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Low-temperature α -alumina thin film growth – *ab initio* studies of Al adatom surface migration

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Abstract

Investigations of activation energy barriers for Al surface hopping on α -Al₂O₃ (0001) surfaces have been carried out by means of first-principles density functional theory calculations and the nudged elastic band method. Results show that surface diffusion on the (most stable) Al-terminated surface is relatively fast with an energy barrier of 0.75 eV, whereas Al hopping on the O-terminated surface is slower, with barriers for jumps from the two metastable positions existing on this surface to the stable site of 0.31 and 0.99 eV. Based on the present study and literature, the governing mechanisms during low-temperature α -alumina thin film growth are summarized and discussed. Our results support suggestions made in some previous experimental studies, pointing to that limited surface diffusivity is not the main obstacle for α -alumina growth at low-to-moderate temperatures, and that other effects should primarily be considered when designing novel processes for low-temperature α -alumina deposition.

1. Introduction

As one of the most important ceramic materials, alumina (Al_2O_3) has been studied extensively in the past. [1] Besides applications as a bulk material, alumina thin films are used in numerous applications, e.g., as a dielectric layer in microelectronics, [2] as a catalyst support,[3] in thermal or diffusion barrier coatings, [4,5] and in wear-protecting layers.[6] The α phase of alumina is the only thermodynamically stable phase. However, metastable (transition) phases such as γ -, κ -, and θ -alumina commonly form, especially during synthesis at reduced temperatures.[3] Since these metastable phases will transform to α -alumina upon heating,[3] the α phase is often the desired phase in the types of applications where stability and preserved mechanical properties at elevated temperatures are necessary. This is of large importance in, e.g., wear-resistant coatings on metal-cutting tools, where phase transformations during operation are detrimental for the coating performance.[7,8] Industrially, α -alumina coatings are usually deposited at substrate temperatures close to 1000 °C using chemical vapor deposition (CVD).[6] To be able to coat a wider range of substrate materials and to avoid unwanted effects arising, e.g., due to different thermal expansion of film and substrate,[8] intense research on deposition methods for α -alumina at reduced temperatures has been conducted during the last decade. However, growing α -alumina at lower temperatures has proved not to be straightforward, and metastable phases often form instead. Using plasma enhanced CVD [9] and physical vapor deposition (PVD) techniques such as arc evaporation [10-12] and different types of magnetron sputtering, [13-15] α phase growth has been achieved at temperatures down to around 600 °C. In these studies, energetic bombardment was found to promote α -alumina growth, but it has also been shown that a too high energy of the bombarding species (i.e., a high substrate bias) again may result in formation of metastable phases. [16] While promotion of surface diffusion is often mentioned as the key role of the energetic bombardment, [9,12,17] other suggestions of the dominating effect of the bombardment have been made in the literature. These suggestions include defect generation and removal of impurities. [18,19] It has, e.g., been shown that residual water present in the deposition chamber might compromise the α -alumina content of the resulting films[18] (as well as deteriorate the properties of amorphous films [20]) and that energetic bombardment can be utilized to reduce the impurity incorporation into alumina coatings.[19] A further indication that promotion of surface diffusivity is not the only role of the bombardment is given by the fact that relatively high bombardment energies are needed (often exceeding 100 eV). [10-12,17] In addition to the results obtained using energetic bombardment, it has been shown that

α -alumina growth can be achieved at even lower temperatures by growth in ultra-high vacuum environment onto controlled nucleation surfaces. This has been done by either depositing alumina epitaxially onto single crystal α -alumina (sapphire) substrates [21] or by growing onto a pre-deposited Cr_2O_3 template layer. [22-24] Cr_2O_3 (more easily) forms the same crystalline structure as α -alumina and therefore promotes nucleation and growth of this phase through epitaxy.[23,25] Overall, the mechanisms governing the phase formation during alumina growth are not well understood and more fundamental knowledge is needed to better optimize deposition processes towards effective synthesis of α -alumina at lower temperatures.

Alumina surfaces have been studied extensively in the past, both experimentally and by theoretical means. This is not only motivated by the importance of alumina as a thin film material, but also by its wide use in catalysis applications and as a substrate material. Moreover, alumina is an often used model system for studies of fundamental properties of oxide surfaces in general. The (0001) surface is by far the most studied one and by many authors, though not all [26], observed to be most stable. [27,28] Three different terminations of this surface can be obtained by cleaving the bulk structure; two Al-terminated ones and one O-terminated surface. It is commonly accepted that the surface terminated by a single Al-layer is most stable,[28-30] although it has been shown that hydrogen on the surface may stabilize an O-terminated surface and alter the relaxation behavior of the surface layers significantly.[28,31-33] Many studies of the interaction between alumina surfaces and other metal atoms or surfaces have been carried out [34-39], mostly in the context of catalysis applications. However, the amount of literature dealing with investigations of the interaction of Al and O species with the surface is limited, in particular in the context of thin film growth. Rosén *et al.*[40,41] studied both adsorption and migration barriers for positively charged Al and O ions on the O-terminated (0001) surface using density functional theory (DFT) calculations. They showed that the adsorption energy of the metal ions was strongly dependent on the ion charge and adsorption site, and suggested that the presence of Al^{3+} or O^+ ions in the deposition flux might inhibit α -alumina growth. [40] The migration energy barrier for Al^+ ions from a metastable position to the stable site on the O-terminated surface was found to be 1.6 eV. [41] More recently, we presented DFT results on adsorption of neutral Al, O, and AlO species on differently terminated (0001) surfaces. [42] It was, e.g., shown that Al adsorption on the Al-terminated surface is quite uncomplicated with the bulk position being the only stable site, while several metastable positions exist on the O-terminated surface. Furthermore, Al adsorption in the bulk position was found to be hindered or weakened on hydrogenated surfaces, suggesting that hydrogen

might inhibit continued α -alumina growth. Here, these results are extended by a thorough investigation of hopping barriers for Al neutrals as obtained using DFT calculations and the nudged elastic band method. The results are analyzed in conjunction with previous experimental results of alumina thin film growth and the importance of surface diffusivity in comparison to other mechanisms is discussed.

2. Computational details

2.1 Calculation methods and parameters

Calculations were performed using the Vienna *ab initio* simulation package (VASP) [43,44], which employs a density functional theory (DFT) [45,46] based plane-wave method. Exchange-correlation effects were included using the generalized gradient approximation (GGA) [47] as proposed by Perdew and Wang. A plane-wave basis set including plane waves up to a cutoff energy of 400 eV, and a k-point mesh containing a single point was used. Dipole corrections were included in the calculations. To treat the ion cores, potentials of the projector augmented wave (PAW) [48,49] type were used. Further details pertaining to the computational setup used and the accuracy of the calculations can be found in ref. 42. The activation energy barriers for surface hopping processes were calculated using a type of nudged elastic band (NEB) method. [50,51] A climbing-image modification [52], where the image having the highest energy is moved towards a high energy position along the minimum energy path (i.e., the saddle point), was applied after the path was first converged without this feature. The positions of the atoms were optimized until the total forces on the (unconstrained) atoms were smaller than 0.03 eV/Å. This method is expected to ensure a very accurate identification of the transition states.

2.2 Slab geometry

The primitive cell of α -alumina is rhombohedral, but the conventional hexagonal cell is often more convenient to use in order to describe the structure, since the O atoms form an approximately hexagonal close packed (hcp) lattice with Al atoms in interstitial positions. [53] Throughout this paper, the hexagonal description will be used. The structure has a ...-O-Al-Al-O-Al-Al-... stacking sequence in the [0001] direction. Thus, three (0001) surface terminations are obtainable by cleaving the bulk structure; two Al- and one O-terminated. In the present study, the termination by a single Al layer as well as the O-terminated surface has been considered. This choice is motivated by the fact that the Al-termination is the most stable one, and therefore should be a commonly occurring surface for diffusion, and that metastable sites have been

found to exist on the O-terminated surface in our previous work on adsorption. [42] The existence and magnitude of energy barriers for jumps from the metastable positions to the bulk site are of course of interest in the context of film growth. Due to the computational demands of this type of calculations, the present study has been limited to representative single Al adatom hopping events, and more complex cases like, e.g., exchange processes and diffusion at steps, edges, and corners have not been studied. The surfaces were modeled using a slab geometry with 2×2 surface unit cells and periodic boundary conditions in all three directions. A total amount of 12 atomic layers was used in the slab (i.e., four full stoichiometric layers), with a vacuum depth separating the slabs in the [0001] direction of 12 Å. Further details can be found in ref. 42.

Recently, Hinnemann and Carter [54] published results on the adsorption behavior of a number of different atoms on the Al-terminated (0001) surface. For Al adsorption, discrepancies were found in the adsorption energies calculated with the bottom layers of the slab frozen in their bulk position, as compared to if all layers were allowed to relax. [54] In our previous work on adsorption,[42] the bottom six layers were fixed in bulk positions, a procedure commonly used to ensure bulk conditions in the bottom of the slab. [35,38-41] Hinnemann and Carter [54] found that the adsorption energy for an Al adatom was 2.3 eV when all layers were allowed to relax, compared to our previous value of 3.9 eV. [42] This was speculated to be due to the creation of an artificial dipole moment across the slab when having fixed layers, arising as a consequence of the ionicity of alumina, and affecting the adsorption energy of Al beyond the test calculations performed in ref. 42. [54] Therefore, the relevant adsorption energies from ref. 42 have in this work been checked with respect to this property. We find the adsorption energy for Al on the Al-terminated surface to be 2.4 eV with all layers relaxing, in agreement with the findings of Hinnemann and Carter. [54] However, adsorption energetics on the O-terminated surface turned out to be essentially unaffected by whether the bottom part of the slab was fixed or not, with changes in adsorption energies < 0.1 eV. Also, the changes in the results for O adsorption on the Al-terminated surface were minor. [54] Hence, it should be emphasized that the general conclusions drawn in ref. 42 still hold. In this paper, the energy barrier presented for the Al-terminated surface was obtained with all layers relaxing, and should consequently be free from errors caused by this type of artifacts. (Relaxing all layers in the slab changed the activation energy barrier by 0.07 eV, as compared to having six frozen layers.) For the O-terminated surface, results for six fixed bottom layers are presented, as motivated by the negligible change in adsorption behavior observed in this case.

3. Results and discussion

3.1 Al surface hops on $\alpha\text{-Al}_2\text{O}_3$ (0001) surfaces

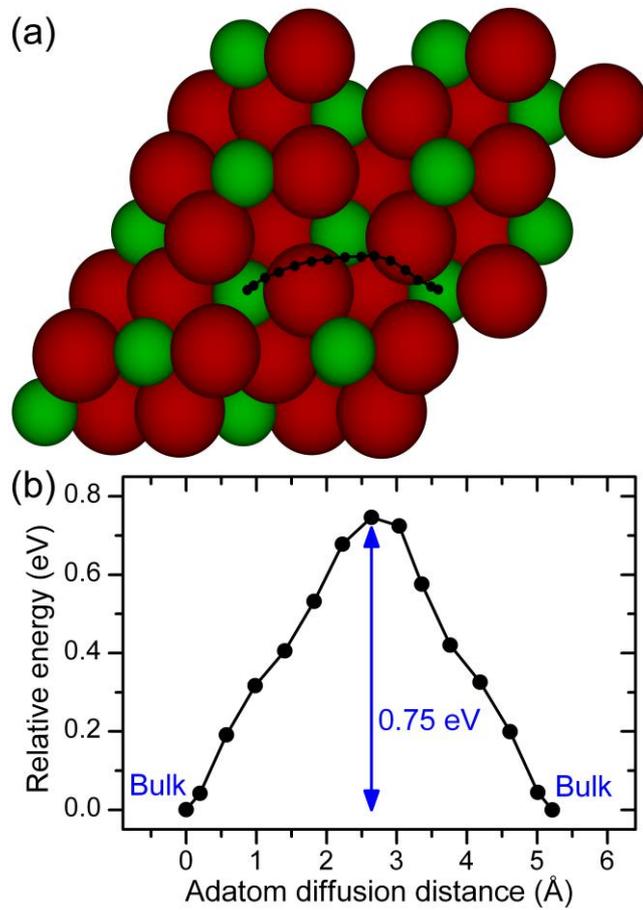


FIG. 1. (Color online) Minimum energy path for Al hops between bulk sites on the Al-terminated surface (a) and the corresponding relative energy along the path (b). O atoms are larger (red) and Al atoms smaller (green). The surface atoms are fixed in the positions obtained for adsorption in the bulk position in this illustration, but were allowed to move during the calculations.

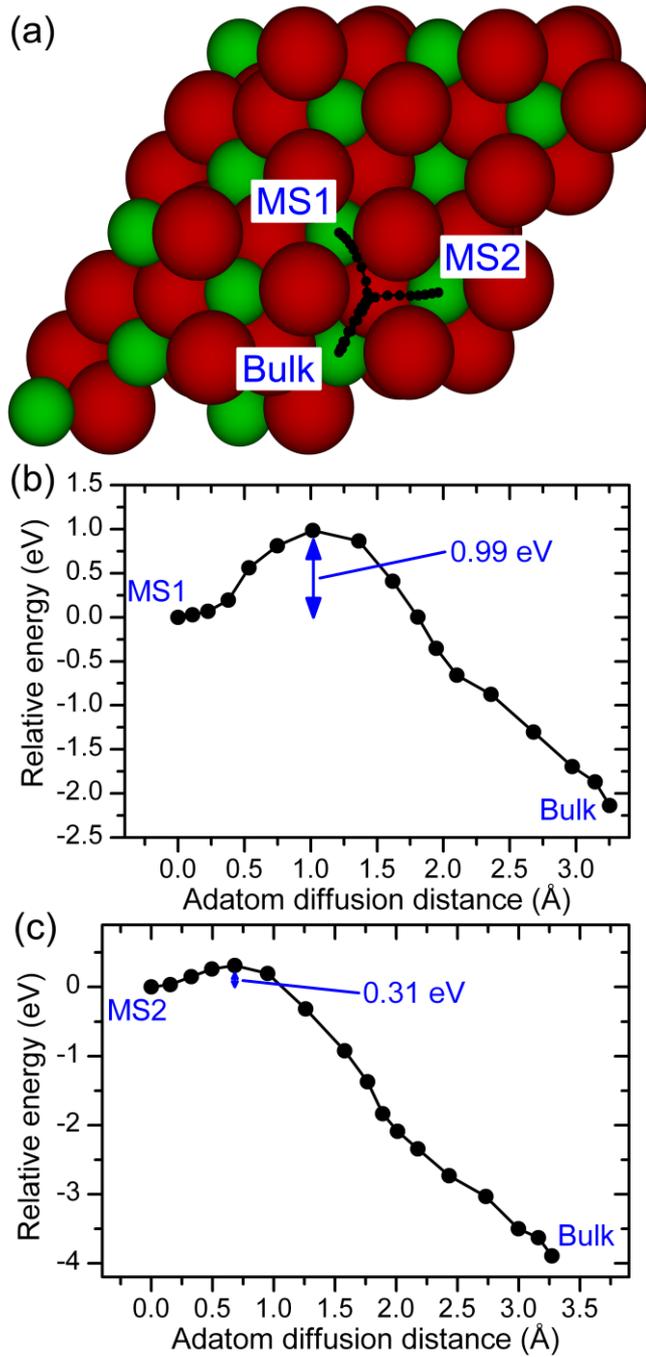


FIG. 2. (Color online) Minimum energy paths for hops from the two metastable sites MS1 and MS2 to the bulk position on the O-terminated surface (a). O atoms are larger (red) and Al atoms smaller (green). The surface atoms are fixed in the positions obtained for adsorption in the bulk position in this illustration, but were allowed to move during the calculations. The corresponding relative energies along the paths are shown for hops from MS1 (b) and MS2 (c) to the bulk position.

Table 1. Activation energies for Al hops on differently terminated α -Al₂O₃ (0001) surfaces, as well as the adsorption energies in the two endpoints [42].

Path	Energy barrier (eV)	Adsorption energies (eV)	
		Initial position	Final position
Al-termination			
Bulk – Bulk	0.75	2.4	2.4
O-termination			
MS1 – Bulk	0.99	11.9	14.0
MS2 – Bulk	0.31	10.1	14.0
Bulk – MS1	3.1	14.0	11.9
Bulk – MS2	4.2	14.0	10.1

Table 1 summarizes the calculated activation energies for the studied cases of Al adatom jumps on the Al- and O-terminated surfaces, as well as the adsorption energies in the two endpoints (see also ref. 42). On the more stable Al-terminated surface, the bulk position (on top of an Al atom in the fourth atomic layer) is the only stable Al adsorption site [42,54] with an adsorption energy of 2.4 eV. The barrier for adatom hops between such sites is moderate; 0.75 eV. The minimum energy path on the surface and the corresponding relative energy is illustrated in Fig. 1. (Note that the surface atoms are drawn in the positions corresponding to adsorption in the bulk site in Fig. 1(a), whereas they were allowed to relax during the actual calculations.) The Al adatom follows a somewhat non-intuitive path on the surface, passing quite close to two O atoms in the second surface layer, with a fairly smooth change in adsorption energy along the path as shown in Fig. 1(b). This can be seen as a consequence of the type of bonding Al has to the surface, which in previous work has been seen to be predominantly due to electrostatic interactions. [42,54] Hence, no abrupt breaking or forming of covalent-like bonds is expected during this hopping process. The point of highest energy along the path is located approximately halfway between the endpoints.

The barriers for adatom jumps on the less stable O-terminated surface, on which two metastable positions exist, [42] are considerably higher as seen from table 1. The metastable position designated MS1 is on top of an Al atom in the third atomic layer and has an adsorption energy of 11.9 eV, while MS2 is on top of an Al atom in the second atomic layer with an adsorption energy of 10.1 eV (cf. positions C and B in ref. 42). The adsorption energy in the bulk position, on top of an Al atom in the fifth atomic layer, is 14.0 eV. The minimum energy paths for hops from the two metastable sites to the bulk position both go via a position on top of an O atom in the fourth atomic layer, as shown in Fig. 2(a). (Note that also here, all surface atoms

are drawn in the positions corresponding to adsorption in the bulk site for clarity.) The transition states are located fairly close to the metastable positions, before the point where the two minimum energy paths merge, as seen from the energy changes along the paths plotted in Figs. 2(b) and (c). Due to the large difference in adsorption energy between the metastable sites and the bulk position, hops from the bulk site to MS1 or MS2 is subject to large barriers of 3.1 and 4.2 eV, respectively.

For Al⁺ ions, Rosén *et al.* [41] only identified one metastable site exhibiting a barrier for migration to the bulk position on the O-terminated surface. The energy barrier for this process was found to be 1.6 eV. [41] Hence, when comparing to our results, there seems to be a large difference in whether the diffusing species are ionized or neutral Al. This could be of practical importance in, e.g., thin film growth, even though in this case, one also needs to consider the probability of ions being neutralized on, or in the vicinity of, the surface and therefore diffusing as neutrals. Pd, on the other hand, has been found to be more mobile than Al on the Al-terminated surface, with the adsorption energies in (assumed) transition sites being only a few tens of meV higher than in the bulk position. [36] This can be attributed to the generally weaker interaction of Pd with the surface. [36] The barriers for Al adatom hopping calculated in the present study are comparable to the ones obtained for Ti on TiN (001) and (111) surfaces by Gall *et al.*[55] TiN is a common thin film material, which is easy to synthesize in crystalline form also at low temperatures. [56] Gall *et al.* [55] found activation energies for Ti diffusion between bulk sites of 0.35 and 1.74 eV on the (001) surface and the N-terminated (111) surface, respectively. Metastable positions were found on both surfaces, with barriers for migration to the bulk site of 0.06 eV on the (001) surface, and 0.78 eV on the N-terminated (111) surface.

3.2 Al surface diffusivity and alumina thin film growth

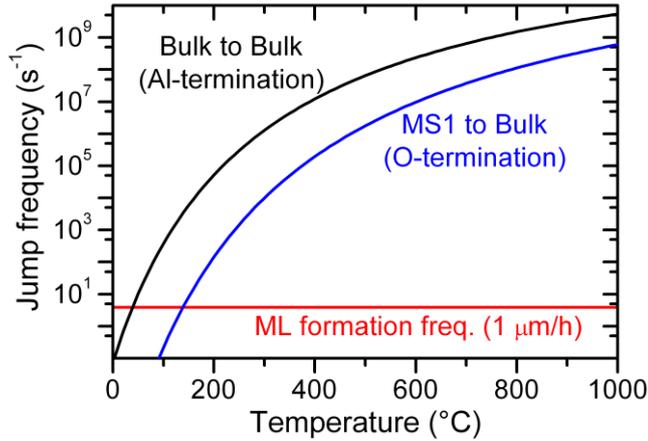


FIG. 3. (Color online) Adatom jump frequencies as a function of temperature for Al diffusion between bulk sites on the Al-terminated surface and for hops between MS1 and the bulk position on the O-terminated surface. An attempt frequency of 5×10^{12} Hz was assumed [cf. B. Hinnemann and E.A. Carter, *J. Phys. Chem. C* **111**, 7105 (2007); P. Gamallo and R. Sayós, *Phys. Chem. Chem. Phys.* **9**, 5112 (2007)]. The monolayer (ML) formation frequency at a film deposition rate of $1 \mu\text{m/h}$ is shown for reference.

In order to correlate the obtained surface hopping activation energies with previous experimental thin film growth results, adatom jump frequencies were estimated from transition state theory. Hence, jump frequencies were calculated as

$$\nu = \nu_0 e^{-E_b/kT}$$

where ν_0 is the attempt frequency, E_b the energy barrier along the minimum energy path, T is the temperature, and k is the Boltzmann constant. Based on previous calculations of vibrational frequencies of adsorbed species on $\alpha\text{-Al}_2\text{O}_3$ (0001) surfaces [54,57], an attempt frequency for adatom jumps of $5 \times 10^{12} \text{ s}^{-1}$ was assumed. To avoid adsorption in the metastable (non α -alumina) positions on the O-terminated surface, both hopping processes from MS1 and MS2 to the bulk site must be active during growth. Here, migration from MS1 is the limiting process as this barrier is considerably higher than for jumps from MS2 (0.99 compared to 0.31 eV). (Migration from the bulk position back to the metastable sites is very rare in the temperature range studied and is therefore not considered.) In addition, diffusion on the stable Al-terminated

surface is important as this surface is expected to be most occurring during growth; growing (0001) surfaces have been observed to exhibit steps with heights corresponding to the layer distance between such terminations [21] thereby suggesting, together with its high relative stability, that this termination is commonly exposed for Al diffusion. In a way, this is also in line with the results of the present study, where the Al adatom mobility on O-terminated surfaces is found to be negligible in the relevant temperature range. This suggests that if O-terminated domains would appear during growth, they would quickly be overgrown by Al adatoms diffusing fairly rapidly on the Al-terminated domains, reaching the edge of these. (The properties of the steps and the behavior of adatoms adjacent to them will of course also be highly relevant, but investigations of these matters are beyond the scope of the present paper.) When summarizing the above, two hopping processes can be identified as most relevant for α -alumina growth on the (0001) surface; hops from MS1 to the bulk position on the O-terminated surface, and diffusion between bulk sites on the Al-terminated surface. Figure 3 shows the obtained Al adatom jump frequencies for these two processes as a function of temperature. For reference the (average) monolayer (ML) formation frequency at a typical thin film deposition rate of 1 $\mu\text{m/h}$ is indicated. As can be seen, both types of hopping events are very rare close to room temperature, with jump frequencies below the ML formation frequency. However, already at temperatures of around 300 °C the jump frequency from MS1 to the bulk site on the O-terminated surface is more than three orders of magnitude higher than the ML formation rate. Moreover, assuming a jump length of 5 Å and a mean free time for diffusion of 1/100 of the ML formation time, the diffusion length on the most stable Al-terminated surface is ~ 90 nm at 400 °C. Hence, these observations indicate that growth of (0001) α -alumina would not be limited by a too low surface diffusivity above temperatures in the range of 300-400 °C. In addition, it is well known that processes with a high activation energy frequently obey the so-called Meyer-Neldel compensation rule, resulting in that a high energy barrier to some extent may be compensated for by an increased pre-exponential factor (attempt frequency). [58,59] Estimations of the magnitude of this effect in the present case (using a value of the Meyer-Neldel energy of 190 meV, based on literature [59]) show that the attempt frequency may increase by up to almost three orders of magnitude for the case of migration from MS1 to the bulk site on the O-terminated surface (with activation energy 0.99 eV). Hence, such an effect would contribute to an even higher mobility on the surface and displace the critical temperature where growth becomes diffusion-limited down to around 200 °C.

In experiments, epitaxial growth of alumina onto α -Al₂O₃ (0001) single crystals using molecular beam epitaxy has been shown possible down to temperatures around 300 °C, while amorphous films formed at lower temperatures. [21] Growth on the (0001) surface was found to be most difficult to maintain at lower temperatures as compared to the other studied surfaces [21], suggesting that this surface is a worst case scenario for surface diffusion. Moreover, sputter deposition of polycrystalline α -alumina has been achieved at temperatures down to 280 °C, when being epitaxially stabilized by chromia nucleation layers. [23] Hence, our results on surface mobilities are in good agreement with these experimental observations. Still, growth of polycrystalline α -alumina onto other substrate materials (e.g., steels and cemented carbides), and under worse vacuum conditions, has proved elusive. Among the many possible hindering mechanisms obstructing the deposition of α -alumina at low temperatures proposed in literature, limited surface diffusion is one of the main candidates. Nevertheless, there are numerous species which should be considered as relevant for surface diffusion during α -alumina thin film growth (Al and O, ions and atoms, Al-O complexes) on several possible surface terminations and/or steps. However, the study of all species and possible surface diffusion processes with DFT methods is currently an extremely computationally demanding, if not impossible, task. Within this context, our results clearly indicate that one of these processes, the limited surface diffusion of neutral Al adatoms, is of little importance in α -alumina thin film growth. In addition, the present results suggest that other obstacles put forward in the experimental literature are equally important, such as the presence of impurities, primarily hydrogen, on growth surfaces, and the inherent difficulty in nucleating α -alumina. For example, it has been shown that residual water in the process chamber hinders continued α -alumina growth and can cause a transition to γ phase growth [18,42], and, as also described above, several studies have shown that once α -alumina nucleation has been facilitated, growth can be carried out at fairly low temperatures. [16,22-25] This points to that the role of the energetic bombardment found necessary for α -alumina synthesis is to remove impurities on growth surfaces, and possibly to promote bulk diffusion in order to achieve a transformation to α -alumina growth if a metastable phase has first nucleated. This also explains the high bombardment energies found necessary. Rosén *et al.* [19] indeed showed that energetic bombardment can reduce the amount of hydrogen incorporated into growing alumina coatings, and consequently can be utilized as an alternative to high surface temperatures or good vacuum conditions in this respect. The nucleation difficulties of α -alumina may be explained by surface energy stabilization of metastable phases, in particular γ -alumina, at small enough grain sizes. [23,60] McHale *et al.* [58] showed

experimentally that, due to the lower surface energy of γ -alumina, the γ phase becomes energetically favored over α -alumina at specific surface areas greater than $125 \text{ m}^2/\text{g}$. Assuming an alumina density of $3.6\text{-}4.0 \text{ g/cm}^3$ (cf. ref. 3) and spherical grains, this corresponds to a grain diameter of $12\text{-}13 \text{ nm}$. Hence, during the initial stage of growth, γ -alumina is actually the energetically preferred phase. A similar effect may explain the transition back to γ -alumina growth at too high bombardment energies [12,16]: As the bombardment starts to induce defects and renucleation events, the grain size gets smaller and at some point the γ phase will be energetically preferred over α -alumina. All in all, the results presented here support previous suggestions made in literature pointing to that the design of future processes for low-temperature α -alumina thin film growth primarily should be focused on reducing the impurity (mainly hydrogen) content in the films and finding efficient ways of facilitating α -alumina nucleation, rather than promoting surface adatom mobilities.

4. Conclusions

Density functional theory calculations in combination with the nudged elastic band method have been utilized to obtain activation energies for Al adatoms surface hopping on the Al- and O-terminated α - Al_2O_3 (0001) surfaces. Diffusion of Al neutrals on the (most stable) Al-terminated surface was found to be relatively fast with an energy barrier of 0.75 eV , while hopping on the O-terminated surface is slower, with barriers for jumps from the two metastable positions existing on this surface to the stable site of 0.31 and 0.99 eV , respectively. These values were used, within transition state theory formalism, to estimate Al adatom jump frequencies as a function of temperature. Based on these results it was concluded that α -alumina thin film growth is not likely to be limited by surface diffusion of neutral Al adatoms at low-to-moderate temperatures. The present results support the suggestions made in some of the previous experimental papers, pointing to that the main obstacles for low-temperature α -alumina growth are impurities, in particular hydrogen, on growth surfaces, and difficulties in nucleating the α phase. Hence, the design of novel processes for low-temperature α -alumina growth could benefit dramatically from focusing on finding ways of overcoming these obstacles.

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