Coarse-grained model for growth of $\alpha$- and $\kappa$-$\text{Al}_2\text{O}_3$ on TiC and TiN(111): thin alumina films from density-functional calculations

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Abstract. We propose a coarse-grained model for growth of $\alpha$- and $\kappa$-$\text{Al}_2\text{O}_3$ on TiX(111) (X=C or N) surfaces, generalisable to similar systems. We perform the first step in the model and investigate the structure and energetics of a thin alumina film on TiX(111) with density-functional theory calculations. Results show that the stable alumina structure consists of two oxygen layers with a full aluminum layer in octahedral coordination in between and that the stability is higher on the TiC surface than on TiN.

1. Introduction

Alumina (aluminum oxide, $\text{Al}_2\text{O}_3$) exists in many different phases with applications ranging from microelectronics and catalysis to wear-resistant coatings. Depending on the application, different phases ($\alpha$, $\gamma$, $\kappa$, $\theta$, ...) and alumina thicknesses (from a few atomic layers to several nanometers) are used. Common to all of them is the presence of interfaces between alumina and other materials. Since these interfaces are often crucial for the device properties there is a need to understand their atomic and electronic structures.

In this paper we focus on the formation of interfaces between $\alpha$-$\kappa$-$\text{Al}_2\text{O}_3$ and titanium carbide/nitride (TiX, X=C or N). Multilayer structures of these materials, grown by chemical vapour deposition (CVD), are commonly used as coating materials on cemented-carbide cutting tools [1]. While the structure of the interface surely determines the growth morphologies observed in TEM analysis [2], the interface is a result of growth itself. Traditional interface modeling, based on calculations on truncated bulk structures, does not take into account the associated growth history. On the other hand, a brute-force kinetic Monte Carlo modeling, which includes all atomic and molecular processes at each growth stage, is superfluous for ionic crystals such as alumina, where the strong electrostatic forces drive the atoms towards only a few allowed sites.

We present a coarse-grained model of growth, which neglects the details of the atomic dynamics but takes into account growth history. When fully applied, it describes the alumina structure at several growth stages (thicknesses) and ultimately yields the atomic structure at the interface to the substrate. Here we study the first stage of the interface formation, the growth of a thin alumina film. Calculations concerning further growth will be published elsewhere.
(a) Coarse-grained model for growth of alumina: The model ignores details of atomic processes; adsorption studies identify the first alumina layer; strong electrostatic forces determine the alumina film geometries in subsequent layers; respecting growth history the relevant interface structures are established. (b) Al vacancy positions in $\alpha$-$\text{Al}_2\text{O}_3$. (c) Al atom positions in $\kappa$-$\text{Al}_2\text{O}_3$.

2. Interface and Growth Modeling

Figure 1(a) illustrates the coarse-grained description of growth that we introduce here and apply in our study. The model relies on the existence of strong electrostatic forces, which allow for only a few atomic configurations even during growth. Motivated by the high growth temperature, we ignore atomic diffusion and focus on larger-scale growth history effects. Hence, instead of studying the details of atomic processes, we describe the growth by depositing a larger portion of alumina in a few different but distinct atomic configurations and then letting the atoms relax to find their optimal positions. The structure with lowest energy represents a relevant growth stage in the coarse-grained model. The candidates for the subsequent growth stage are found by depositing alumina on this stable structure. Iterating the procedure gives an accelerated description of the growth and leads ultimately to the atomic structure at the interface.

2.1. The First Atomic Alumina Layer on Titanium Carbide/Nitride

In the multilayer CVD coatings, alumina grows on TiX(111) with the orientations $\alpha$-$\text{Al}_2\text{O}_3(0001)$ || TiX(111) and $\kappa$-$\text{Al}_2\text{O}_3(001)$ || TiX(111) [2]. Studies on atomic adsorption on Ti-terminated TiX(111) [3] show a much stronger adsorption for O than Al and a preference for the fcc adsorption site. Our monolayer-adsorption calculations [4] confirm the fcc site preference. Thus, we choose an O monolayer in fcc as first atomic alumina layer on the Ti-terminated TiX(111) surfaces and restrict ourselves to these substrate terminations.

2.2. Structural Analysis of the $\text{Al}_2\text{O}_3$/TiX Interface

The stacking sequences of the $\alpha$- and $\kappa$-$\text{Al}_2\text{O}_3$ bulk structures can be described as [5, 6]:

$$
\alpha[0001] : Ac^a Bc^\beta Ac^\gamma Bc^\alpha Ac^\beta Be^\gamma, \quad (Ba^a Ca^\beta Ba^\gamma Ca^\alpha Ba^\beta Ca^\gamma, \quad Cb^\alpha Ab^\beta Cb^\gamma Ab^\alpha Cb^\beta Ab^\gamma), \\
\kappa[001] : Ac_b^\alpha Bc_a^\gamma Ab_{\gamma,c_{\alpha,b_{\beta}}} Cb_{\alpha,b_{\beta}}, \quad (Ba_{\beta,c_{\gamma}} Ca_{\alpha,a_{\gamma}} Bc_{\gamma,b_{\beta}} Ac_{\alpha,c_{\beta}}, \quad Cb_{\beta,a_{\gamma}} Ab_{\gamma,b_{\alpha}} Ca_{\gamma,b_{\beta}} Ba_{\alpha,\beta}). \quad (1)
$$

Capital letters denote O planes and small letters with greek super-/subscripts ($\alpha/\kappa$) denote Al vacancies/positions, see Figure 1(b)-(c). In each line, the standard notation, with the first O plane in A sites, is followed by translated equivalent notations in parentheses. The presence of the TiX substrates breaks the equivalence and all three expressions need to be considered.

Bulk TiX adopts the NaCl structure. We define the $ABC$ stacking of the TiX(111) to end with a $C$ plane. The fcc site corresponds then to $A$ stacking. All possible stackings of the
grown alumina follow from Eq. 1 by starting from all possible oxygen A planes and choosing one of the two stacking directions. The number of different $\alpha$ structures is then reduced by symmetry: [0001] is equivalent to [000 ¯1] and the superscripts one of the two stacking directions. The number of different $\alpha$ films composed of two O layers. Furthermore, since the stable films composed of two O layers. Furthermore, since the stable $\alpha(0001)$ and $\kappa(001)$ surfaces are terminated by half an Al layer [8, 9], we terminate the films with half an Al layer.

As each Al layer contains four occupied Al sites there are six different termination possibilities for each film structure. In each $\alpha$-$\text{Al}_2\text{O}_3$ layer, two Al atoms have vacancies and two have Al neighbors in the layer below. Since the former are electrostatically more favorable we choose those as terminating Al positions in the $\alpha$-derived films. This choice also conserves the $R\overline{3}c$ bulk symmetry of $\alpha$-$\text{Al}_2\text{O}_3$ in the surface region.

In the same way, in the $\kappa$-derived films, we consider those terminations that conserve the $Pna2_1$ symmetry of bulk $\kappa$-$\text{Al}_2\text{O}_3$ in the surface Al layer, that is, we do not allow mixed occupations of different stacking symbols [6], e.g., $b_\alpha b_\beta$ is replaced by $b_\alpha$ or $b_\beta$ but not by any other combination of the four positions. This choice avoids an increased electrostatic repulsion due to shorter Al-Al distances when mixing $\alpha$ sites with $\beta$ or $\gamma$ [see Figure 1(b)].

We have successfully tested these restrictions by performing calculations on all rejected geometries for one $\alpha$- and one $\kappa$-derived film. The final thin-film configurations, listed in Figure 2(a), are the starting structures for our density-functional theory (DFT) calculations.

3. Computational Method

All calculations are performed with the DFT pseudopotential plane-wave code dacapo using ultrasoft pseudopotentials and the PW91 exchange-correlation functional [10].

We employ the supercell approach and model the $\text{Al}_2\text{O}_3$/$\text{TiX}$ system by slab geometry. Each unit cell contains 4 TiX bilayers, 2 O layers, 1 1/2 Al layers (66 atoms in total), and additional vacuum of 12 Å. We use a 400 eV plane-wave cutoff and a $4 \times 2 \times 1$ Monkhorst-Pack k-point sampling. These choices have proven to yield high accuracy at acceptable CPU times [7].

We include a dipole correction to correct for electrostatic effects arising from slab asymmetry. Atomic relaxations are performed until all interatomic forces are smaller than 0.05 eV/Å.

4. Results & Discussions

Figure 2(a) shows the energies of all considered structures before and after relaxation. After relaxation, the energetically lowest-lying structures do not display an $\alpha$- or $\kappa$-$\text{Al}_2\text{O}_3$ structure but consist of $AbC$ (lowest energy) or $AcB$ (next-lowest energy) stackings, with all six Al atoms in octahedral coordination in between the O planes, see Figure 2(b). All other relaxed films display highly distorted $\kappa$ structures and are separated by fairly large energy differences from the $AbC$ structure.

The total-energy differences per unit cell between the three lowest-lying structures are $\Delta E_{\text{Tic}}^{\text{0.78 eV}}$ and $\Delta E_{\text{TiC}}^{\text{1.24 eV}}$ on TiC, and $\Delta E_{\text{TiN}}^{\text{0.65 eV}}$ and $\Delta E_{\text{TiN}}^{\text{1.58 eV}}$ on TiN. Assuming a Boltzmann distribution $P_{\text{struct}}(T) \propto \exp(-\Delta E_{\text{struct}}/k_B T)$ to describe the probability for a surface region of one unit cell area to display one of the found film structures at finite temperature, we find that at $T = 1300$ K (CVD temperatures: 1100–1300 K) $P_{\text{ABT}}^{\text{TiC}} \approx 0.9992$ and $P_{\text{ABT}}^{\text{TiN}} \approx 0.9970$. Thus, we can expect the $AbC$ structure to be the one obtained in the first step of the alumina growth on TiX(111).
Figure 2. (a) Energies before and after relaxation. Only the lowest-lying AbC structures are present at temperatures below 1300 K. (b) Layer distances for these stable structures on both substrates after relaxation. On TiC two energetically almost equivalent structures are possible (AbC or AbC\(^*\)).

The difference in formation energy of the AbC film on the two substrates, TiC(111) and TiN(111), \(\Delta E_f = (E_{\text{tot}}^{\text{AbC/TiC}} - E_{\text{tot}}^{\text{AbC/TiN}}) = -0.27\) eV, where \(E_{\text{tot}}^{\text{AbC/TiX}}\) is the calculated total energy of the relaxed clean TiX(111) slab, shows also that growth is more stable on TiC than on TiN. This result agrees with experimental findings [11] and shows the importance of electronic interactions over elastic contributions [4] for the interfacial stability.

Finally, we note that in our calculations the AbC structure is obtained from relaxation of both an \(\alpha\) and several \(\kappa\) structures [see Figure 2(a)]. Thus, at this stage, there is no way to infer the phase content of a thicker alumina film grown on TiX(111).

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