Theory of the clean and hydrogenated $Al_2O_3(0001)$-(1×1) surfaces

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We present the results of a first principles investigation of the equilibrium properties of c-plane α-Al_2O_3 surfaces. The stable structure for the 1×1 clean surface is Al terminated with a stoichiometric composition, while other terminations are unstable independent of surface preparation conditions. We discuss the implications of our results in the frame of possible extended reconstructions. For 1 monolayer of H coverage, we find that the preferred structure has OH dimers both perpendicular and nearly parallel to the surface. H-terminated surfaces may form in suitable preparation conditions. We discuss our results in terms of water adsorption and atomic layer epitaxy of α-$Al_2O_3(0001)$. [S0163-1829(99)51848-1]

Corundum (α-Al_2O_3) is a colorless ceramic material, best known for its doped colored forms sapphire and ruby, obtained by substituting a fraction of Al atoms with Ti (and/or Fe) and Cr atoms, respectively. Corundum is one of the many possible allotropic forms of aluminas, which have a broad range of applications in the automobile industry, in atmospheric treatments, in catalytic reactions, and in the microelectronic industry. In microelectronics, aluminum oxide plays important roles both as a dielectric in devices, and as a substrate for other active materials. In recent years, it has been widely employed as a substrate for nitride growth.[1] The surfaces of aluminas were widely studied in the past, both experimentally[2–4] and theoretically.[5–8] However, most theoretical studies were limited to semiempirical calculations. The earliest first principles computations[6] employed thin supercell geometries to analyze selected surface terminations. Progress in numerical methods and in computer power has made the application of first principles methods to extended modifications of various oxide structures feasible. As a consequence, there has been a renewed interest in the surfaces of Al_2O_3 very recently, with a focus on more complicated issues than those studied in the past. The dissociation kinetics of H_2O,[9] and metal adsorption,[10] have been studied with state-of-the-art first principles calculations using extended supercells.

In this paper, we address the important issue of surface stoichiometry for the α-$Al_2O_3(0001)$ surfaces. We present results of first principles calculations of the structure and the energetics for various possible reconstructions. We have calculated the formation energy for several surface structures, including clean surfaces and H-covered surfaces, as a function of the Al and H chemical potentials. While for the clean surface the termination with 1/3 monolayer (ML) of Al atoms was commonly accepted[6] (or tested without allowing for atomic relaxation,[5]) we studied its stability in comparison with other low-energy structures obtained by adding various amounts of Al to the surface.

We have performed *ab initio* calculations in the framework of density functional theory in the local density approximation (DFT-LDA).[11] The electron-ion interaction has been treated by norm-conserving soft pseudopotentials,[12] and

the electronic wave functions have been expanded in plane waves up to a kinetic energy cutoff of 50 Ry. The crystal structure of corundum has a rhombohedral unit cell with two molecules per cell. The hexagonal cell contains 12 Al atoms and 18 O atoms.[13] The surfaces have been modeled by 1×1 repeated supercells containing 6 layers of oxygen atoms with 3 atoms/layer. The O atoms are stacked in hexagonal close packed planes parallel to the (0001) basal plane of the hexagonal cell. The Al atoms in the bulk occupy 2/3 ML of the octahedral sites in two different planes between any two oxygen planes, as illustrated in the side view in Fig. 1. We have performed structural optimizations by allowing all the atoms to move, until the atomic forces vanished within a required precision of 0.05 eV/Å, while the electron wave functions adjusted to the atomic displacements.

The bulk properties of corundum are well described with our computational technique. There are four structural parameters:[14] the side of the rhombohedral cell a_R, the angle α_R, and two internal parameters u and v fixing the Al-O distances. Previous calculations[6,14] have demonstrated that
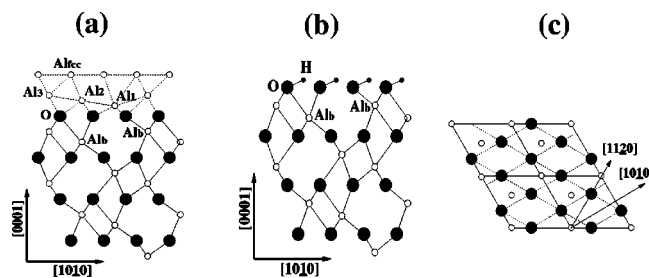

FIG. 1. Microscopic models for clean (a) and hydrogenated (b) corundum (0001) surfaces in side view. A top view is shown in panel (c). Large (small) dots represent O (H) atoms; circles represent Al atoms. The panel (a) models an Al-rich surface terminating with 2 ML's of Al atoms (the $Al_{6/3}$ structure). Removing the outermost Al_{fcc} layer, we have the $Al_{3/3}$ structure. If we further take out first the Al_3 atom and then the Al_2 atom, we obtain, respectively, the $Al_{2/3}$ structure and the $Al_{1/3}$ structure. Finally, if we take out only atom Al_3 from the structure of panel (a), we obtain the $Al_{5/3}$ structure. The $Al_{4/3}$ structure results from removing atoms Al_3 and Al_2. In this fractional labeling, the subscript indicates the number of top aluminum monolayers. The panel (b) models the $OH_{\parallel}(0001)$ hydrogenated surface with in-plane OH dimers. At the $OH_{\perp}(0001)$ surface, the out-of-plane dimers lie along the [0001] direction.

the internal parameters are identical to the experimental values, hence we have kept them fixed [$u=0.352, v=0.556$ (Ref. 13)]. We have calculated the equilibrium values of a_R and α_R as a function of the plane wave kinetic energy cutoff. Using a 50 Ry cutoff, a converged bulk structure is obtained with $a_R=5.054$ Å and $\alpha_R=55°18'$. The experimental values are $a_R=5.128$ Å and $\alpha_R=55°20'$.[13] The side a of the hexagonal cell and the c/a ratio are defined in terms of a_R and α_R, as $a=2a_R \sin(\alpha_R/2)=4.69$ Å, $c/a=3/2\sqrt{1/\sin^2(\alpha_R/2)-4/3}=2.729$. We have calculated the formation enthalpy ΔH of bulk corundum from bulk Al_{fcc} and O_2 molecules. Including the spin-polarization correction for the O_2 molecule,[15] our calculated value of ΔH is 18.0 eV, in good agreement with the experimental value, $\Delta H_{exp}=17.2$ eV. We find an electronic direct band gap at Γ of 6.7 eV, with a typical DFT-LDA underestimate of 25% with respect to the experimental value of 8.8 eV.[16]

We have performed simulations of different clean and hydrogenated (0001) surfaces in 1×1 supercells having the lattice dimensions that we have calculated. Each supercell contained two equivalent surfaces. For the clean surfaces, we have considered several atomic terminations, ranging from 0 ML to 2 ML of Al atoms. Figure 1(a) models a termination with two full ML's of Al (the structure labeled $Al_{6/3}$). The other structures that we have studied ($Al_{5/3}$, $Al_{4/3}$, $Al_{3/3}$, $Al_{2/3}$, $Al_{1/3}$) can be obtained from Fig. 1(a) by removal of some atoms, as explained in the caption of Fig. 1. For the 1×1 hydrogenated surfaces (generically labeled OH), we have considered different terminations with 1 ML of H atoms, that can be obtained, with reference to Fig. 1(a), by removing the top Al layers and attaching one H atom to each O atom that remains uncovered. We have allowed for different orientations of the O-H bonds, resulting in three distinct structures: the $OH_\parallel(0001)$ surface [see Fig. 1(b)] with in-plane OH dimers lying nearly parallel to the (0001) plane, the $OH_\perp(0001)$ surface with out-of-plane OH dimers perpendicular to the (0001) plane, and the $OH_\parallel^\perp(0001)$ surface with a mixture of in-plane and out-of-plane OH dimers. The structures $OH_\parallel(0001)$ and $OH_\perp(0001)$ have the full hexagonal symmetry of the O sublattice of bulk corundum, while the structure $OH_\parallel^\perp(0001)$ has reduced hexagonal symmetry. We have calculated the formation energy of the structures as a function of the Al chemical potential (μ_{Al}) assuming equilibrium with bulk Al_2O_3 ($2\mu_{Al}+3\mu_O=\mu_{Al_2O_3}$):

$$E_{form}=E_{form}(Al\text{-}rich)-\left(n_{Al}-\frac{2}{3}n_O\right)(\mu_{Al}-\mu_{Al(fcc)}).$$

μ_i and n_i indicate the chemical potential and the number of atoms of species i; $\mu_{Al(fcc)}$ is the chemical potential of Al in its fcc phase, and $E_{form}(Al\text{-}rich)$ is the formation energy for $\mu_{Al}=\mu_{Al(fcc)}$. In Fig. 2 we present our results for the energetics of α-$Al_2O_3(0001)$ surfaces. To eliminate the dependence of E_{form} on the H chemical potential (μ_H) for comparing the energies of the clean and hydrogenated surfaces, we have taken μ_H to be equal to the energy per H atom in molecular H_2. This value for μ_H is an upper bound on its true value, and corresponds to an extremely H-rich environment.
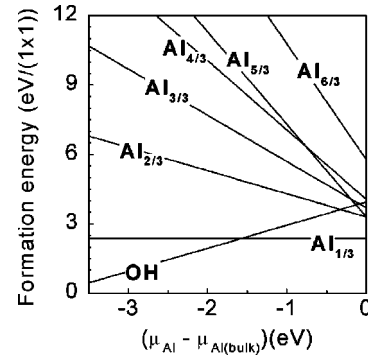

FIG. 2. Formation energy of clean and hydrogenated $Al_2O_3(0001)$ surfaces as a function of the Al chemical potential, in equilibrium with bulk Al_2O_3. We take the H chemical potential μ_H to be equal to its maximum possible value, which is $\mu_H(\text{max})=1/2E(H_2)$.

Independently of the Al chemical potential (see Fig. 2), the most stable clean 1×1 surface has bulk stoichiometry. It is terminated by 1/3 ML of Al atoms and has a surface energy of 1.98 Jm^{-2} (124 $meV/Å^2$): this value is in agreement with molecular dynamics simulations.[7] The $Al_{1/3}$ surface is nonmetallic: The three valence electrons of the top Al atoms are donated to the bonds with subsurface O atoms, and the empty Al p_z orbital is located 5.1 eV above the bulk valence band maximum. Surfaces terminating with 2/3 ML or 1 ML of Al atoms are not energetically favorable. For the latter stoichiometry, we have even considered alternative stackings of the outermost Al layer, none of which results in energy reduction. The lowest energy structure $Al_{1/3}$ exhibits large atomic displacements in the [0001] direction. In Table I, we report the first four interlayer spacings: the good agreement between the different calculations listed there demonstrates that the vertical relaxations are converged to within ±0.02 Å, with respect to the slab thickness[17] and other numerical approximations. Large lateral relaxations characterize the oxygen planes: we report the atomic co-ordinates in Table II. Guo and co-workers, by means of semiempirical calculations, established the stability of the $Al_{1/3}$ surface with respect to other cleavage terminations.[5] However, as a consequence of inhibiting atomic relaxation, they obtained a very high formation energy of 3.7 Jm^{-2} for the stable surface geometry.[18]

The regime with Al coverage (Θ_{Al}) larger than 1 ML has been studied in order to gain insight into the nature of the

TABLE I. Interlayer distances in the ideal (Δz_{id}) and relaxed geometries (Δz_{rel}) for the $Al_{1/3}$ structure of the $Al_2O_3(0001)$ surface. The numbers in parentheses (first column) label the layers starting from the topmost layer. The vertical relaxation is very large, especially for the Al(1)-O(2) interlayer distance. The surface Al atoms become almost coplanar with the subsurface O atoms. The percentage relaxation (fourth column), with respect to the ideal configuration, is in very good agreement with the results of other calculations (Refs. 9 and 10).

	Δz_{id} (Å)	Δz_{rel} (Å)	Relaxation (%)		
			Present	Theory[a]	Theory[b]
Al(1)-O(2)	0.828	0.128	-85	-82	-87
O(2)-Al(3)	0.828	0.853	$+3$	$+7$	$+3$
Al(3)-Al(4)	0.478	0.265	-45	-52	-42
Al(4)-O(5)	0.828	0.991	$+20$	$+25$	$+19$

[a]Reference 9.
[b]Reference 10.

TABLE II. Atomic coordinates of the atoms in the supercell simulating the $Al_{1/3}$ surface geometry, in the units of the lattice vectors $(\mathbf{a_1},\mathbf{a_2},\mathbf{a_3})$ of the hexagonal supercell: $\alpha = \mathbf{r}/\mathbf{a_1} = (x+y/\sqrt{3})/a$, $\beta = \mathbf{r}/\mathbf{a_2} = (2/\sqrt{3})y/a$, $\gamma = \mathbf{r}/\mathbf{a_3} = z/c$, with $a = 4.69$ Å and $c = 12.799$ Å. The other half of the supercell is obtained by inversion symmetry.

Species	Ideal geometry			Relaxed geometry $Al_{1/3}$		
	α	β	γ	$\Delta\alpha$	$\Delta\beta$	$\Delta\gamma$
Al	0.66667	0.33333	0.48133	0.00000	0.00000	−0.05582
O	0.33333	0.36067	0.41667	−0.01466	−0.01774	−0.00088
O	0.63933	0.97267	0.41667	0.01775	0.00241	−0.00088
O	1.02733	0.66667	0.41667	−0.00292	0.01424	−0.00088
Al	0.00000	0.00000	0.35200	0.00000	0.00000	−0.00249
Al	0.33333	0.66667	0.31467	0.00000	0.00000	0.01355
O	0.30600	0.00000	0.25000	0.00612	0.00098	0.00111
O	0.69400	0.69400	0.25000	−0.00500	−0.00595	0.00111
O	1.00000	0.30600	0.25000	−0.00094	0.00510	0.00111
Al	0.66667	0.33333	0.18533	0.00000	0.00000	−0.00220
Al	0.00000	0.00000	0.14800	0.00000	0.00000	0.00095
O	0.36067	0.33333	0.08333	−0.00150	−0.00118	0.00004
O	0.97267	0.63933	0.08333	0.00034	0.00152	0.00004
O	0.66667	0.02733	0.08333	0.00119	−0.00031	0.00004
Al	0.33333	0.66667	0.01867	0.00000	0.00000	0.00128

Al-rich $\sqrt{31}\times\sqrt{31}$ reconstruction that is observed following high-temperature annealing.[2] This structure contains a high density of Al atoms, arranged in two fcc layers on top of the last plane of O atoms. It was argued that it could be obtained through the evaporation of two oxygen layers during annealing, leaving behind 5/3 ML of Al on the surface. Indeed, the observed stoichiometry was 1.6867 ML,[2] very close to the 5/3 value which is compatible with the constraint of 1×1 cells. Hence, we have calculated the formation energies of structures with 2 ML, 5/3 ML, and 4/3 ML of Al top atoms, to investigate the possible mechanisms of formation of the extended reconstruction. The structure terminating with 5/3 ML of Al atoms can be regarded as a topmost complete fcc Al layer separated from the last O plane of the oxide by an interface Al layer with 2/3 ML composition. Our results in Fig. 2 show that, while even in Al-rich conditions the $Al_{6/3}$ structure is energetically unfavorable, the formation energy can be significantly reduced by depleting the subsurface layer, as in the $Al_{5/3}$ structure. In Al-rich conditions, e.g., in equilibrium with the fcc bulk aluminum phase that is forming, the energy drops by 2.5 eV/(1×1) by removing 1 out of every 3 Al atoms in the layer bonded to the last O plane. Furthermore, while the addition of 1 Al ML on top of a complete initial Al ML costs 2.1 eV/(1×1) (energy difference between the structures $Al_{3/3}$ and $Al_{6/3}$ for $\mu_{Al} = \mu_{Al(fcc)}$), the addition of 1 Al ML on top of a 2/3 Al ML is exothermic (vanishing energy difference between the structures $Al_{2/3}$ and $Al_{5/3}$ for $\mu_{Al} = \mu_{Al(fcc)}$). For completeness, we have also calculated the formation energy of the $Al_{4/3}$ structure, obtained from the $Al_{5/3}$ structure by removing one interface Al atom. This further depletion of the oxide/metal interface layer is energetically unfavorable for $\mu_{Al(fcc)} - 0.8$ eV $\leq \mu_{Al} \leq \mu_{Al(fcc)}$. In particular, in Al-rich conditions, it is unfavorable by 0.75 eV/(1×1). The presence of the incomplete Al layer with 2/3 ML stoichiometry is conducive to the formation of an Al-rich surface via the ad-

dition of an fcc Al(111) wetting layer on α-$Al_2O_3(0001)$. Summarizing the results of our calculations for structures with 1 ML $\leq \Theta_{Al} \leq 2$ ML, we conclude that the observed $\sqrt{31}\times\sqrt{31}$ reconstruction[2] is most likely to consist of a top Al fcc layer bonded to the underlying oxide through an incomplete Al layer, containing a fraction of Al atoms much closer to 2/3 ML than to 3/3 ML or 1/3 ML.

We now turn to the hydrogenated surface with 1 ML of H [see Fig. 1(b)]. As seen in Fig. 2, the lowest-energy OH surface, which we discuss below, is stable with respect to the $Al_{1/3}(0001)$ surface for extremely H-rich conditions only when the chemical potential of Al is more than 1.6 eV below its maximum value. Conversion of the stable clean surface $Al_{1/3}$ to the hydrogenated surface OH requires a low Al chemical potential and a high H chemical potential simultaneously. We shall see below that such conditions may be achieved in the dissociative adsorption of H_2O.

For OH structures that maintain the symmetry of corundum, we find that the $OH_\parallel(0001)$ surface is energetically favorable by 0.11 eV/(OH bond) with respect to the $OH_\perp(0001)$ surface.[19] At the $OH_\parallel(0001)$ surface, the O-H bonds form an angle of $\sim 19°$ with respect to the (0001) plane. The O-H bond lengths are 0.98 and 0.96 Å for the in-plane and out-of-plane OH dimers, respectively. Hass et al.[9] performed dynamical simulations of the OH(0001) surface in a 3×3 simulation supercell, as an idealized model for a fully hydroxylated $Al_2O_3(0001)$ surface. They found that 1/3 of the OH dimers were in-plane and 2/3 were out-of-plane at room temperature, and that the in-plane dimers had a smaller vibrational frequency than the out-of-plane dimers (by 4%). Accordingly, we find a larger bond length for the in-plane dimers with respect to the out-of-plane dimers, by about 2%. Moreover, if we relax symmetry constraints in our simulations, we find that there is an energy gain of 0.18 eV/(OH bond) upon mixing 1/3 in-plane and 2/3 out-of-plane dimers and forming the $OH_\parallel^\perp(0001)$ surface. At the $OH_\parallel^\perp(0001)$ surface, the in-plane dimers form an angle of $\sim 5°$ with the basal plane and are 1 Å long. The bending and elongation of the O-H bonds at the $OH_\parallel^\perp(0001)$ surface, with respect to the $OH_\parallel(0001)$ surface, may be due to a compromise between reducing the H-H repulsion and optimizing the coordination of the O atoms with respect to the corundum lattice. The H-H distance is increased from 1.9 Å to 2.3 Å in going from the $OH_\parallel(0001)$ surface to the $OH_\parallel^\perp(0001)$ surface. It could be further increased to 2.5 Å in the full-symmetry $OH_\perp(0001)$ surface. However, this structure constrains the O atoms to a dramatic change of coordination with respect to the bulk, and we find it to be unfavorable.

We have attempted to identify pathways leading to the formation of the H-covered surface by studying the energetics of H_2 and H_2O adsorption on the $Al_{1/3}(0001)$ surface, with consequent desorption of AlH_3 or $Al(OH)_3$ molecules, or formation of bulk Al. The reactions that we have considered, and the calculated reaction energies, are summarized in Table III. Reactions $r1$ and $r3$ involve dissociative adsorption of H_2: When $r1$ occurs, AlH_3 molecules are evolved, when $r3$ occurs, one of the reaction products is bulk Al. These reactions are both endothermic. Thus, dissociative adsorption of H_2 on $Al_{1/3}(0001)$ is not energetically favorable

TABLE III. Energetics of surface chemical reactions for adsorption of H_2 or H_2O molecules on the $Al_2O_3(0001)$ surface.

Surface chemical reaction	Label	Reaction energy $[eV/(1\times1)]$
$Al_{1/3}(0001) + 3H_2 \rightarrow OH_{\parallel}^{\perp}(0001) + AlH_3$	$r1$	$+3.1$
$Al_{1/3}(0001) + 3H_2O \rightarrow OH_{\parallel}^{\perp}(0001) + Al(OH)_3$	$r2$	-0.5
$2Al_{1/3}(0001) + 3H_2 \rightarrow 2OH_{\parallel}^{\perp}(0001) + 2Al_{fcc}$	$r3$	$+1.6$
$2Al_{1/3}(0001) + 3H_2O \rightarrow 2OH_{\parallel}^{\perp}(0001) + Al_2O_3(bulk)$	$r4$	-2.9

via reactions $r1$ and $r3$. In contrast, surface chemical reactions involving adsorption of H_2O ($r2$ and $r4$ in Table III) are exothermic. Reaction $r2$ results in the desorption of $Al(OH)_3$ and is exothermic by 0.5 eV/(1×1), and reaction $r4$ is exothermic by a large amount: 2.9 eV/(1×1). In this latter reaction, Al must diffuse from one part of the surface to another. The mobile Al is created by replacing the three O-Al bonds per (1×1) cell of the $Al_{1/3}(0001)$ surface with three O-H bonds in a given surface region, which is thus converted to the $OH_{\parallel}^{\perp}(0001)$-$(1\times1)$ reconstruction. The displaced Al may then diffuse across the surface, either as Al atoms, or possibly as mobile $Al(OH)_3$ molecules that remain bonded to the surface. As the mobile Al species arrives on an $Al_{1/3}(0001)$ terrace, it will be incorporated into the surface, converting the terrace to the $OH_{\parallel}^{\perp}(0001)$ reconstruction. If the mobile species is an Al atom, then incorporation requires additional OH molecules that are available from the dissociated H_2O. If the mobile species is an $Al(OH)_3$ molecule, then no additional OH is required. In a temperature regime where step flow growth is possible, this process would correspond to the motion of steps across the surface. The reaction $r4$ can be viewed as the first stage (stage A) of atomic layer epitaxial (ALE) cyclic growth of Al_2O_3.[20] The second stage (stage B) of the cycle would convert the surface back

to the $Al_{1/3}$ structure by the addition of 1/3 ML of Al and the desorption of H atoms. Stage B of the ALE process could be any exothermic reaction that added 1/3 ML of Al to the surface. The reverse of reaction $r1$ or $r3$ would be a suitable stage B of an $ABAB\dots$ ALE growth cycle. Each AB segment of the cycle would lead to the deposition of 1 ML of Al_2O_3 on half of the surface. Growth of a full monolayer of the oxide requires two cycles, $ABAB$. Since the step height on sapphire is $c/6=2.16$ Å, the growth rate is 1.08 Å per AB cycle. Thus, our results indicate that reaction $r4$ may be used as a self-limiting[20] reaction for ALE growth of Al_2O_3 in a step-flow growth regime.

In summary, we have characterized clean and hydrogenated α-$Al_2O_3(0001)$-(1×1) surfaces by first principles total-energy-and-force calculations. The study of the energetics of clean surfaces reveals the stability of a stoichiometric surface termination, with 1/3 ML of Al atoms on top. Our results suggest that the establishment of the Al-rich $\sqrt{31} \times \sqrt{31}$ surface occurs via the formation of a 2D layer of fcc Al on the $Al_{2/3}(0001)$ termination of the oxide. Finally we have shown that a stable $OH_{\parallel}^{\perp}(0001)$-$(1\times1)$ H-terminated surface may be formed by dissociative adsorption of H_2O on the $Al_{1/3}(0001)$ surface, and that this reaction may serve as the first step of an ALE growth process of $Al_2O_3(0001)$.

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[17] The vertical relaxation is accurately described as far as the seventh inner layer: the spacing between the 5th and the 6th layers relaxes by $+5.1\%$, and that between the 6th and 7th layers by -8.2%. ($+6\%$ and -8.4%, respectively, in Ref. 10, with an 18-O-layer supercell).

[18] We calculate a formation energy of 4.07 Jm^{-2} (255 meV/Å^2) for the unrelaxed $Al_{1/3}$ surface. Compared to 1.98 Jm^{-2} for the stable surface, this corresponds to a large relaxation energy of 131 meV/Å^2, consistent with other first principles calculations (Refs. 10 and 6).

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