Ab initio studies of Al, O, and O_2 adsorption on α-Al$_2$O$_3$ (0001) surfaces

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(Received 12 July 2006; published 8 September 2006)

The interactions of Al, O, and O_2 with different α-Al$_2$O$_3$ (0001) surfaces have been studied using *ab initio* density functional theory methods. All three surface terminations obtainable by cleaving the bulk structure [single Al-layer (AlO), double Al-layer (AlAl), and O terminations] have been considered, as well as a completely hydrogenated O-terminated surface. Adsorbed Al shows strong ioniclike interaction with the AlO- and O-terminated surfaces, and several metastable adsorption sites are identified on the O-terminated surface. On the completely hydrogenated surface, however, Al adsorption in the bulk position is found to be unstable or very weak for the studied configurations of surface H atoms. Atomic O is found to interact strongly with the AlAl-terminated surface, where also O_2 dissociative adsorption without any appreciable barrier is observed. In contrast, O adsorption on the AlO-terminated surface is metastable relative to molecular O_2. On the O-terminated surface, we find the creation of O surface vacancies to be plausible, especially upon exposure to atomic O at elevated temperatures. The results are mainly discussed in the context of alumina thin film growth and provide insight into phenomena related to, e.g., preferred adsorption sites and effects of hydrogen on the growth.

I. INTRODUCTION

Alumina, Al$_2$O$_3$, is one of the technologically most important ceramic materials. It can be found in microelectronics, thermal and diffusion barrier coatings, as well as catalysis and cutting-tool applications. Part of the explanation for the broad applicability of alumina is the existence of several polymorphs with different properties.[1] For example, the α phase, also known as corundum and the only thermodynamically stable form of alumina, is commonly utilized in wear-resistant coatings and as a substrate material in, e.g., optics and electronics, whereas metastable alumina phases (e.g., the γ phase), are often used in catalysis applications due to their high specific surface areas.

Applications in catalysis, as thin films, and as substrate material, explain the importance of alumina surfaces and, consequently, much work has been devoted to both experimental and theoretical studies of, in particular, α-alumina surfaces. Previous reports[2,3] have, although not completely unanimously,[4] identified the (0001) surface as the most stable α-Al$_2$O$_3$ surface. It is also, by far, the most studied one and often serves as a prototype for oxide surfaces in general. It is well established that this surface is unreconstructed under most conditions, but a rotated $\sqrt{31} \times \sqrt{31}$ surface reconstruction occurs at elevated temperatures (>1250 °C).[5–7] The amount of relaxation of the outermost layers and the stable termination of the surface have however been a matter of controversy, and it was not until recently that some plausible explanations for the discrepancies between different studies were presented. Many authors have observed a surface terminated with a single Al-layer,[8] whereas, e.g., Jaeger *et al.*[9] reported an O-terminated surface for ultrathin films, and Toofan and Watson,[10] a mixture of Al- and O-terminated domains. From a chemistry point of view, one may expect the O-terminated surface to be less stable since it, contrary to the Al-terminated surface, has a nonzero dipole moment. This is

also in line with what computational studies have showed.[11,12] However, the amount (and in some cases also the direction) of the relaxations of the outermost layers show a spread in values both in experimental investigations and early theoretical studies.[8,10,13,14] More recent first-principles calculations have revealed that the origin of the experimental inconsistencies could be hydrogen on the surface. For example, Wang *et al.*[15] showed that the single Al-terminated surface is stable up to high oxygen partial pressures with large inward relaxations, but that the O-terminated surface can be stabilized by hydrogen. Other calculations have confirmed that hydrogen strongly affects the surface,[3,16–18] and different terminations of the clean and hydrated surface have also been observed experimentally.[19] Moreover, the dissociation mechanism of water on the surface has been thoroughly investigated, and H$_2$O has been shown to dissociate readily.[20] Hence, the general belief at present is that the stable clean (0001) surface is Al-terminated with large relaxations, whereas hydrogen on the surface, stemming from, e.g., residual water, strongly affects the properties and can stabilize an O-terminated surface.

Previous adsorption-related studies have mainly concerned investigations of the interaction between different metals and the (0001) surface. For example, Lodziana and Norskov[21] studied the interaction of Cu and Pd with different (0001) surfaces and found that it was weak and covalentlike for the Al-rich surface, whereas it was stronger and more ioniclike for the O-terminated surface. Similar observations have been made for the adhesion between α-Al$_2$O$_3$(0001) and metal surfaces, e.g., Al(111), Cu(111), and Ag(111).[22,23] Bogicevic and Jennison[24] studied metal adsorption on ultrathin (5 Å) Al$_2$O$_3$ films on Al(111) and found that the bonding for most studied metals was ionic at low coverages.

The motivation behind the present study is primarily to increase the understanding of alumina thin film growth. Owing to the wide range of applications for alumina coatings, a

considerable amount of growth studies has been made, as exemplified in Refs. 25–30. Often, the α phase is the desired polymorph in growth situations. However, this phase is difficult to deposit at low substrate temperatures ($<$1000 °C), and to be able to reduce the temperature, energetic bombardment,[26,27] nucleation layers,[29,30] or a combination of these[31] have been shown to be necessary. Proposed explanations for the difficulties in growing the thermodynamically stable phase at lower temperatures include too high diffusion energy barriers[26] and surface energy stabilization of metastable phases during the nucleation stage of growth.[30] However, no coherent picture of the mechanisms behind the phase formation and structure evolution exists. An increased atomic scale understanding of alumina surface processes would thus be an important step toward a more complete control of the deposition process. The only adsorption study related to alumina thin film growth found in literature is the computational work by Rosén *et al.*[32] They studied Al$^+$, Al^{2+}, Al^{3+}, and O$^+$ adsorption on the O-terminated surface with results showing a strong site and charge dependence of the adsorption energies.

In this paper, we report on first-principles computational studies of Al, O, AlO, and O$_2$ adsorption on alumina using the (0001) surfaces of α-Al$_2$O$_3$ as a model system. All three surface terminations obtainable by cleaving the bulk structure, as well as a H-covered O-terminated surface, have been studied to be able to relate to not only ultrahigh vacuum (UHV) equilibrium situations, but also non-UHV conditions and nonequilibrium processes occurring, e.g., during thin film growth. Al, O, and O$_2$ species are unarguably the most important species present in many such situations. The results are relevant for the understanding of crystalline alumina thin film growth processes and are mainly discussed in this context. They can, however, also provide important understanding of alumina surfaces in, e.g., catalysis applications, as well as for properties of oxide surfaces in general.

II. METHODS

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 approximately form a hexagonal close packed (hcp) lattice with Al atoms occupying 2/3 of the octahedrally coordinated interstitial positions.[33] Throughout this paper, hexagonal indexing is therefore used. The structure has a …-O-Al-Al-O-Al-Al-… stacking sequence in the [0001] direction, with $\sim$2.2 Å between the O planes in the bulk configuration. Thus, three (0001) surface terminations are obtainable by cleaving the bulk structure: two Al- and one O-terminated. These three surfaces together with the completely H-covered O-terminated surface are the ones that have been considered in this work. We will refer to the surface terminated by two Al layers as AlAl terminated, and to the surface terminated with a single Al layer as AlO terminated. The surfaces were modeled using a slab geometry with 2×2 surface unit cells and periodic boundary conditions in all three dimensions. This configuration results in a separation between the periodic replicas of the adsorbates in the (0001) plane of

$\sim$9.6 Å. For all terminations, a total amount of 12 layers was used in the slab (i.e., four O layers), out of which the six bottom layers were frozen in their bulk positions (as calculated prior to the surface calculations). The topmost six layers were allowed to relax in all calculations. The vacuum depth separating the slabs in the [0001] direction was 12 Å. The number of layers in the slab, as well as the vacuum depth needed, were carefully tested and are consistent with what has been found sufficient in previous studies of alumina surfaces.[20,21] For example, our test calculations show that increasing the number of free layers to 12 while keeping six frozen layers, alters the adsorption energy of an Al adatom on the AlO-terminated surface by $<$0.1 eV.

All calculations were carried out using a density functional theory (DFT)[34,35] based plane-wave method, as implemented in the Vienna *ab initio* simulation package (VASP).[36,37] The generalized gradient approximation (GGA) proposed by Perdew and Wang was used with spin-polarization included.[38] It is known that the local density approximation (LDA) in some cases better succeeds to describe properties like surface and interfacial energies, due to a fortunate cancellation of errors.[39] However, other studies have shown that adsorption behavior is more accurately described by GGA functionals,[40,41] and we have therefore made the choice to perform our calculations within the GGA. To treat the ion cores, the standard potentials of the projector augmented wave (PAW)[42,43] type supplied with VASP were used. The atomic positions were optimized using a conjugate gradient algorithm until the forces on the unconstrained atoms were smaller than 0.03 eV/Å. Careful convergence tests showed that 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, give energies computationally converged to within 2 meV/atom. Results for bulk alumina using these approximations are in good agreement with previous experimental and computational studies, as described in detail elsewhere.[44] Since some of the studied surfaces are polar, dipole corrections were included in the calculations to avoid errors introduced by electrostatic effects.

Adsorption energies E_{ads} were obtained by subtracting the energy of the clean surface and free atom-molecule, from the energy of the system with adsorbate on the surface, i.e., $E_{ads}=E_{s+a}-(E_s+E_a)$, where E_{s+a} is the energy of the surface with adsorbate, E_s is the energy of the clean surface, and E_a is the energy of the free atom or molecule. The vacancy formation energy E_{vac} and the energy required to form a vacancy and a diatomic molecule instead of an adsorbed atom $E_{vac+mol}$ were calculated in a similar manner. Thus, $E_{vac}=(E_{s+vac}+E_a)-E_s$, and $E_{vac+mol}=(E_{s+vac}+E_{mol})-E_{s+a}$, where E_{s+vac} is the energy for the surface with vacancy and E_{mol} the energy of the free molecule. The energies of the isolated Al and O atoms, and the O$_2$ molecule were presented in a previous work,[44] while the energies of the H atom and AlO molecule were calculated to be -1.11 and -7.97 eV, respectively, using settings in analogy with Ref. 44. The obtained bonding distance for the AlO molecule, 1.63 Å, is in excellent agreement with the experimental value of 1.62 Å, and the estimated binding energy (using a tabulated value for the entropy) of -5.60 eV at 298 K is in fair agreement with the experimental value of -5.20 eV.[45,46]

TABLE I. Relaxation (in percent) of the topmost layer distances of the clean Al-terminated surface compared to previous results. The changes reported are with respect to calculated plane spacings for the perfect bulk.

Layers	Present	Ref. 17	Ref. 21
Al-O	−90.1	−82.5	−87.5
O-Al	3.9	4.2	3.2
Al-Al	−45.0	−43.0	−46.4
Al-O	19.6	19.2	20.4

To gain further understanding of the interaction between the adatoms and the surface, charge density and charge density difference plots are presented in some cases.[47] The charge density difference was calculated as the density of the slab with adsorbate minus a superposition of the density of an isolated adatom and the slab (in the same geometry as with adsorbate), i.e., $\Delta\rho(\mathbf{r}) = \rho_{s+a}(\mathbf{r}) - [\rho_a(\mathbf{r}) + \rho_s(\mathbf{r})]$.

III. RESULTS AND DISCUSSION

A. AlO-terminated surface

As mentioned in the Introduction, the AlO termination is believed to be the most stable one, at least under UHV conditions, and is accordingly the most studied (0001) surface termination. Our results for the relaxations of the topmost layers are in good agreement with previous DFT studies, as seen from Table I, and we therefore conclude that our model correctly reproduces the properties of the clean surface. The top Al atoms on this surface relax heavily, almost down to the same plane as the O layer (Al-O layer distance 0.08 Å, compared to 0.85 Å for bulk alumina).

Figure 1 shows the attempted adsorption sites on the AlO-terminated surface. Position D is on top of an Al atom in the fourth atomic layer and corresponds to the Al position in bulk Al$_2$O$_3$. Positions A and C are on top of Al atoms in
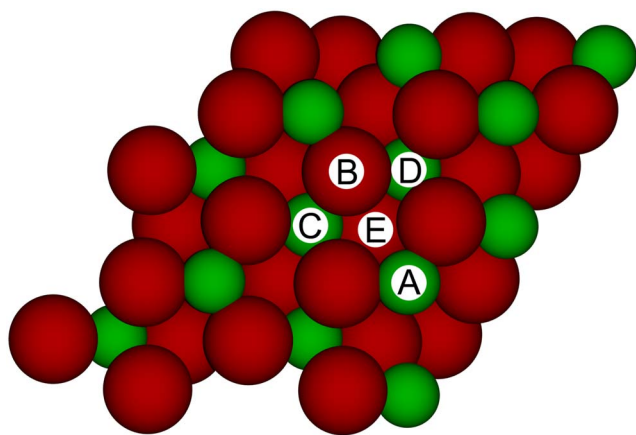

FIG. 1. (Color online) Studied adsorption sites on the AlO-terminated surface. O atoms are drawn larger. The image shows the full computational cell, i.e., 2×2 primitive surface unit cells.

TABLE II. Adsorption energies (in electron volts) for Al and O on the five different adsorption sites studied on the AlO-terminated surface. A dash indicates that no adsorption occurred in that position. Note that sites A and C correspond to saddle points for Al adsorption (see text).

	E_{ads} (eV)	
Position	Al	O
A	(−2.9)	−1.8
B		−2.3
C	(−3.1)	
D	−3.9	
E		

the first (top) and third atomic layer, respectively, while positions B and E are on top of O atoms in the second and fifth layer. The calculated adsorption energies for Al and O in the different positions are shown in Table II. The only stable adsorption site for Al on this surface is the bulk position D, with an adsorption energy of −3.9 eV. Consequently, incoming Al atoms during alumina growth would spontaneously occupy their bulk positions without any need for activated surface diffusion. The distance between the Al adsorbate in position D and the O layer, 1.3 Å, is only slightly smaller than the layer separation found for the AlAl-terminated surface. Upon Al adsorption in this position, the surface structure changes so that all Al atoms in the top layer, except the one closest to the adsorbate, move to positions just below the O layer. No barrier for this process was observed, indicating that the top Al atoms easily move to occupy positions below the O layer, close to the free interstitial positions found there. Results from adsorption attempts in positions A and C indicate that these positions are saddle points. Hence, weak forces act on the adatoms in the exact adsorption positions, but a slight perturbation causes the adatoms to move to position D seemingly without barrier. The adsorption energies in the saddle points A and C are −2.9 and −3.1 eV, respectively, indicating that the activation barrier for Al adatom surface diffusion between bulk sites on this surface is of the order of 0.8 eV (assuming diffusion via site C). However, to fully elucidate the barrier height, more careful investigations would be necessary. Adsorption in position B or E, i.e., on top of O atoms, is unstable and the adatoms spontaneously move to bulk positions during the energy minimization process. An electron density plot for adsorption in the stable position D is shown in Fig. 2. The charge density indicates a predominantly ionic bonding, with extensive charge transfer from the Al adatom to the surface, resulting in a slightly polarized Al charge density.

Recent mass spectrometry characterization of magnetron sputtering plasmas during alumina growth has shown large fractions of AlO molecules in the deposition flux.[48] For this reason, adsorption of AlO complexes in positions A, C, and D was attempted. Only starting configurations with the molecule "standing" on the surface, with the Al atom closest to the surface and the Al-O bond being perpendicular to it, was tested. The molecules adsorbed without dissociating and remained standing, with a trend closely resembling that of in-
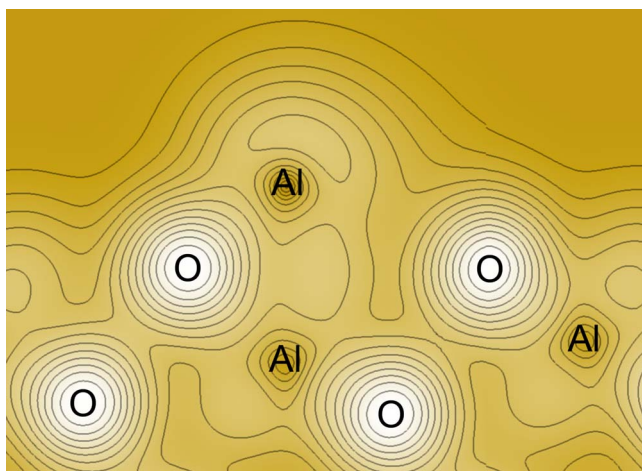
FIG. 2. (Color online) Charge density plot in logarithmic scale for an Al adatom (top atom) adsorbed in position D. The plane corresponds to a cut through sites B and D in Fig. 1 (perpendicular to the surface). Brighter areas correspond to higher charge density.
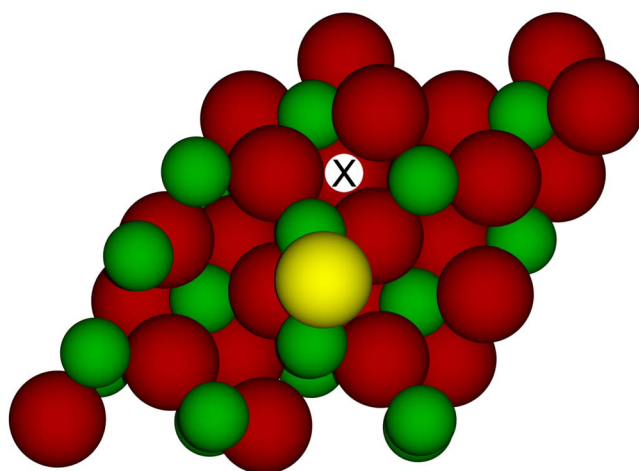

FIG. 3. (Color online) The stable O adsorption site on the AlAl-terminated surface. O atoms are drawn larger with the O adatom being brighter. The adatom resides close to its bulk position (another equivalent position is marked X). The image shows the full computational cell, i.e. 2×2 primitive surface unit cells.

dividual Al atoms. Hence, position D was found to be the only stable site, with an adsorption energy of −3.7 eV.

O exhibits stable adsorption on only two sites on this surface: A and B. The interaction is fairly weak in both cases, with adsorption energies of −1.8 and −2.3 eV, respectively. Consequently, adsorption of isolated O atoms is stable in these positions, but adsorption on both sites is unstable relative to O in the O_2 molecule form, with adsorption energies of 1.3 and 0.8 eV in this case. Hence, our results show no driving force for interruption of the crystalline sequence through dissociative adsorption of O_2 on this surface during thin film growth, even though single O atoms, at least temporarily, might reside on the surface.

B. AlAl-terminated surface

Table III shows the calculated relaxations for the Al-rich termination. The agreement between different studies in this case is inferior compared to the AlO-terminated surface. Our results show an outward relaxation of the top Al layer, which is in agreement with Ref. 17. However, the relaxation in their case is considerably smaller. No data for the relaxation of the first layer distance is published in Ref. 21, but the trend in

TABLE III. Relaxation (in percent) of the topmost layer distances of the clean AlAl-terminated surface compared with previous results. The changes reported are with respect to calculated plane spacings for the perfect bulk. The two results from the present study are for two different slab geometries (see text).

Layers	Present 6+6 layers	Present 6+12 layers	Ref. 17	Ref. 21
Al-Al	32.4	35.0	12.1	
Al-O	−13.1	−13.1	2.0	−19.4
O-Al	7.4	7.3	1.7	15.2
Al-Al	−2.4	−5.3	−4.7	8.6

the relaxations of the underlying layers shows a good agreement with our calculations. Possible sources for the discrepancies could be the use of different exchange-correlation functionals and different slab geometries. For example, in Ref. 17 a different computational setup was used with, among other things, the local density approximation instead of the GGA. In Ref. 21, the GGA and the same total number of atom layers (i.e., 12) as in our case were used, but fewer layers were frozen in their bulk position. This could cause unphysical relaxations on the "bulk" (frozen) side of the slab, since the relaxations seem to go fairly deep into the material.[21] Similarly, too few free layers might also introduce errors. One of our test calculations with an additional six free atomic layers (i.e., six frozen and 12 free layers in total) resulted in a relaxation behavior very close to the one observed with six free layers, as seen from Table III. Hence, we judge that six free layers describe the surface sufficiently well to enable predictions of adsorption behavior.

Al adsorption was found stable only on the site corresponding to the bulk Al position after an O layer has been added (i.e., on top of an Al atom in the fourth atomic layer). The adsorption energy at this position, −3.7 eV, is comparable to the adsorption energies calculated for the AlO-terminated surface. This might be interpreted as an indication that stable adsorption corresponding to an interruption of the crystalline stacking sequence is likely. However, as was pointed out for the AlO-terminated surface in the preceding section, the Al atoms easily move "through" the O layer on the AlO-terminated surface and, hence, Al adsorbed in this position is likely to spontaneously occupy its correct position when an O overlayer is formed. Indeed, when an O adatom is placed in the bulk position (see Fig. 3), after an Al atom has been adsorbed, they relax (seemingly without barrier) to positions with the Al atom in the top atomic layer and the O atom closer to the surface. Thus, our results show no possibilities of interruption in the crystalline stacking sequence through Al adsorption on this surface, e.g., during thin film growth.
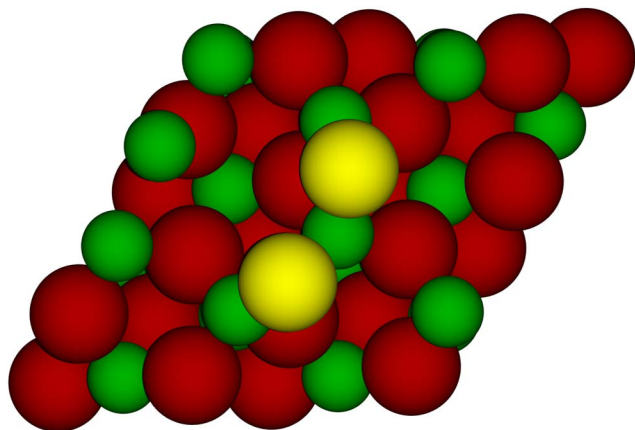
FIG. 4. (Color online) A dissociated O$_2$ molecule on the AlAl-terminated surface. O atoms are drawn larger, and the O adatoms are bright.
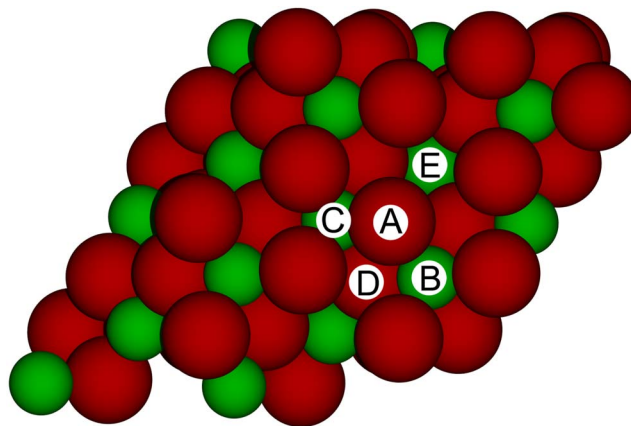

FIG. 5. (Color online) Studied adsorption sites on the O-terminated surface. O atoms are drawn larger. The image shows the full computational cell, i.e., 2×2 primitive surface unit cells.

All attempted starting configurations for O adsorption resulted in relaxations to positions equivalent with the one shown in Fig. 3, i.e., close to the bulk position, but slightly displaced toward neighboring Al atoms. The adatom adsorbs strongly, with an adsorption energy of −8.0 eV. Hence, the adsorption energy relative to O in molecular form is as large as −4.9 eV. The charge density (not shown) reveals a mainly ioniclike interaction between the adsorbate and the surface, with charge transfer to the O adatom. When both an Al and an O atom are adsorbed on the surface, as discussed in the preceding paragraph, some additional charge is transferred to the O adsorbate and it is displaced toward its bulk position.

O$_2$ molecular adsorption was attempted with three different starting configurations: two with the molecule lying parallel to the surface and one with the molecule perpendicular to the surface (all with the molecule in its triplet ground state). Interestingly, all three initial configurations result in spontaneous dissociation of the molecule, with O atoms moving to occupy positions equivalent with the stable adsorption sites identified for atomic O. A typical relaxed configuration is shown in Fig. 4. Thus, our results suggest thin film growth to be relatively unproblematic on this surface, with no metastable adsorption sites and without any appreciable activation barrier for dissociative adsorption of O$_2$ molecules.

C. O-terminated surface

The relaxations of the topmost layers of the clean O-terminated surface are shown in Table IV. The inward

relaxation of the top layer is seen to be smaller than for the AlO-terminated surface, but still considerable. This is in agreement with previous studies, indicating that the properties of the surface are correctly reproduced. The top layer O atoms produce a net magnetic moment at the surface, with the low-energy state having the individual magnetic moments aligned in parallel.

Figure 5 shows the studied adsorption sites for atoms on this surface and Table V, the calculated adsorption energies for Al. Position E is on top of an Al atom in the fifth atomic layer and corresponds to the Al position in bulk alumina. Positions B and C are on top of Al atoms in the second and third atomic layer, respectively, while positions A and D are on top of O atoms in the topmost and fourth layer. Al adsorbs strongly in all three positions B, C, and E, but distinctively strongest in position E, which corresponds to the bulk position. The electron density indicates an ionic type of bonding with extensive charge transfer from the adsorbed Al atom in all three cases, as exemplified in the charge density plot shown in Fig. 6. The ionic type of bonding is consistent with what has been observed previously for adsorption of other metals at low coverages on this surface.[21,24] A clear difference in the distance between the adsorbate and the surface can be made in the three cases. For adsorption in position E, the atom relaxes down to a position almost at the same level as for the relaxed AlO-terminated surface (a relaxation in the Al-O layer distance of −65%). In positions B and C, however, the atom resides at a distance from the surface compa-

TABLE IV. Relaxation (in percent) of the topmost layer distances of the clean O-terminated surface compared with previous results. The changes reported are with respect to calculated plane spacings for the perfect bulk.

Layers	Present	Ref. 17	Ref. 21
O-Al	−13.2	−7.2	−14.4
Al-Al	−6.9	−1.5	−10.3
Al-O	13.5	7.3	15.3
O-Al	−7.7	−0.6	−5.9

TABLE V. Adsorption energies (in electron volts) for Al on the five different adsorption sites studied on the O-terminated surface. No adsorption occurred in position A or E.

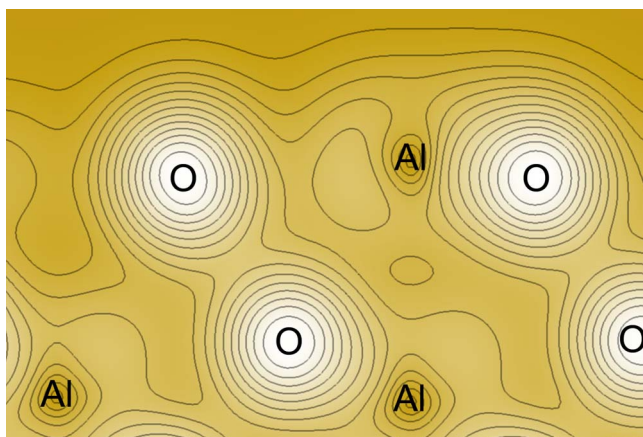| Position	E_{ads} (eV)
A	
B	−10.1
C	−11.7
D	
E	−14.0

FIG. 6. (Color online) Charge density plot in logarithmic scale for an Al adatom (top atom) adsorbed in the bulk position E. The plane corresponds to a cut through sites A, D, and E in Fig. 5 (perpendicular to the surface). Brighter areas correspond to higher charge density.
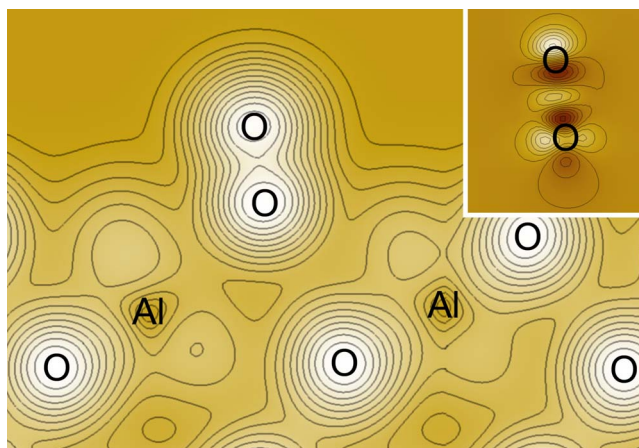

FIG. 7. (Color online) Charge density plot in a plane perpendicular to the surface for an O atom adsorbed on top of an O surface atom on the O-terminated surface (logarithmic scale). The inset shows the charge density difference induced by the adatom (linear scale). Bright areas correspond to charge accumulation and dark areas to charge depletion.

rable to, or slightly larger than, the layer distance in bulk alumina. Adsorption attempts of Al in positions A or D (on top of O atoms) resulted in barrierless relaxations to positions equivalent with C or E. Also for this surface, adsorption of AlO molecules was attempted for the positions found stable for Al atoms. Only starting configurations with the molecule standing on the surface, with the Al atom near the surface, were tested. Similar to the case of the AlO-terminated surface, the complex adsorbs in a standing position without dissociating. The adsorption energies were found to be -7.2, -8.6, and -11.9 eV for positions B, C, and E, respectively. Hence, the trend follows that of individual Al atoms also on this surface.

The stronger interaction with this surface, as compared to the previously discussed cases, further demonstrates the relative instability of the O-terminated surface. The strong bonding of Al, also at nonbulk positions, is consistent with what has been calculated for positive Al ions.[32] This might indicate that an interruption in the crystalline sequence, resulting in amorphous growth, growth of another phase, or introduction of lattice defects, would occur if the energy supplied to a growing film surface is too low, so that the diffusion from the metastable sites to the bulk position is limited. Similar suggestions have been made based on experimental investigations of thin film growth, where a larger momentum transfer to the growth surface has been found to promote crystalline alumina growth,[26] and based on the theoretical results for ions by Rosén *et al.*[32] However, as was mentioned in the Introduction, other experimental studies point out the importance of the nucleation stage of growth and suggest that the stabilization of other phases at this stage might be a strong reason for the observed difficulties in synthesizing the α phase.[30,49] Further investigations of, e.g., the diffusion barriers between the metastable Al sites and the bulk position, are needed in order to gain a more complete understanding of these issues.

O adsorbs significantly weaker on this surface. In the vicinity of positions B–E, there are adsorption states where the O adatom stabilizes close to one or two of the surrounding O

atoms. The surface atoms move upward, indicating that their bonding to the surface is weakened. The electron density indicates a covalentlike type of bonding between the adsorbate and either one or two surface O atoms. An example of the charge density and charge density difference for an O adatom adsorbed on top of an O surface atom is shown in Fig. 7, with a density difference revealing charge accumulation between the O atoms, indicating covalentlike interaction. The adsorption energies range from -3.9 to -4.5 eV, depending on the bonding configuration. In position A, no stable adsorption occurs. Instead, the adatom forms a covalentlike bond to the underlying O atom (with a bonding distance close to that of O_2), and both atoms move away, indicating spontaneous formation of a (very weakly bound) O_2 molecule on the surface. In positions B and E, an additional weak (metastable) adsorption state is found, where the magnetic moment of the O adatom is aligned with those of the surface O atoms. The adsorption energies in this state are -0.8 and -1.2 eV, respectively.

In view of these observations, the formation energy of an O surface vacancy was calculated, yielding a value of 2.5 eV. This means that the formation of an O_2 molecule and two O vacancies is energetically favored by 1.2 eV (assuming the formation energy of the second vacancy to be identical to that of the first one), even though the kinetic barrier for this process is unknown. Hence, the reaction where O_2 molecules might desorb from the O-terminated surface competes with the process of O_2 dissociative adsorption on the AlAl-terminated surface discussed in the preceding section. This result further emphasizes earlier findings by, e.g., Wang *et al.*[15] showing that the O-terminated surface is unstable also at high O_2 partial pressures and that O deficient configurations are favored. Moreover, our results show that only 0.8 eV is gained by atomic O adsorption at the strongest adsorption site, compared to the formation of a vacancy and an O_2 molecule. It is important to note that the present calculations are done at 0 K and that entropy effects might very
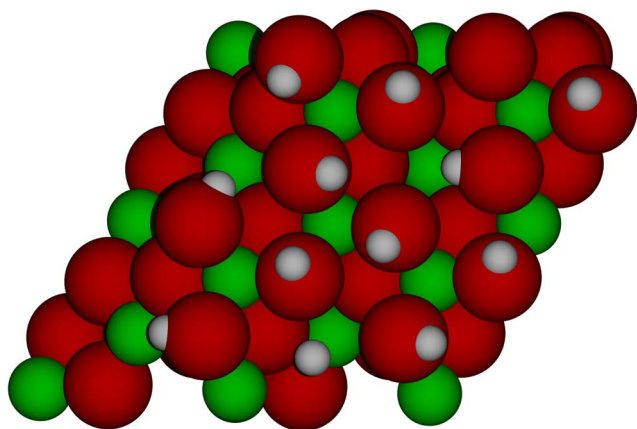
FIG. 8. (Color online) The completely hydrogenated O-terminated surface. O atoms are drawn larger and H atoms are small and bright.
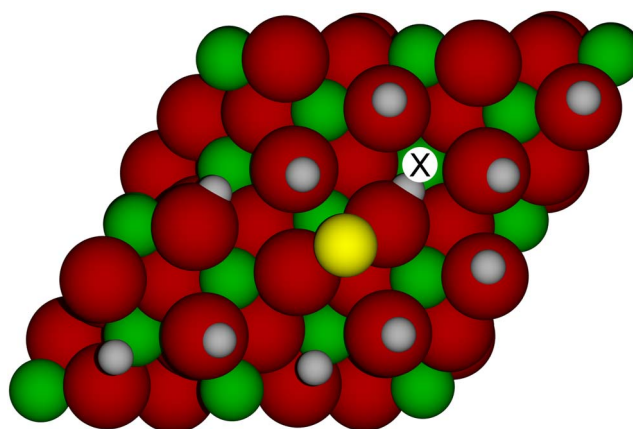

FIG. 9. (Color online) A relaxed configuration after an attempt of Al adsorption in the bulk position (marked X) on a hydrogenated surface. O atoms are drawn larger and the added Al atom is bright.

well cause the formation of a vacancy and an O$_2$ molecule to be the energetically stable configuration at higher temperatures. Indeed, an estimation of this effect, using a tabulated value for the entropy of O$_2$ (Refs. 46 and 50) and neglecting the entropy of the surfaces, shows that the free energy of the molecule is lowered by 0.8 eV at ~360 K and, accordingly, that the formation of an O vacancy upon exposure to atomic O is energetically favored at higher temperatures. (The energy differences here are quite small in relation to the approximations made. Hence, the exact numbers presented should be interpreted with care.) This result for neutral O is somewhat in contrast to that obtained for O ions by Rosén *et al.*[32] They find that O$^+$ ions adsorb strongly on the O-terminated surface and state that this might be a reason for the evolvement of an amorphous structure when O$^+$ ions are present in the deposition flux during thin film growth. Our results do not provide any evidence that this is the case for neutral O. Instead, we find that atomic O is likely to create O surface vacancies, with consequent formation, and possible desorption, of O$_2$. It should, however, be noted that a barrier for desorption probably exists, even though the result from the adsorption attempt in position A suggests that it is small. These results indicate that the presence of excess atomic O during alumina growth might inhibit growth of (0001) planes and therefore, e.g., alter the resulting texture of polycrystalline thin films. A similar influence of whether gas species at the surface are molecules or atoms has been observed for TiN and has been proposed as an explanation for the experimentally observed change from a 111 to a 001 textured growth as the amount of atomic nitrogen present on the growth surface increases.[51]

D. Hydrogenated O-terminated surface

In high-vacuum systems used for, e.g., thin film synthesis, water is the most occurring residual gas. Since hydrogen previously has been found to stabilize the O-terminated surface[15] and water has been shown to readily dissociate on alumina surfaces,[20] we have chosen to also study a hydrogenated O-terminated surface. Only the fully hydrogenated

(gibbsitelike) surface,[52] with one H per surface O atom, was studied. Six different starting configurations were attempted, with different starting positions of the H atoms relative to the surface O atoms. They all relaxed to structures resembling the one shown in Fig. 8. One out of three OH bonds is lying parallel to the surface with the in-plane H atoms being close to the Al bulk positions, while the rest of the OH bonds point upward from the surface. Table VI shows the calculated surface relaxations, which are seen to agree well with previous reports for the gibbsitelike surface. The H atoms cause a change in the relaxation behavior, as compared to the clean O-terminated surface (Table IV), with outward relaxation of the outermost O layer and a reduced distance between the two Al layers closest to the surface. Hydrogen also compensates for the dangling bonds of the O-terminated surface and is therefore found to decrease the surface energy, as seen in previous studies.[15]

In order to gain some further insight into the behavior of crystalline alumina growth in the presence of hydrogen, Al adsorption on the hydrogenated surface was studied. Adsorption was attempted on several surfaces with different configurations of the H atoms, but only close to the site corresponding to the bulk Al position. A typical end result is visualized in Fig. 9. The adatom was placed over the surface in position X, but moved significantly during minimization, adsorbing only weakly in its final position. The resulting adsorption energies range from −0.4 to −0.6 eV, depending on the configuration of the surface H atoms. For one surface

TABLE VI. Relaxation (in percent) of the topmost layer distances of the completely hydrogenated O-terminated surface compared to previous results. The changes reported are with respect to calculated plane spacings for the perfect bulk.

Layers	Present	Ref. 17	Ref. 21
O-Al	7.9	2.3	6.0
Al-Al	−39.3	−25.6	−36.4
Al-O	13.5	8.3	10.4
O-Al	−1.4	−0.8	−0.4

where the H atoms are "forced" away from the Al bulk position (with all OH bonds pointing upwards or away from this site), the Al atom stays close to its bulk position. However, the adsorption is still very weak (-0.9 eV), and the distance to the surface considerably larger than for the case of a clean O-terminated surface. The weak interaction between the adatom and the hydrogenated surface has also been observed for adsorption of other metals on this type of surface.[21] However, interestingly enough, our results suggest that Al adatoms do not adsorb in their bulk positions at all on many hydrogenated surfaces.

Hydrogen has previously been shown to alter the conditions for crystalline alumina thin film growth, and incorporation of hydrogen in amorphous films has been shown to cause drastic changes in their properties.[53] Our results suggest that hydrogen on the surface disturbs the crystalline growth. Moreover, the calculations indicate that a large incorporation of hydrogen into α-Al$_2$O$_3$ crystallites during thin film growth is unlikely, since adsorption attempts corresponding to a continuation of the stacking sequence results in no, or weak, adsorption on the hydrogenated surface. Consequently, we propose that hydrogen in such samples, to a large extent, originates from grain boundaries or amorphous parts of the films. This is supported by experimental studies of bulk boehmite-derived γ-alumina, in which hydrogen in the samples has been found to be located in amorphous regions or at the surface, and not in the bulk.[54]

IV. CONCLUSIONS

We have performed density functional theory based *ab initio* calculations to investigate Al, O, AlO, and O$_2$ adsorption processes on different α-Al$_2$O$_3$ (0001) surfaces. The three terminations obtainable by cleaving the bulk structure (AlO, AlAl, and O terminations) have been studied, as well as a completely hydrogenated O-terminated surface.

Al interacts strongly with all surfaces except the hydrogenated one. On the hydrogen-covered surface, we find Al adsorption in the bulk position to be very weak or not stable at all, depending on the configuration. On the O-terminated surface, several metastable adsorption sites are identified. In most cases, Al binds to the surfaces through ioniclike inter-actions, with strongest interaction occurring on the O-terminated surface, reflecting the relative instability of this surface. AlO complexes are found to follow the same binding trends as Al atoms for the situations studied here.

O binds strongly to the AlAl-terminated surface, and O$_2$ molecules are found to readily dissociate on this surface. In contrast, O atom adsorption on the AlO-terminated surface is unstable relative to O in O$_2$ molecular form. On the O-terminated surface, we find the formation of two O surface vacancies and an O$_2$ molecule to be energetically favored compared to the perfect surface. Hence, two competing processes exist here: one where O$_2$ molecules readily dissociate on the AlAl-terminated surface and one where O$_2$ desorbs from the perfect O-terminated surface if the kinetic barrier for this process is overcome. This further emphasizes results in previous reports, demonstrating the relative instability of the O termination and a driving force towards O deficient configurations.[15] Moreover, we show that atomic O might adsorb on the O-terminated surface but that the formation of a vacancy and an O$_2$ molecule becomes the thermodynamically stable configuration at elevated temperatures due to entropy effects.

Concerning α-Al$_2$O$_3$ thin film growth, the identification of several metastable adsorption sites on the O-terminated surface provides a possible explanation for the difficulties in growing α-alumina at low temperatures. The calculations also indicate that growth of (0001) surfaces might be inhibited if excess atomic O is present during growth. Moreover, our results suggest that H disturbs α-Al$_2$O$_3$ growth and that H incorporation into α-Al$_2$O$_3$ crystallites during growth is unlikely, since adsorbed H on the O-terminated surface seems to hinder, or at least considerably weaken, further Al adsorption corresponding to the bulk crystal stacking sequence.

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