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Atomistic simulation and virtual diffraction characterization of stable and metastable alumina surfaces

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Abstract

The structures of select alumina surfaces are studied using molecular statics and molecular dynamics simulations and are characterized using virtual diffraction methods. First, bulk alumina simulations are performed to validate the transferability of the ReaxFF potential to model different alumina phases. Bulk alumina simulations accurately predict α-Al_2O_3 as the lowest energy crystalline phase; however, they unexpectedly predict an even lower-energy amorphous phase. At 0 K, virtual X-ray diffraction patterns of the bulk crystalline phases and select alumina surfaces are validated by experimental studies. Molecular statics simulations of select alumina surfaces are consistent with prior first-principles studies. However, molecular dynamics simulations show that many surfaces experience significant reconstructions at temperatures below what is expected from experiments. It is believed that premature surface reconstructions are biased by the predicted lower-energy amorphous phase and occur due to the extra degrees of freedom allowed by the free surfaces as well as the available thermal energy during dynamics. Discrete peaks appearing in virtual selected-area electron diffraction patterns indicate that the reconstructions are not fully amorphous due to lattice constraints imposed by the internal bulk structure. Bulk and surface energies are tabulated for each simulation to be used in future predictive mesoscale models of polymorphic alumina.
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1. Introduction

Alumina (Al_2O_3) is an abundant ceramic material that exhibits extraordinary structural flexibility [1–5]. The different Al_2O_3 phases display a range of unique physical properties which make them useful in a variety of coating applications [6,7]. These properties stem from subtle differences within the crystal structure of its phases. In general, the alumina phases are composed of a close-packed O sublattice surrounded by Al interstitials filling two-thirds of the octahedral and tetrahedral sites to maintain stoichiometry [8]. The type of close-packed arrangement of the O sublattice and the degree of symmetry of the Al interstitials within each alumina unit cell determines the phase and properties of the material. Corundum, α-Al_2O_3, is the only thermodynamically stable alumina phase, and contains the most symmetric ordering of the Al interstitials [1]. High symmetry leads to the high density of α-Al_2O_3 compared to the other phases and promotes directionality and ionic bonding between the atoms, leading to high hardness. The metastable alumina phases have decreasing symmetry of the Al interstitials, which decreases their density and weakens their bond strength by reducing bond directionality. Due to subtle structural differences, phase identification within atomistic simulations based solely on local atomic positions is difficult; however, experimental characterization

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techniques such as X-ray diffraction (XRD) and selected-area electron diffraction (SAED) have proven successful in distinguishing between alumina phases [9–13].

Selective vapor deposition of single-phase alumina thin films is often desired in order to take advantage of specific material properties, but is difficult due to the complexity of the alumina material system. For example, κ- and α-Al_2O_3 surfaces are widely regarded as ideal protective coatings due to their wear resistance, chemical inertness, resistance to thermal shock, and high hardness [14,15]. However, several metastable alumina phases demonstrate properties less ideal for these purposes and can form during deposition depending on the processing conditions [16]. For example, θ- and γ-Al_2O_3 metastable phases may form at lower processing temperatures ($T_m \approx 0.3$) [16]. These metastable phases have lower surface energies and therefore exhibit higher surface areas, making them more appropriate as catalytic supports. In addition, selective vapor deposition of single-phase alumina proves difficult due to alumina's complex phase transition series that is dependent on the material precursors and processing conditions [17–19]. To determine the current state under a particular synthesis process, researchers and manufacturers must continually characterize the surface structure.

Predictive mesoscale material simulations can aid in the search for the ideal processing conditions that produce tailored alumina coatings, similar to solidification studies of multicomponent systems [20–22]. By considering the mechanisms governing phase formation and evolution, predictive models can computationally explore the unique processing conditions that achieve single-phase coatings in polycrystalline materials. Analogous experimental approaches, such as those taken to develop structure zone diagrams [23,24], rely on phenomenological observations requiring an exhaustive experimental study for a polymorphic material system and are only predictive within the same processing space. Mesoscale models, such as phase-field methods [25], for physical vapor deposition of polymorphic materials require energetic data (i.e. bulk, surface, and interface energies) that can be easily computed from atomistic simulations. However, to quantitatively compare these data the relevant energies need to be computed using the same computational model, as is done in this work.

Specifically, this work investigates select bulk and surface alumina structures using atomistic simulations modeled with the reactive force-field (ReaxFF) potential [26]. This article begins with a detailed discussion of previous atomistic simulations performed on alumina bulk and surface structures, highlighting the need for a consistent computational model to provide quantitatively comparable data. This is followed by a description of the current simulation methods using ReaxFF as well as the virtual diffraction method [27,28] used to characterize the nanoscale structure of the alumina simulations. Next, computed surface energies as well as characterization results are reported and analyzed. This paper concludes with a summary and discussion of the future work needed to develop predictive mesoscale models of vapor deposition for polymorphic alumina.

2. Previous atomistic studies of alumina

Because of its important material properties and wide industrial use, the alumina system has been studied extensively using molecular dynamics (MD), molecular statics (MS), and first-principles computational models. However, none of these previous atomistic studies has attempted to catalog the structural and energetic properties of bulk and surface structures across more than two alumina phases using the same computational model. By narrowing the focus on select alumina components, prior atomistic simulation studies have avoided the challenges of uniquely characterizing the subtle structural differences among the various alumina phases as well as the distortion created by atomic relaxations near surfaces. More importantly, because prior alumina studies used different computational models, direct comparisons between computed energetic values cannot be made.

First-principles simulations have studied alumina bulk and surface structures at 0 K using models based on quantum mechanics which rely on approximations to describe the electron interactions explicitly (cf. [29–31]). These approximations can be divided into three classes: (i) Hartree–Fock (HF) theory; (ii) density functional theory with local density approximations of the electron exchange-correlation (DFT-LDA); and (iii) density functional theory with generalized gradient approximations of the electron exchange-correlation (DFT-GGA). Unlike first-principles simulations, MS and MD simulations use models based on Newtonian physics which represent atoms as point masses in space that encompass both the nucleus and the orbiting electrons. Interactions between atoms are governed by an interatomic potential to describe the potential energy of the system. Prior MS and MD simulations have employed a variety of interatomic potentials with different approximations for electrostatic and non-electrostatic interactions (i.e. the styles describing pair, many-body and bonded interactions). The approximations used to describe the electrostatic interactions in alumina can be divided into three different classes: (i) fixed point charges [32–43]; (ii) charged shell models [44–48]; or (iii) dynamic geometry dependent charges [49–52]. Each of these increases in complexity in an attempt to better represent the polarization of the O ions.

2.1. Bulk alumina studies

Prior atomistic simulations of alumina modeled bulk systems in order to assess the transferability of the computational model to multiple phases. Because α-Al_2O_3 is the only thermodynamically stable phase, transferable computational models should predict α-Al_2O_3 as the lowest potential energy structure per Al_2O_3 unit. Table 1 lists a sample of previous atomistic simulation studies that compared the

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