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Ab initio molecular dynamics of Al irradiation-induced processes during Al₂O₃ growth

Denis Music,^{1,a)} Farwah Nahif,¹ Kostas Sarakinos,² Niklas Friederichsen,¹ and Jochen M. Schneider¹

¹Materials Chemistry, RWTH Aachen University, D-52056 Aachen, Germany

²Plasma and Coatings Physics Division, Linköping University, SE-58183 Linköping, Sweden

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Al bombardment induced structural changes in α -Al₂O₃ (*R*-3*c*) and γ -Al₂O₃ (*Fd*-3*m*) were studied using *ab initio* molecular dynamics. Diffusion and irradiation damage occur for both polymorphs in the kinetic energy range from 3.5 to 40 eV. However, for γ -Al₂O₃(001) subplantation of impinging Al causes significantly larger irradiation damage and hence larger mobility as compared to α -Al₂O₃. Consequently, fast diffusion along γ -Al₂O₃(001) gives rise to preferential α -Al₂O₃(0001) growth, which is consistent with published structure evolution experiments. © 2011 American Institute of Physics. [doi:10.1063/1.3570650]

Alumina (Al₂O₃) exhibits many polymorphs, ranging from thermodynamically stable α -Al₂O₃ (space group *R*-3*c*) to various metastable crystallographic modifications, such as γ -Al₂O₃ (space group *Fd*-3*m*).¹ The structure of γ -Al₂O₃ is still disputed upon.² Generally, alumina is a stiff, refractory compound with commercial relevance.^{3–5} α -Al₂O₃ is nowadays widely used for instance in surface protection applications as well as microelectronics.^{6,7} On the other hand, γ -Al₂O₃ is exceedingly valuable in catalysis.⁸ For many of these applications, it is imperative to form thin films. It is a common practice to synthesize thermodynamically stable α -Al₂O₃ at temperatures ≥ 1000 °C using chemical vapor deposition,⁹ but this high thermal load restricts the range of possible substrates and hence hinders widespread applications. To reduce the deposition temperature, ion-assisted synthesis methods have been used.^{10–13} From these studies, it is apparent that the understanding of the effect of the energetic bombardment on the phase formation of alumina is central for further development of experimental methodologies that would in turn facilitate a decrease in the temperature limit for the growth of α -Al₂O₃. It has been suggested that energetic bombardment affects (i) nucleation of various Al₂O₃ polymorphs,¹⁴ (ii) bulk and surface diffusion,^{10,12,15} and (iii) incorporation of impurities.¹⁰ All these factors may in turn control the phase formation. In our previous work, we have used a monoenergetic Al⁺ beam to synthesize α -Al₂O₃ at energies of 40 eV.¹⁶ It has been shown, using Monte Carlo simulations, that in this energy range a fraction of Al⁺ ions is subplanted into the growing film highlighting, in addition to the above mentioned factors, the role of subsurface processes for the phase formation of Al₂O₃.¹⁶ However, the effect of the ion irradiation in this energy range on the structure evolution of Al₂O₃ has not yet been explored on the atomic and electronic level.

Molecular dynamics (MD) has been beneficial for unraveling physics of ion-surface processes on the atomic level in many systems.^{17–22} In the case of alumina, there are some MD studies available. For instance, Rosén *et al.*¹⁵ have showed that bombardment of O-terminated α -Al₂O₃(0001)

with 3.5 eV Al⁺ results in local structural disorder. However, no phase transitions were identified. Interestingly, the same ion energies were reported to be responsible for removal of hydrogen from a gibbsite surface.^{23,24} It is expected that larger ion energies induce changes significant for structure evolution. For instance, 20 eV N₂⁺ ions have been argued to alter the preferred orientation of TiN from (111) to (001).²⁵ Furthermore, in diamondlike carbon subplantation has been shown to promote *sp*³ bonding.¹⁹

In this work, α -Al₂O₃(0001) and γ -Al₂O₃(001) are bombarded with Al at 330 K using *ab initio* MD simulations and structural changes are observed. Diffusion and damage occur for both polymorphs in the kinetic energy range from 3.5 to 40 eV. This energy range has been chosen based on our previous experimental report,¹⁶ where evidence for subplantation of impinging Al in γ -Al₂O₃, which in turn causes significantly larger irradiation damage and hence larger mobility as compared to α -Al₂O₃, is presented. We suggest that Al bombardment induced fast diffusion along γ -Al₂O₃(001) gives rise to preferential α -Al₂O₃(0001) growth, which is consistent with the previously reported structure evolution experiments.¹⁶

Ab initio MD was performed using the OPENMX code,²⁶ based on the density functional theory²⁷ and basis functions in the form of linear combination of localized pseudoatomic orbitals.²⁸ The electronic potentials were fully relativistic pseudopotentials with partial core corrections^{29,30} and the generalized gradient approximation was applied.³¹ The basis functions used were generated by a confinement scheme^{28,32} and specified as follows: Al_{6.0} *s*²*p*² and O_{4.5} *s*²*p*¹. Al and O 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 and bulk modulus. The energy cutoff (150 Ry) and *k*-point grid (1 × 1 × 1) within the real space grid technique³³ were adjusted to reach the accuracy of 10^{−6} H/atom. Canonical ensembles at 330 K (slightly above room temperature due to irradiation from plasma) were used to simulate Al bombardment of alumina slabs (vacuum thickness 10 Å) containing 392 and 420 atoms for O-terminated

^{a)}Electronic mail: music@mch.rwth-aachen.de. Tel.: +49-241-8025892. FAX: +49-241-8022295.

FIG. 1. (Color online) Structure evolution of O-terminated α - Al_2O_3 (0001) upon 40 eV bombardment with Al. An arrow indicates the bombardment site. Large and small spheres designate Al and O atoms, respectively.

α - Al_2O_3 (0001) and Al-O terminated γ - Al_2O_3 (001), respectively. Monoenergetic Al^+ beams are readily available in filtered cathodic arc deposition, which allows for a direct comparison with experiments.^{16,34} Structural description of α - and γ - Al_2O_3 bulk/surfaces was adopted from literature.^{35–37} The MD time step was 1.0 fs and the total MD simulation time was 400 fs, namely 100 fs for surface relaxations and 300 fs after bombardment events. These MD time scales are large enough to model fast irradiation-induced processes, according to a previous study.¹⁵

We start the discussions with ion-surface interactions for α - Al_2O_3 (0001). Figure 1 shows the structure evolution for this particular surface upon 40 eV bombardment with Al. It is clear that substantial irradiation-induced damage occurs. Many O-surface atoms are displaced in this MD snapshot at 300 fs. To evaluate the irradiation-induced damage of α - Al_2O_3 (0001), we have calculated the mean square displacements before and after Al bombardment. The mean square displacement for α - Al_2O_3 (0001) bombarded with 40 eV Al is $2.48 \text{ \AA}^2$. This indicates that some bonds may be broken and rearranged. However, there is no evidence for substantial diffusion. We have also analyzed the electronic structure before and after Al bombardment using electron density distributions and Mulliken analyses. The nature of chemical bonding is conserved. The 3.5 eV bombardment case has already been addressed in literature.¹⁵ We have also simulated 3.5 eV bombardment of Al_2O_3 (0001) and obtained consistency with Rosén *et al.*¹⁵ in terms of the maximum displacements. Furthermore, the mean square displacement for α - Al_2O_3 (0001) bombarded with 3.5 eV Al is $0.45 \text{ \AA}^2$. Since α - Al_2O_3 (0001) is O-terminated during vapor phase condensation in the presence of O_2 , unlike γ - Al_2O_3 (001) which is known to exhibit a mixed termination,³⁷ the bombardment of O-surface sites with and without underlying Al can be studied. However, all irradiation studies on Al_2O_3 (0001) were performed for O without underlying Al so that possible irradiation damage is maximized. We observe larger irradiation-induced surface damage for the 40 eV case. In both cases, α - Al_2O_3 (0001) is damaged, but there is no evidence for phase transitions or substantial diffusion.

In the case of bombardment of γ - Al_2O_3 (001) with Al, considerable differences occur in comparison with α - Al_2O_3 (0001). Figure 2 shows the structure evolution for γ - Al_2O_3 (001) upon 3.5 and 40 eV bombardment with Al. It

FIG. 2. (Color online) Structure evolution of Al-O terminated γ - Al_2O_3 (001) upon 3.5 and 40 eV bombardment with Al. Arrows indicate two bombardment sites probed. Large and small spheres designate Al and O atoms, respectively.

is apparent that substantial irradiation-induced damage occurs. A significant fraction of surface atoms are displaced in all MD snapshot at 300 fs. Most importantly, subsurface layers are affected for all cases to a larger extent. It is obvious that more damage occurs for larger kinetic energy. To evaluate the irradiation-induced damage of γ - Al_2O_3 (001), we have calculated the mean square displacements before and after Al bombardment. The mean square displacement for γ - Al_2O_3 (001) bombarded with Al is $20.05 \text{ \AA}^2$, $24.76 \text{ \AA}^2$, and $23.27 \text{ \AA}^2$ for 3.5 eV Al at site I, 40 eV Al at site I, and 40 eV Al at site II, respectively. This indicates that a significantly larger fraction of bonds may be broken and rearranged as compared to α - Al_2O_3 . Hence, more pronounced diffusion may occur for γ - Al_2O_3 than α - Al_2O_3 . We have also analyzed the electronic structure before and after Al bombardment. The nature of chemical bonding is conserved.

We have analyzed the temporal evolution of the penetration range of Al interacting with α - Al_2O_3 (0001) and γ - Al_2O_3 (001) surfaces. Figure 3 shows the relative z-coordinate of impinging Al with respect to surface of both polymorphs as a function of time. The maximum penetration for impinging Al with 3.5 eV and 40 eV onto α - Al_2O_3 (0001) is $0.71 \text{ \AA}$ and $1.87 \text{ \AA}$ and its final position at 300 fs is $2.07 \text{ \AA}$ and $2.20 \text{ \AA}$ above the pristine surface, respectively. For the γ - Al_2O_3 (001) case, we observe a site and kinetic energy dependence. As Al impinges onto O (site I) with 3.5 eV, the maximum penetration is $1.20 \text{ \AA}$, while the penetration depth after 300 fs is $0.49 \text{ \AA}$ only. As the kinetic energy increases from 3.5 to 40 eV, two effects can be observed. The maximum penetration increases to $3.82 \text{ \AA}$. The penetration depth after 300 fs is still $3.17 \text{ \AA}$, which in turn implies that subplantation of the impinging Al occurs. For the site II (surface Al) and kinetic energy of 40 eV, the maximum penetration is $1.83 \text{ \AA}$, while the penetration depth after 300 fs is $0.77 \text{ \AA}$. Obviously, subplantation occurs for γ - Al_2O_3 (001), but not for α - Al_2O_3 (0001). To justify that 300 fs is large enough

FIG. 3. (Color online) Relative z -coordinate of bombarding Al with respect to pristine surface of α - Al_2O_3 (0001) and γ - Al_2O_3 (001) as a function of MD time. Only last 300 fs are shown corresponding to relaxations after Al bombardment. Site I and site II correspond to O and Al surface atoms of γ - Al_2O_3 (001), respectively. For site II of γ - Al_2O_3 (001), additional 400 fs are considered and the data are provided as an inset.

time to grasp the underlying atomic mechanisms, we have extended the simulation time to 700 fs in the case of γ - Al_2O_3 (001), site II, 40 eV (see inset in Fig. 3). The fluctuation in the z -coordinate of impinging Al within 110 and 290 fs continues for the additional simulation time. Hence, it is reasonable to assume that 300 fs simulation time is sufficient. Based on the results from these MD simulations, we propose the following growth scenario. Impinging Al with a kinetic energy of 40 eV is subplanted and preferentially irradiation damages the γ - Al_2O_3 grains. At the same time, the Al bombardment triggers a more pronounced diffusion in these grains. Anisotropic diffusion in these two polymorphs may result in larger residence time of adatoms in α - Al_2O_3 than in γ - Al_2O_3 grains. Assuming that both polymorphs nucleate on the substrate surface, fast diffusion along γ - Al_2O_3 (001) causes preferential α - Al_2O_3 (0001) growth. This mechanism may explain the experimentally observed structure evolution of Al_2O_3 as a function of kinetic energy of impinging Al.¹⁶

In summary, we have studied irradiation-induced processes during alumina growth using *ab initio* MD at 330 K. We have correlated Al bombardment of α - Al_2O_3 (0001) and γ - Al_2O_3 (001) with structure evolution thereof. Independent of kinetic energy of impinging Al and irradiated surface site, diffusion and local structural disorder occur. Contrary to α - Al_2O_3 (0001), γ - Al_2O_3 (001) exhibits kinetic energy and site dependence. For γ - Al_2O_3 , subplantation of impinging Al causes extensive irradiation damage and hence larger mobility as compared to α - Al_2O_3 . It is expected that this finding has consequences for the structure evolution. If both polymorphs nucleate on the substrate surface, the Al bombardment induced mobility is proposed to enable fast diffusion along γ - Al_2O_3 (001) giving rise to preferential α - Al_2O_3 (0001) growth. This work is relevant for design of

experimental strategies to decrease the deposition temperature of α - Al_2O_3 .

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