

Effect of the Environment on α - Al_2O_3 (0001) Surface Structures

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We report that calculating the Gibbs free energy of the α - Al_2O_3 (0001) surfaces in equilibrium with a realistic environment containing both oxygen and hydrogen species is essential for obtaining theoretical predictions consistent with experimental observations. Using density-functional theory we find that even under conditions of high oxygen partial pressure the metal-terminated surface is surprisingly stable. An oxygen-terminated α - Al_2O_3 (0001) surface becomes stable only if hydrogen is present on the surface. In addition, including hydrogen on the surface resolves discrepancies between previous theoretical work and experimental results with respect to the magnitude and direction of surface relaxations.

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The nature of the corundum surface (α - Al_2O_3) is of considerable importance in a wide variety of technological applications. These range from catalytic supports and thin-film substrates to corrosion and wear protection in mechanical systems. Yet, despite considerable experimental and theoretical efforts over the years [1], the surface structure, and even the surface stoichiometry, is a matter of strong controversy. The principal reason for this is that it is difficult to prepare clean, uniform surfaces with specific, well-defined structures and stoichiometries. The typical heterogeneity of the surface makes the interpretation of low energy electron diffraction (LEED) and other surface spectroscopic data difficult. In addition, corundum is an insulator which makes the application of scanning tunneling microscopy and other techniques based on electron spectroscopy problematic.

Knowing the structure and stoichiometry of the corundum surface, however, is essential for understanding the electronic, mechanical, and chemical properties which determine its reactivity and performance in various applications. Yet it has only been within the past two years that new experimental techniques have enabled the chemical identification of the surface terminations for these systems. Renaud has reported a (1×1) structure, prepared by heating in an oxygen-rich atmosphere, which could reasonably be interpreted as being O terminated [2]. Toofan and Watson found in a tensor LEED experiment both Al- and O-terminated domains in a 2:1 ratio, respectively [3]. Ahn and Rabalais annealed the surface under ultrahigh vacuum (UHV) conditions and determined the detailed structure of the Al-terminated surface using time-of-flight scattering and recoiling spectrometry (TOF-SARS) [4]. The sensitivity of TOF-SARS also enabled the detection of hydrogen randomly distributed on the surface which was stable even at an annealing temperature of 1100 °C.

Despite recent advances in experimental techniques, however, many questions and inconsistencies remain that theoretical calculations performed to date have not been able to resolve. Corundum (α - Al_2O_3) crystallizes in a structure which can be described by a primitive rhombo-

hedral unit cell with two Al_2O_3 formula units (10 atoms) or by a conventional hexagonal unit cell with six Al_2O_3 formula units (30 atoms). For the hexagonal unit cell, the atoms are stacked along the (0001) direction according to the sequence R - AlAlO_3 - AlAlO_3 - R , where R represents the continuing sequence in the bulk. The oxygen atoms form hcp layers, and the metal atoms fill two-thirds of the octahedral sites between these layers [5].

In the R - Al-Al-O_3 - R corundum structure (0001) stacking sequence, there are three unique stoichiometric slice planes. Yet theoretical methods ranging from the empirical to the *ab initio* [6–11] have so far identified only one stable termination stoichiometry for the α - Al_2O_3 (0001) surface: an Al monolayer indicated by $\text{AlO}_3\text{Al-R}$ in Fig. 1. No stable O-terminated surface has been found, so how can the experimentally observed O terminations be explained? In addition to the surface stoichiometry, there is considerable disagreement with respect to the magnitude and direction of the surface relaxations. For the Al-terminated surface, experimentally observed relaxations range from -51% [12] to -63% [4], whereas the density-functional theory pseudopotential calculations predict a relaxation of about -87% [9,11], and Hartree-Fock gives -40% [7]. Toofan

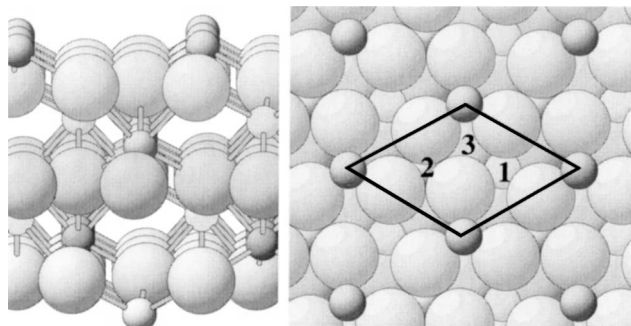


FIG. 1. Side and top view of the $\text{Al-O}_3\text{-Al-R}$ surface of α - Al_2O_3 , in which 1, 2, and 3 indicate three sites which could be occupied by the topmost Al instead of the bulk site. The large circles denote O atoms and the small circles denote Al atoms.

and Watson reported an outward relaxation for their two-domain system, which is the opposite of what other experimental and theoretical investigations had concluded. These discrepancies are significant and need to be resolved.

What has not been previously considered in the theoretical treatment of the α -Al₂O₃ (0001) surface is the effect of the environment on the surface structures and stoichiometry. Under realistic conditions, a surface will exchange atoms with its surroundings. Hence in this paper we present the first analysis of the Gibbs free energy of the system with respect to its dependence on the chemical potentials of the components present in the material and the environment at 0 and 1000 K. For a metal oxide such as α -Al₂O₃, the O₂ partial pressure is obviously the most important factor in the analysis, as well as temperature. In addition, the presence of stable hydrogen on the surface also needs to be addressed, as it can be incorporated into the bulk structure during growth, remain from calcination of Al(OH)₃ in the synthesis of α -Al₂O₃, or may result from exposure of the surface to water vapor prior to placement in the UHV chamber. Yet to our knowledge the presence of hydrogen on the corundum surface has not yet been investigated in theoretical studies. In this paper we report that the surface stoichiometries, structures, and properties change significantly depending upon the chemical potential of O₂, H₂, and H₂O gases in equilibrium with the surface at different temperatures. We use the full-potential linearized augmented plane wave (FP-LAPW) method to solve the Kohn-Sham equations and calculate the total energies, forces, and chemical potentials for all reasonable (1 × 1) corundum (0001) surface geometries. We find that the metal-terminated surface is surprisingly stable across the range of a physically realistic oxygen chemical potential. An oxygen-terminated surface becomes stable only if hydrogen is present on the surface, even at partial O₂ pressures which are too high for standard UHV equipment. In addition, including hydrogen on the surface of both the aluminum- and oxygen-terminated surfaces results in calculated relaxations which agree with the latest experimental results, in both magnitude and direction.

To systematically investigate the (1 × 1) (0001) surface which is observed at annealing temperatures below 1250 °C, we have generated what we believe are all the possible (1 × 1) (0001) Al- and/or O-surface terminations of Al₂O₃, plus several additional surfaces containing hydroxyl groups. Previous studies which investigated possible (1 × 1) (0001) surface terminations examined only the three types of structures obtained by simply cleaving the unit cell at unique positions [8,10]: AlO₃Al-*R*, O₃AlAl-*R*, and AlAlO₃-*R*. For the single Al-terminated layer there are three other possible locations for the Al atom in addition to the corresponding bulk site, as shown in Fig. 1. For the O-terminated surface, other investigations have not considered the possibility of oxygen vacancies which could occur and still maintain a perfect (1 × 1) surface periodicity. Two additional O-terminated structures

can be created by introducing one or two oxygen vacancies per unit cell, indicated by O₂AlAl-*R* and O₁AlAl-*R*, respectively. Hence, there are a total of at least eight possible (1 × 1) geometries of the (0001) surface which we investigate to determine their relative stability.

In our calculations, the (1 × 1) α -Al₂O₃ surface is modeled by a slab which consists of a finite number of layers and is infinite in the plane of the surface. The slabs are repeated periodically along the [0001] direction and separated by 10 Å of vacuum. The slab contains six oxygen O₃ layers and from ten to fourteen aluminum layers, depending upon the specific surface studied. We carefully tested that the thickness of the vacuum as well as that of the slabs is sufficiently large to ensure that surface-surface interactions through both the vacuum and the slab are negligible [13]. The two surfaces of the slab are identical and inversion symmetry is maintained.

For our total-energy calculations we use the generalized gradient approximation of Perdew *et al.* [14] for the exchange-correlation potential and the FP-LAPW method as implemented within the WIEN97 program [15–17] to solve the Kohn-Sham equations [18]. A uniform **k**-point mesh with ten points is used for the entire surface Brillouin zone. An identical mesh is used for the bulk calculations to ensure consistency. The calculated equilibrium lattice constants for the hexagonal unit cell and the nonsymmetry fixed positions of the atoms agree with experimental values to within 0.7%. The calculations give the heat of formation at 0 K of the bulk Al₂O₃, $\Delta H_f^0 = 17.37$ eV, which is in good agreement with the experimental value of 17.24 eV [19].

To compare the stability of surfaces with different stoichiometries in chemical and thermal equilibrium with the gas phase and with the bulk, we calculate the Gibbs free energy Ω of the surface relative to the chemical potential of oxygen. The Gibbs free surface energy Ω of a slab at temperature T and partial pressure p is given by $\Omega = E^{\text{total}} + \Delta G^{\text{vib}} - \sum N_i \mu_i(T, p)$, where E^{total} is the self-consistent-field energy of the slab, ΔG^{vib} is the vibrational contribution to the Gibbs free energy, N_i is the number of i th type of atoms in the slab, and $\mu_i(T, p)$ is the chemical potential of the i th type of atom at a given temperature and pressure. The sum is over all of the types of atoms in the slab. To calculate the values of the chemical potential for all species we use $\mu_i(T, p) = \mu_i^0 + \Delta \mu_i(T, p)$, where 0 K is taken as the reference state, and $\Delta \mu_i(T, p)$ is the change in free energy from that reference state to the system at a given temperature and pressure. The 0 K values for surfaces and for bulk Al and Al₂O₃ are taken from our total-energy calculations. For the dissociation energies of the H₂, O₂, and H₂O molecules, we use experimental values. The $\Delta \mu_i(T, p)$ values for all crystalline and gas phase species are taken from the JANAF thermochemical tables [20].

As each surface is considered here to be in chemical and thermal equilibrium with the bulk and the

environment, the chemical potentials are constrained, so, for the clean surface, $2\mu_{\text{Al}} + 3\mu_{\text{O}} = E_{\text{Al}_2\text{O}_3}^{\text{bulk}}$, $\mu_{\text{Al}} < E_{\text{Al}}^{\text{bulk}}$, and $\mu_{\text{O}} < \frac{1}{2}E_{\text{O}_2}^{\text{molecule}}$, where $E_{\text{Al}_2\text{O}_3}^{\text{bulk}}$ is the total energy per bulk Al_2O_3 formula unit. The limits of the chemical potential for oxygen are determined by conditions of equilibrium with relevant oxygen-containing species in the system. The maximum oxygen chemical potential is that of a maximum concentration of O_2 molecules at 0 K, which corresponds to O_2 condensing on the surface. This is the reference value of the oxygen chemical potential, which is the zero on the right-hand side of the graph in Fig. 2. Since the system is in equilibrium with bulk Al_2O_3 the minimum μ_{O} occurs when μ_{Al} is at a maximum and $\mu_{\text{O}} = \frac{1}{3}E_{\text{Al}_2\text{O}_3}^{\text{bulk}} - \frac{2}{3}E_{\text{Al}}^{\text{bulk}}$. Below this range, aluminum metal would condense on the surface.

For the surfaces where hydrogen is adsorbed, the free energy of the surface is calculated relative to the chemical potential of hydrogen μ_{H} in both H_2 and H_2O , as desorption of hydrogen as either molecular species is possible. The lines for the $\text{HO}_3\text{AlAl-R}$ and $\text{H}_3\text{O}_3\text{AlAl-R}$ surface energies calculated with respect to μ_{H} in equilibrium with H_2 and H_2O cross at μ_{O} equal to -2.7 eV at 0 K. Below -2.7 eV, μ_{H} is determined by the equilibrium with H_2 , and above with H_2O . Below these lines, either H_2 or H_2O would condense on the surface. It should be noted that the only independent variables in our system are μ_{O} , in equilibrium with bulk Al_2O_3 , and μ_{H} . From these the dependent Al, O_2 , H_2 , and H_2O chemical potentials follow.

The results are shown in Fig. 2. The Gibbs free energies per surface area for various (1×1) geometries of the

(0001) surface are displayed as a function of μ_{O} . The dashed black vertical lines bracket the allowed range of μ_{O} . For the systems containing just aluminum and oxygen, there is clearly only one overwhelmingly low energy surface stoichiometry: the $\text{AlO}_3\text{Al-R}$ structure. This is consistent with the previous theoretical results. Our results show, however, that this stability extends across the entire range of the oxygen chemical potential, even up to the limit where an O_2 condensate would form on the surface. The empirical models explain this remarkable stability on the basis of simple ionic considerations, as it is the only structure without a significant surface dipole. The actual situation is a bit more complicated, of course, and the quantum mechanical calculations performed by us and others [8,10] indicate that the surface aluminum atom relaxes inward until it is practically coplanar with the oxygen layer, and rehybridizes to an sp^2 orbital configuration which is dramatically stabilized by autocompensation and bonding considerations. That is, the structure relaxes and charge is transferred so that the sp^2 bonds between the aluminum atoms and the three oxygens are filled, the aluminum $3p_z$ orbital perpendicular to the surface is empty, and there are no partial occupancies of dangling bonds at the surface. In our calculations the lowest empty surface state, which is primarily the Al $3p_z$ with some Al $3s$ and O $2p$ character, is 4.5 eV above the Fermi level. This is very high and contributes to the relative chemical inertness of the relaxed Al-terminated surface. Moving the topmost aluminum atom of the Al-terminated surface from its position to one of the three nonbulk positions indicated in Fig. 1 increases the surface energy dramatically from $133 \text{ meV}/\text{\AA}^2$ to 355, 282, and $228 \text{ meV}/\text{\AA}^2$ for the three sites, respectively.

The O_3 -terminated surface has a very unfavorable energy, although this decreases sharply as μ_{O} increases. This stoichiometry has the highest dipole at the surface, which is reflected in a very large work function of 9.66 eV, compared to 5.97 eV for the Al-terminated surface above. In addition, there are partially filled open valencies on the surface oxygens which are not relieved by relaxation. Our results indicate, however, that this high energy surface can become more stable through oxygen evaporation. The O_2 -terminated surface has a consistently lower free energy than the $\text{O}_3\text{AlAl-R}$, and the $\text{O}_1\text{AlAl-R}$ surface is more stable than $\text{O}_2\text{AlAl-R}$, except at the highest range of the oxygen chemical potential. At 1000 K the metal-terminated surfaces become the lowest energy surface under the most oxygen-deficient conditions. This is consistent with what happens at annealing temperatures above 1250°C , where oxygen evaporation leaves behind a metallic aluminum overlayer [1]. The figure does not convey the kinetic barriers required to move from one surface stoichiometry to another, but the relative thermodynamic stability is clear and is consistent with experimental observations.

The large surface dipole and dangling bonds of the O_3 -terminated surface can also be compensated by the

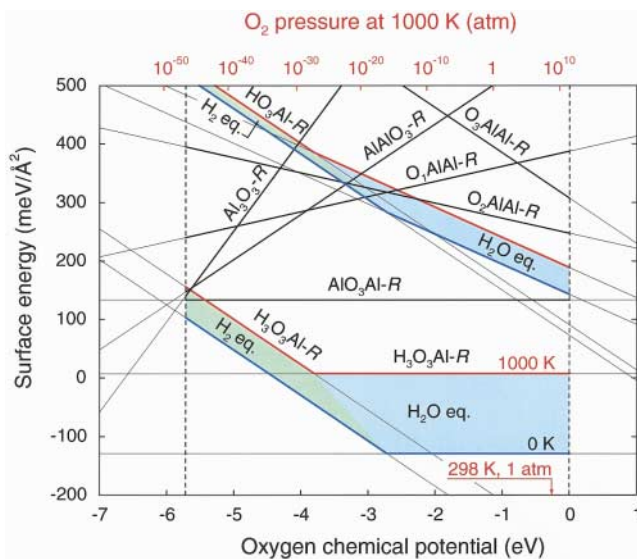


FIG. 2 (color). Surface energies of different Al_2O_3 (0001) surface terminations. The dashed vertical lines indicate the allowed range of the oxygen chemical potential, μ_{O} . Values in red indicate examples of higher temperatures and pressures. The green and blue regions indicate the range where hydrogen on the surface is in equilibrium with H_2 and H_2O , respectively, from 0 K up to 1000 K and 1 atm pressure (red lines).

TABLE I. Interlayer relaxations at the Al-terminated surface in percent of the corresponding bulk spacings.

Interlayer		Theory of Refs.			Experiment of Refs.		
		This	[9]	[11]	[4]	[12]	[3]
Al-O ₃	1-2	-86	-86	-87	-63	-51	+30
O ₃ -Al	2-3	+6	+3	+3	-	+16	+6
Al-Al	3-4	-49	-54	-42	-	-29	-55
Al-O ₃	4-5	+22	+25	+19	-	+20	-
O ₃ -Al	5-6	+6	-	+6	-	-	-

addition of hydrogen to the surface. Adding one hydrogen per unit cell to the surface [21] dramatically lowers the free energy and the work function from 9.66 to 7.06 eV. This surface is much more stable than the O₃-terminated surface at all oxygen partial pressures. Saturating all surface oxygens with hydrogen, indicated by the H₃O₃AlAl-R line in Fig. 2, results in the lowest free energy and greatest stability across the entire range of physically realistic conditions. The oxygen open valencies are filled, charge transfer occurs from the H to the topmost O layer, and the work function is reduced to 3.44 eV, the lowest of all surfaces examined. The region of negative surface energy of the H₃O₃-terminated surface indicates that the hydroxylated surface is lower in energy than bulk α -Al₂O₃ plus free H₂O. This negative surface energy reflects the strength of the H-OAl bond and is consistent with the negative heat of the α -Al₂O₃ + 3H₂O → 2Al(OH)₃ reaction. This reaction is exothermic by 0.19 eV per Al₂O₃ formula unit relative to liquid water at 298.15 K and 1 atm pressure [22].

We find that in addition to explaining the relative stabilities of the (0001) (1 × 1) surfaces observed experimentally, considering the presence of hydrogen on the surface is essential to resolve the controversy surrounding the surface relaxations. Our results are shown in Table I. In the absence of hydrogen, our full potential results find a large inward relaxation of 86% for the first layer, in very close agreement with previous pseudopotential calculations [9,11], although there is less agreement for subsequent layers. When a hydrogen atom occupies site 1, however, the contraction between the first Al and O layers is ~69%, in very close agreement with the experimental result of Ahn and Rabalais [4]. Several other locations for the hydrogen atom were investigated, with similar results.

For the oxygen-only terminated surface, theoretical predictions have indicated an inward relaxation of the top layer of 0.05 Å. Yet the experimental results of Toofan and Watson, in which one of the two domains observed was O terminated, clearly showed an outward relaxation of 0.12 Å [3]. Placing a hydrogen at site 1, however, results

in a predicted outward relaxation of 0.11 Å, in excellent agreement with experiment. Saturating the surface with hydrogen, the H₃O₃AlAl-R structure, increases the predicted relaxation to 0.19 Å. Hence, even though H was not detectable with the instrumentation used by Toofan and Watson, our free energy calculations and predicted relaxations provide strong evidence that H was most likely present on the surface.

Real surfaces are usually much more complicated and heterogeneous than the model (1 × 1) system studied here, but incorporating the effects of chemical and thermal equilibrium with the environment into the model provides a sound framework for interpretation of experimental results on these real systems.

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