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Pathway for a low-temperature deposition of α-Al_2O_3: A molecular dynamics study

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ABSTRACT

Thin films of α-Al_2O_3 are of high interest because of their mechanical properties. Previously, the preparation of Al_2O_3 has been described in terms of extrinsic process parameters, such as total pressure, oxygen partial pressure or substrate bias potential. In this paper, the growth of Al_2O_3 is studied by atom-by-atom molecular dynamics simulations, focused on intrinsic process parameters such as ion energy, ion fraction in the particle flux, growth temperature and growth template. While the preparation of α-Al_2O_3 by currently available techniques requires temperatures of around 1000 °C (well above the typical softening temperature of tool steel substrates), the paper presents a narrow window of intrinsic process parameters which leads to an uninterrupted epitaxial growth or growth of previously nucleated α-Al_2O_3 at low temperatures.

1. Introduction

Aluminium oxide, Al_2O_3, is a widely used thin film material. It forms many polymorphs [1] including α (thermodynamically stable phase), γ (the most common metastable phase), κ, θ, δ, η and χ, let alone the amorphous phase. Different properties of the aforementioned polymorphs lead to numerous applications as wear-resistant protective coatings (α and κ phase) [2,3], in catalysis (γ and χ phase) [4,5], in microelectronics (e.g., waveguides) or as diffusion and thermal barriers. Properties reported for all polymorphs include high optical transparency, excellent chemical inertness and zero electrical conductivity. Ion-assisted deposition techniques constitute a common method of Al_2O_3 fabrication. Films covering a wide range of structures can be prepared by varying extrinsic deposition parameters such as substrate bias voltage, substrate temperature, discharge gas composition and pressure or (in the case of pulsed sputtering) duty cycle and frequency. These quantities control the intrinsic deposition parameters such as the particle flux composition, ion fraction in the particle flux, ion energy and substrate temperature (affected by both the ohmic heating and the ion bombardment). A large experimental effort is being devoted to investigating the relationships between deposition technique, deposition parameters, phase structure and material properties [6–11]. This is a complex task due to a high number of Al_2O_3 polymorphs, uncertainties concerning the exact atomic structures of metastable Al_2O_3 (particularly the γ-phase [12,13]) and the fact that a large portion of as-deposited Al_2O_3 is amorphous.

The α-Al_2O_3 phase (corundum) is of particular worldwide interest because of its mechanical properties. However, its preparation by currently available techniques requires temperatures of around 1000 °C (well above the typical softening temperature of tool steel substrates of 550 °C). The deposition of α-Al_2O_3 coatings at low substrate temperatures constitutes a big challenge which has not been solved yet. This may be partially due to the fact that the aforementioned intrinsic deposition parameters are more difficult both to adjust and to measure than the extrinsic parameters, and consequently, the effect of the intrinsic parameters (which really control the film growth, independently of, e.g., the deposition system geometry) is less known. There were attempts to capture this effect theoretically, using Monte-Carlo simulations [14] or ab-initio simulations describing an impact of a single atom [15]. The usefulness of these techniques for this purpose is however limited because they cannot yield grown atomic structures containing thousands of atoms, either by definition (in the former case) or because of computational costs (in the latter case). On the contrary, classical molecular dynamics (MD) simulations can reproduce the atomic-scale processes that control the growth of individual Al_2O_3 phases and provide the experimentally inaccessible information about the complex relationships between these processes and the intrinsic deposition parameters.

This approach has been used to describe the growth of numerous ceramics, see e.g., Refs. [16–21]. Cooper et al. [16] studied the growth of a-C, and successfully reproduced, for example, the experimentally measured relationship between the length of surface chains and their sputter frequency. In parallel, limitations resulting from the short-range nature of the interatomic interactions (both empirical potentials and tight-binding) were found. In Ref. [17], Hensel et al. studied the epitaxial growth of crystalline Si and its amorphization (or at least

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formation of a surface amorphous layer—this seems to be difficult to distinguish as the authors "deposited" only 320 atoms) using various energies of arriving atoms. Note that the topic of Ref. [17] is very similar to the present work, except dealing with a covalent instead of an ionic crystal (which affects the choice of a proper interaction potential). Ivaschenko et al. [18] simulated the chemical vapor deposition (CVD) of SiC films under varied conditions (growth temperature, vapor temperature and substrate bias) and their subsequent annealing. The authors, for example, qualitatively reproduced the experimentally measured changes in the radial distribution function upon annealing. In Ref. [19], classical MD was used to reproduce CVD of SiNH in even more detail: the parameters of control included not only particle energies but also the particle flux composition (SiH_x + N radicals in this case). There is an excellent agreement with experimental results (e.g., increasing utilization of SiH_4 with decreasing fraction of SiH_4 in a $SiH_4 + N_2$ gas mixture, higher sticking coefficient of SiH_x for lower x, H/Si ratio or volume fraction of intentionally formed pores). Lefevre et al. [20] used classical MD to study the growth of a-SiO_2 and (most importantly) to predict an optimum energy of arriving particles leading to low-stress, high-density films. In our recent work [21], we used classical MD to study the growth of crystalline TiO_2 (both rutile and anatase). The results are not only consistent with all phenomena observed experimentally but also include information not accessible experimentally. For example, while published experiments indicate that the deposition of rutile is more "difficult" compared to anatase, simulations indicate that the growth of previously nucleated rutile takes place in a wider range of process parameters compared to anatase. This illustrates a significant advantage of classical MD simulations compared to many experiments: easy disentanglement of crystal nucleation and crystal growth. Georgieva et al. [22] used classical MD for a single simulation of a non-ion-assisted growth of (consequently amorphous) Al_2O_3. There is no work using this approach for a physics-based description of the growth of α-Al_2O_3 (or any other crystalline Al_2O_3 phase).

The above overview constitutes a proof that the film growth can be successfully reproduced using classical MD. Moreover, it indicates what one has to avoid in order to capture as many phenomena as possible (e.g., using a short-range potential for describing structures which depend also on long-range interactions [16], or "depositing" too low number of atoms [17]). In parallel, it is desirable to keep in mind the differences between the growth of crystalline and amorphous materials. On the one hand, the crystal phase of interest can be (and α-Al_2O_3 is) thermodynamically stable, and it can even be used for fitting the interaction potential (see the next section). On the other hand, the modeling can be more time consuming (especially due to the higher number of atoms leading to a "converged" structure), one can model only the crystal growth (not the nucleation which takes place on much longer time scales) and the comparison with experiment can be less straightforward (because of the experimentally difficult disentanglement of the nucleation and the growth; although at the same time this underlines the value of the simulations).

In this paper, the growth of Al_2O_3 in general and α-Al_2O_3 in particular is systematically investigated in a wide range of process parameters by MD simulations. There are five parameters of interest: the energy of arriving ions, E_i, the ion fraction in the particle flux, f_i, the growth temperature, T, the orientation of the growing crystal and the lateral size of the growing crystal. The film characteristics of interest include the short-range order (coordination numbers and radial distribution functions), the medium-range order (network ring statistics), crystal structure and the fact whether an amorphization takes place. The aim is to contribute towards understanding the complex relationships between growth conditions and phase formation of the Al_2O_3 thin films and to use this understanding for defining new pathway(s) for a low-temperature deposition of α-Al_2O_3. Note that this aim also constitutes a challenge from a methodology point of view because most of the structures of binary or "higher" materials obtained (predicted) previously by classical MD simulations are amorphous (exceptions include TiO_2 [21] and simple rock salt structures of Mg-rich MgAlO [22] or Ti-rich TiSiN [23]).

2. Methodology

2.1. Simulation protocol and structure analysis

All simulations performed in this work use classical MD as implemented in the LAMMPS code [24]. The film growth simulations use periodic boundary conditions in horizontal directions and a vacuum slab in the vertical direction. The recursive atom-by-atom simulation protocol includes the following:

(1) generation of the growth template and a 1-ps long "thermalization run" (canonical ensemble) at T up to 1300 K (Nose–Hoover thermostat);
(2) generation of 3 new atoms above the film surface (not bonded to each other), with velocities (towards the surface) corresponding to a given E_i (up to 100 eV) in the case of ions and 1 eV in the case of slow neutrals;
(3) a 5-ps long "collisional run" without controlling the temperature of film atoms (microcanonical ensemble), in order to simulate particle collisions and energy dissipation;
(4) a 1-ps long "thermalization run" (canonical ensemble) at given T, in order to reestablish the deposition temperature;
(5) removal of resputtered (desorbed) atoms and return to item 2.

The growth template can represent not only an amorphous substrate or a crystalline substrate/seed layer for an epitaxial growth, but also previously grown part of the film/previously nucleated crystal. The ion fraction in the total particle flux, f_i, was 25%–100%. Note that throughout this paper the words "ions" and "neutrals" refer to particle kinetic energy, not to particle charge (in other words, from an experimental point of view the "ion flux" can include also fast neutrals). The time step used (1 fs at $E_i \leq 100$ eV) and the aforementioned durations of the MD runs needed (5 and 1 ps) were identified and successfully used previously [19,21]. The composition of the film-forming flux was adaptively changed (depending on sticking coefficients on Al and O) in order to keep the Al/O = 2/3 composition of the films. The two bottom monolayers were frozen in all simulations. See Fig. 1 (discussed in detail below) for an example of grown structures. In most cases (all cases except testing of interaction potentials), ≥3000 atoms were deposited in ≥1000 cycles of the above algorithm.

The short-range order in materials was examined in terms of coordination numbers and distribution of interatomic distances (radial distribution functions, RDF). In the case of coordination numbers, the bonding cutoff distance of 2.5 Å (upper bound of first RDF peaks) was used. Because the sets of RDF peaks characterizing various Al_2O_3 phases are numerous and overlapping, the medium-range order in materials was examined in parallel and expressed in terms of network ring statistics [25] shown in Fig. 2. In the high-density phase α-Al_2O_3, there are only rings containing up to 8 atoms (see Fig. 2a), while longer rings can be considered as a fingerprint of γ-Al_2O_3 and other low-density phases (see Fig. 2c) and amorphous structures (see Fig. 2d). The γ-Al_2O_3 phase was described as hausmannite with Al vacancies [12]. The presence of rings containing up to 12 atoms is qualitatively independent of the positions of vacancies (Fig. 2c is based on positions recommended in Ref. [12]), while special positions of vacancies can even lead to rings containing 14 atoms (not shown). Hausmannite itself has only short network rings (see Fig. 2b), but a stoichiometry of 3:4 (not 2:3).

2.2. Interaction potential

It is well known that the interaction potential choice is critical for the success and reliability of classical MD simulations. For example, the fact