubic TiN forming Ti\textsubscript{1-x}Al\textsubscript{x}N, these adsorption processes may be altered, but this has not yet been explored.

In this work, we use ab initio MD simulations to explore surface processes on Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) interacting with residual and environmental gases, O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2}. Dissociative adsorption of O\textsubscript{2} induces preferred Ti–O bond formation and extraction of Ti from the TiAlN(001)/O interface, generating Ti vacancies at the interface. H\textsubscript{2}O gives rise to O–H and N–H dipoles. Adsorption of CO\textsubscript{2} is responsible for C–O dipole formation and free atomic O triggers similar physics as the adsorption of O\textsubscript{2}. These data explain on the atomistic level several experimental observations, such as preferred TiO\textsubscript{2} formation of Ti–Al–N surfaces \cite{29,30} and nucleation and growth of Ti–Al–O–N thin films \cite{36}.

2. Methodology

Ab initio MD simulations of Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) interacting with O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} were performed using the OpenMX code \cite{37}, based on the density functional theory \cite{38} and basis functions in the form of linear combination of localized pseudoatomic orbitals \cite{39}. The electronic potentials were fully relativistic with partial core corrections \cite{40,41} and the generalized gradient approximation was applied \cite{42}. The basis functions used were generated by a confinement scheme \cite{39,43} and specified as follows: Ti5.0-s2p2d1, Al6.0-s2p2, N4.5-s2p1, O4.5-s2p1, H4.5-s2 and C4.5-s2p1. Ti, Al, N, O, H and C designate the chemical name, followed by the cutoff radius (Bohr radius units) in the confinement scheme and the last set of symbols defines primitive orbitals applied. The confinement radii as well as the basis set were carefully checked with respect to basic elemental data, such as equilibrium volume (or bond length in the case of free molecules) and bulk modulus. The energy cut off 2040 eV (150 Ryd) and the 96 × 96 × 240 grid within the real-space grid technique \cite{44} were adjusted to reach the accuracy of 3 × 10\textsuperscript{-5} eV atom\textsuperscript{-1} (10\textsuperscript{-6} H atom\textsuperscript{-1}). Canonical ensembles at 300 K were used to simulate Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) surface (six atomic layers, surface area 12.536 × 12.536 Å\textsuperscript{2}, 216 atoms, random distribution of Al and Ti \cite{15}) interacting with O\textsubscript{2}, H\textsubscript{2}O and CO\textsubscript{2} gases as a function of coverage. The coverage was calculated based on ideal dissociative adsorption. These molecules were initially placed 3 Å from the Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) surface at ad hoc positions. The bottom layer of Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) slab was always frozen to mimic the infinitive bulk. The MD time step was 1.0 fs and the simulation time was 2000 fs for each coverage. The total MD time for all simulations performed was 54 000 fs. The adsorption energy (ΔE\textsubscript{ad}) was calculated at 0 K as

\[
\Delta E_{\text{ad}} = \frac{E_{\text{slab}} - nE_{\text{molecule}} - E_{\text{TiAlN}}}{mn},
\]

where \(E_{\text{slab}}\), \(E_{\text{molecule}}\), \(E_{\text{TiAlN}}\), \(n\) and \(m\) designate the total energy of a Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) slab with adsorbed molecules, total energy of a molecule, total energy of the pristine Ti\textsubscript{0.5}Al\textsubscript{0.5}N(001) surface, number of adsorbed molecules and number of atoms in a molecule, respectively. All total energies at 0 K were obtained after full structural relaxations by minimizing the interatomic forces.
3. Results and discussion

We start the discussions on the Ti$_{0.5}$Al$_{0.5}$N(001) surface interaction with residual and environmental gases by considering the O$_2$ case. Figure 1 shows the fundamental atomic process occurring during Ti$_{0.5}$Al$_{0.5}$N(001)–O$_2$ interactions as a function of coverage. Dissociative adsorption of O$_2$ occurs for all coverages probed. We observe the interaction of individual O atoms with surface metal atoms, but never with N. Ti sites are preferred over Al sites for the O$_2$ coverage up to 0.17 monolayers (ML). At an O$_2$ coverage of 0.17 ML, Ti escapes from the Ti$_{0.5}$Al$_{0.5}$N(001)/O interface layer, which is induced by an increased Ti–O coordination (three O nearest neighbours) compared to the Ti–O coordination (one O nearest neighbour) at lower O$_2$ coverages. This generates Ti vacancies in the Ti$_{0.5}$Al$_{0.5}$N(001)/O interface layer. This is consistent with the literature, since metal vacancies were suggested to form in Ti$_{0.5}$Al$_{0.5}$N [45] and isostructural Cr–Al–O–N [46]. We observe the apical Ti–O bond length of 1.66 Å at an O$_2$ coverage of 0.06–0.11 ML, which is not consistent with TiO$_2$ [47]. However, as soon as Ti escapes from the Ti$_{0.5}$Al$_{0.5}$N(001)/O interface layer at an O$_2$ coverage of 0.17 ML, the Ti–O bond adopts the length of 1.87–1.96 Å, which is in turn consistent with TiO$_2$ [47]. Hence, it is reasonable to assume that the O adsorption induces Ti extraction and the associated vacancy formation enables and constitutes the initial stage of TiO$_2$ formation. At an O$_2$ coverage of
0.22 ML, Al–O bonds begin to form, but it is only Ti that escapes from the Ti$_{0.5}$Al$_{0.5}$N(001)/O interface layer. This Al–O bond formation may be due to a decreased population of Ti atoms in the surface exposed to additional O$_2$ molecules. In this case, there is a broader distribution of O–metal bond lengths, from 1.65 to 2.18 Å. This structural disorder (broad bond length distribution) was also observed for the oxidation of Al(111) [48]. At an O$_2$ coverage of 0.44 ML, a Ti atom coordinated with five nearest O neighbours is observed. This is consistent with TiO$_2$ [47]. Our data also support the suggestion by Gnoth et al [49] that surface oxidation of cubic Ti–Al–N thin films is caused by reaction with atmospheric oxygen and/or residual gas immediately after synthesis [49]. to Baben et al [50] showed that the incorporation of O into cubic Ti–Al–N is energetically favourable and Sjölen et al [36] have observed the incorporation experimentally. Hence, the above discussed phenomena are also relevant for nucleation and growth of Ti–Al–O–N thin films. This may be a general feature of cubic transition metal Al nitrides, as O incorporation is energetically also favoured for Sc-, V- and Cr-containing phases [51].

We continue to discuss the structure evolution as a function of coverage in terms of energetics. Figure 2 contains the corresponding adsorption energy data for O$_2$ molecules. As the O$_2$ coverage is increased from 0.06 to 0.50 ML, the adsorption energy increases from $-5.8$ to $-3.5$ eV per adatom. Clearly, the affinity of O towards Ti$_{0.5}$Al$_{0.5}$N(001) decreases with larger O$_2$ coverages. This trend as well as the absolute values is consistent with the literature [52, 53].

The fact that Ti–O bond formation is preferred at low O$_2$ coverages is counter-intuitive as Al$_2$O$_3$ is known to be more stable than TiO$_2$ [54]. This apparent inconsistency can be understood based on the electronic structure. Figure 3 shows the density of states for Ti$_{0.5}$Al$_{0.5}$N(001)–O$_2$ interaction at a coverage of 0.06 ML. We explore two cases: (i) O adsorbed on Ti sites, which is preferred according to our ab initio MD data presented above and (ii) O adsorbed on Al sites. The general features in the density of states for Ti$_{0.5}$Al$_{0.5}$N(001) are consistent with bulk.

**Figure 2.** Adsorption energy for O$_2$, H$_2$O and CO$_2$ on Ti$_{0.5}$Al$_{0.5}$N(001) as a function of coverage.
Figure 3. Density of states for Ti$_{0.5}$Al$_{0.5}$N(001)–O$_2$ interaction at a coverage of 0.06 ML. Two partial densities of states for O 2p orbitals are shown: (i) O adsorbed on Ti sites and (ii) O adsorbed on Al sites. The Fermi level is set to 0 eV.

Ti$_{0.5}$Al$_{0.5}$N [18], so no detailed discussions are provided here. O 2p states are localized in the range of approx. $-4$ to $-2$ and $-2$ to 0 eV for O adsorbed on Ti and Al sites, respectively. The O 2p states are hybridized with Ti 3d in case of adsorption on the Ti sites and Al 3p states in case of adsorption on the Al sites (partial density of states analysis is not shown here). A shift to lower energies, as observed for the O adsorption on the Ti sites, is consistent with an increase in the bond energy and hence bond strength. This is consistent with the electronic structure of bulk Ti$_{0.5}$Al$_{0.5}$N with incorporated O [50]. We suggest that the increased Ti–O bond strength constitutes the electronic origin for the preferred Ti–O bond formation compared to (the initially expected) Al–O formation and represents the early stages of TiO$_2$ formation on Ti$_{0.5}$Al$_{0.5}$N(001). These data explain on the electronic structure level the experimental observation of the selective oxidation of Ti on Ti–Al–N [29, 30] and TiAl [55] surfaces.

After considering the Ti$_{0.5}$Al$_{0.5}$N(001) surface interaction with O$_2$, we continue with the exposure to H$_2$O and CO$_2$. Figure 4 shows the fundamental atomic process occurring during Ti$_{0.5}$Al$_{0.5}$N(001)–H$_2$O and Ti$_{0.5}$Al$_{0.5}$N(001)–CO$_2$ interactions as a function of coverage. Dissociative adsorption of H$_2$O is observed for the coverage of 0.06–0.11 ML. O–H and N–H dipoles are formed. O–H dipoles have a tendency to align laterally. This may be relevant for tribological properties of these surfaces [34, 56]. At an H$_2$O coverage of 0.17 ML, a non-dissociated H$_2$O molecule is observed. Molecular H$_2$O adsorption was reported on TiN(001) [35]. On the other hand, dissociative adsorption of H$_2$O on Al$_2$O$_3$(0001) occurs [57]. At H$_2$O coverages larger than 0.22 ML, all H$_2$O molecules dissociate. Clearly, dissociative adsorption is the dominating physical mechanism. Figure 2 also contains the corresponding adsorption energy data for H$_2$O molecules. The average adsorption energy is $-0.7$ eV per adatom, which is the lowest value observed here. The adsorption energy appears not to be a function of H$_2$O coverage. It seems that the affinity of H$_2$O towards Ti$_{0.5}$Al$_{0.5}$N(001) is rather small.
Figure 4. $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$–$\text{H}_2\text{O}$ and $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$–$\text{CO}_2$ interactions as a function of coverage. MD snapshots at 300 K are shown after 2000 fs at each coverage. Nearest neighbours are connected and only outermost surfaces are shown.

The last molecule interacting with $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ to be considered is $\text{CO}_2$ (see figure 4). Non-dissociative adsorption of $\text{CO}_2$ occurs for the lowest coverage of 0.06 ML. Already at a $\text{CO}_2$ coverage of 0.11 ML, $\text{CO}_2$ dissociates and C–O and Ti–O dipoles are formed. Evidently, surface oxidation can also be $\text{CO}_2$ driven. The observed dissociative adsorption of $\text{CO}_2$ on $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}(001)$ is consistent with the interaction of $\text{CO}_2$ and many metal surfaces, such as

Al, Bi, Fe, Mg, Ni, Pd, Re, Rh and Ru [58]. At a CO\(_2\) coverage of 0.22 ML, Ti escapes from the Ti\(_{0.5}\)Al\(_{0.5}\)N(001)/O interface layer, induced by an increased Ti–O coordination. Here, Al–O bonds already coexist. This is the same physical mechanism as in the case of Ti\(_{0.5}\)Al\(_{0.5}\)N(001)–O\(_2\) interaction, which is discussed above. Dissociative adsorption is continued for all coverages probed except of a CO\(_2\) coverage of 0.44 ML, where a non-dissociative adsorption of CO\(_2\) occurs at very large distance from the surface, namely ~5 Å which is in the order of two interplanar distances. Since a relatively large CO\(_2\) coverage is reached, Coulomb repulsion may occur with already adsorbed CO\(_2\) molecules. However, already at a CO\(_2\) coverage of 0.50 ML, dissociative adsorption is continued including the dissociation of the non-dissociated molecule at a CO\(_2\) coverage of 0.44 ML. Clearly, dissociative adsorption is the dominating physical mechanism. Figure 2 also contains the corresponding adsorption energy data for CO\(_2\) molecules. As CO\(_2\) coverage is increased from 0.06 to 0.50 ML, the adsorption energy increases from −1.6 to −1.0 eV per adatom. This is the same trend as in the case of O\(_2\) adsorption and the affinity of CO\(_2\) towards Ti\(_{0.5}\)Al\(_{0.5}\)N(001) is in the range between those of O\(_2\) and H\(_2\)O. This implies that the Ti\(_{0.5}\)Al\(_{0.5}\)N(001) surface would mainly be covered with O, while C-containing species should be seen as minor impurities.

4. Conclusions

Using \textit{ab initio} MD simulations at 300 K, we have studied fundamental surface processes on Ti\(_{0.5}\)Al\(_{0.5}\)N(001) interacting with residual and environmental gases, O\(_2\), H\(_2\)O and CO\(_2\). Dissociative adsorption of O\(_2\) occurs for all coverages probed. Surprisingly, Ti sites are preferred for an O\(_2\) coverage of 0.06–0.17 ML. This may be understood based on the electronic structure. We suggest that the increased Ti–O bond strength relative to the Al–O surface bond strength is the electronic origin for the early stages of TiO\(_2\) formation on Ti\(_{0.5}\)Al\(_{0.5}\)N(001), which explains the experimental observation of the selective oxidation of Ti on Ti–Al–N surfaces [29, 30] as well as nucleation and growth of Ti–Al–O–N thin films [36]. At an O\(_2\) coverage of 0.17 ML, Ti escapes from the Ti\(_{0.5}\)Al\(_{0.5}\)N(001)/O interface layer, generating Ti vacancies. At a O\(_2\) coverage of 0.22 ML, Al–O bonds begin to form. In the case of H\(_2\)O, dissociative adsorption, where O–H and N–H dipoles are formed, is a dominating mechanism for all coverages. O–H dipoles have a tendency to align laterally. At a H\(_2\)O coverage of 0.17 ML, a non-dissociated H\(_2\)O molecule is observed. This may be due to a competition of two mechanisms. Molecular H\(_2\)O adsorption was reported on TiN(001) [35], while dissociative adsorption occurs on Al\(_2\)O\(_3\)(0001) [57]. In the case of CO\(_2\), non-dissociative adsorption occurs for the lowest coverage of 0.06 ML. Already at a CO\(_2\) coverage of 0.11 ML, CO\(_2\) dissociates and C–O and Ti–O dipoles are formed. At a CO\(_2\) coverage of 0.22 ML, Ti escapes from the Ti\(_{0.5}\)Al\(_{0.5}\)N(001)/O interface layer, induced by an increased Ti–O coordination. This is the same physical mechanism as in the case of Ti\(_{0.5}\)Al\(_{0.5}\)N(001)–O\(_2\) interaction. Larger CO\(_2\) coverages are dominated by dissociation. The identified physical mechanisms are relevant for various processes, ranging from initial stages of oxidation and surface diffusion to nucleation of reaction layers upon exposure to residual and environmental gases.

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