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Atomistic simulation and virtual diffraction characterization of homophase and heterophase alumina interfaces

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Abstract—The objective of this work is to elucidate the structure and energy of 12 homophase and heterophase alumina interfaces using atomistic simulations with the ReaxFF potential. First, the computational methods are validated by exploring a set of five α-Al_2O_3 symmetric tilt twin interfaces. The interface structures and energies for most homophase α-Al_2O_3 twins are in good agreement with prior atomistic studies; however, small deviations occur for select α-Al_2O_3 interfaces due to the larger, more appropriate interface areas explored in this work. Next, select experimentally observed κ-Al_2O_3, γ-Al_2O_3, and θ-Al_2O_3 homophase interfaces as well as heterophase α-Al_2O_3//γ-Al_2O_3 and θ-Al_2O_3//γ-Al_2O_3 interfaces are investigated for the first time using atomistic simulations to elucidate their atomic structure, including terminating plane(s) and relaxations, and to compute interface energies. ReaxFF predicts that the γ-Al_2O_3 $\{111\}$ twin and the θ-Al_2O_3 $\{200\}$ twin interfaces have energies of the same order as the lowest-energy α-Al_2O_3 prismatic twin boundary and that the heterophase α-Al_2O_3 (0001)//γ-Al_2O_3 (111) interface has the lowest energy of all interfaces studied. Lastly, virtual selected-area electron diffraction patterns of select interfaces are used to experimentally validate the predicted interface structures. Because a consistent computational method is implemented throughout this work, the computed interface energies can be incorporated in future predictive mesoscale simulations of polymorphic alumina.

Keywords: Alumina; Molecular dynamics simulation; Grain boundary; Interfaces; Diffraction

1. Introduction

Alumina (Al_2O_3) films are used in a variety of applications, ranging from electronic and catalytic supports [1,2] to thermal barrier and protective coatings [3,4], due to the wide range of material properties exhibited by the various polymorphs of Al_2O_3. Deposition methods and processing conditions influence the microstructure and morphology of the alumina films, which influence the overall performance of the coatings. Both physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes commonly result in the formation of mixtures of γ-Al_2O_3, θ-Al_2O_3, κ-Al_2O_3 and α-Al_2O_3 phases [5–13]. Generally, higher percentages of γ-Al_2O_3 and θ-Al_2O_3 metastable phases form using PVD methods or at lower processing temperatures [5–8], whereas higher percentages of κ-Al_2O_3 and α-Al_2O_3 phases form using CVD methods or at elevated temperatures [9–12]. The γ-Al_2O_3 and θ-Al_2O_3 metastable phases are desired for catalytic support applications due to their high surface area and acid-basic properties [14,15]. However, κ-Al_2O_3 and α-Al_2O_3 phases are sought after for protective coating applications due to their wear resistance, chemical inertness, high hardness and resistance to thermal shock [16,17]. Because α-Al_2O_3 is the only thermodynamically stable alumina phase, researchers and manufacturers seeking protective coatings will often employ thermal treatments to induce the necessary phase transformations to form α-Al_2O_3 [18,19]. Of course, the morphology of heat-treated films is dependent on the microstructure of the as-deposited polymorphic coatings [18,20].

As-deposited alumina films can be fully amorphous, nanocrystalline or coarse-grained depending on the processing conditions used to create the coating [21]. Internal interfaces within polycrystalline alumina films can affect the properties and performance of the coating [22–26] as well as influence microstructure evolution during thermal treatment [27–29]. For example, it is known that abnormal grain growth in alumina occurs due to the presence of impurities and pores at the interfaces [30,31]. However, the effects of interface misorientation on grain growth in polycrystalline alumina films is not fully known [32–34], in particular for heterophase interfaces constructed from different adjoining alumina polymorphs. Despite not fully understanding the structure and role of interfaces, researchers and manufacturers commonly create interfaces through

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deposition of multilayers which have been shown to be more wear resistant and easier to manufacture than single-phase coatings [35,36].

The objectives of this work are (i) to predict the minimum-energy structure of experimentally relevant [22–29] homophase and heterophase interfaces in alumina, including the terminating plane(s) and structural relaxations that may occur asymmetrically in the neighborhood of the interface; and (ii) to compute interface energies to determine rankings between interfaces and to ascertain whether certain heterophase interfaces may have commensurate or lower energies than interfaces in homophase systems. This work uses molecular statics simulations with the reactive force-field (ReaxFF) potential [37]. ReaxFF showed promising accuracy when modeling polymorphic alumina at 0 K in a previous study performed by the authors on Al_2O_3 bulk and surfaces [38], and the consistent use of ReaxFF within this study enables quantitative comparison of computed energetic data. In the current work, virtual diffraction methods [39,40] are used for the first time to aid the construction of complex, heterophase alumina interfaces. In addition, the virtual diffraction methods are used to validate select interface models via direct comparisons to experimental characterization results.

This article begins with a detailed discussion of previous studies performed on alumina interfaces, focusing on prior atomistic simulations and the need for a consistent computational method to provide quantitatively comparable data. This is followed by a description of the current simulation methods used to create, optimize and characterize the alumina interfaces as well as the analysis techniques imposed to extract interface energies. Next, structural characterization results for each alumina interface are presented alongside their computed interface energies, with quantitative comparisons between interfaces. Lastly, select alumina interfaces are further characterized using virtual selected-area electron diffraction (SAED) patterns [39,40], enabling a direct comparison to experimental results.

2. Previous alumina interface studies

Alumina interfaces have been studied using a variety of experimental and computational methods. The majority of previous atomistic simulation studies focused on five twin interfaces in α-Al_2O_3, as described in Table 1, using (i) molecular dynamics (MD), (ii) molecular statics (MS), (iii) density functional theory with local density approximations of the electron exchange–correlation (DFT-LDA), and (iv) density functional theory with generalized gradient approximations of the electron exchange–correlation (DFT-GGA). Each of these interfaces is created by a rotation of the basal plane about the $[12\bar{1}0]$ axis as shown schematically in Fig. 1. Computed α-Al_2O_3 interface energies collected from previous atomistic simulations are listed in Table 2. Four previous research studies examined multiple α-Al_2O_3 interfaces using a consistent computational method within each study. These results showed that the ordering of interface energies can depend on several factors, including the computational method. For example, MS simulations performed by Galmarini et al. predicted the lowest-energy interface to be the basal twin structure (A), whereas the DFT-LDA study performed by Elsässer et al. [41–48] and the MD studies performed by Suzuki et al. [49] predicted the prismatic twin structure (B) to have the lowest energy.

Deviations among the computed interface energies result partially from the different approximations used to model electrostatic interactions. The different approximations for electrostatic interactions affect the ability of the computational method to capture the correct polarization of the O ions, which directly affects the accuracy of the energy calculation [59]. In addition, some of the deviations among the computed interface energies result from the construction of different energy-minimized interface structures when different periodic simulation cell dimensions are used. Different periodic simulation cell dimensions impose different image forces that affect the interface structure. Both the computational method and available computational resources can limit the simulation cell dimensions, which restricts the variety of interface structures capable of being modeled. To the authors' knowledge, no prior atomistic study has examined homophase interfaces constructed from a metastable alumina phase, nor has any atomistic study examined heterophase interfaces constructed from multiple alumina polymorphs, as is done in this work.

A much wider variety of alumina interfaces has been studied using experimental methods, such as high-resolution transmission electron microscopy and electron diffraction. Several research groups have characterized the structure [60–64], analyzed impurities [65,66] and determined interface energies [67,68] in diffusion bonded α-Al_2O_3 bicrystals, while others have performed similar analyses using polycrystalline α-Al_2O_3 [69–71]. Experimentally measured interface energies for α-Al_2O_3 are reflective of the type of samples considered. For example, the $0.85\ \mathrm{J\,m^{-2}}$ interface energy measured by Shin et al. [71] using polycrystalline α-Al_2O_3 represented an averaged value for all interfaces sampled. However, analysis of α-Al_2O_3 [0001] symmetric tilt bicrystals conducted by Sakuma and coworkers [67,68] revealed three classifications of interfaces with different energy values: (i) special $\Sigma 7$ $(2\bar{3}10)//(\bar{3}210)$ and $\Sigma 3$ prismatic twin boundaries with low-energy interfaces of $\sim 0.054\ \mathrm{J\,m^{-2}}$; (ii) low-angle, $\Sigma 21$ $(4\bar{5}10)//(\bar{5}410)$ and $\Sigma 13$ $(3\bar{4}10)//(\bar{4}310)$ boundaries with interface energies of $\sim 0.4\ \mathrm{J\,m^{-2}}$; and (iii) large-angle and $\Sigma 19$ $(3\bar{5}20)//(\bar{5}320)$ boundaries with interface energies of $\sim 0.7\ \mathrm{J\,m^{-2}}$.

Homophase interfaces constructed from a metastable alumina phase and heterophase interfaces constructed from multiple alumina phases have also been observed experimentally, as described in Table 3. Multiple {111} γ-Al_2O_3 twins (F) were observed during CVD, which promoted texture within the films grown [72,73]. An analysis of pure κ-Al_2O_3 observed platelet-like crystal formations oriented along ⟨001⟩ containing 120° twinning (G) of three crystal regions, which mimicked pseudo-hexagonal structures [74]. Twinning also occurred in θ-Al_2O_3 on the {200} [75] and the {110} [76] mirror planes (H and I, respectively). Five heterophase alumina interfaces were identified from studies exploring the phase transition series of alumina which exhibit good crystallographic compatibility [72–80]. These included two θ-Al_2O_3//γ-Al_2O_3 interfaces (J–K) and three α-Al_2O_3//γ-Al_2O_3 interfaces (L–N).

3. Methods

Atomistic simulations of alumina are performed with LAMMPS [82] using the ReaxFF potential [37]. ReaxFF is chosen for this work because of its transferability to