The Effect of the Environment on $\alpha$-Al$_2$O$_3$ (0001) Surface Structures

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We report that calculating the Gibbs free energy of the $\alpha$-Al$_2$O$_3$ (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 $\alpha$-Al$_2$O$_3$ (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 ($\alpha$-Al$_2$O$_3$) 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 STM 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 $(1 \times 1)$ structure, prepared by heating in an oxygen-rich atmosphere, which could reasonably be interpreted as being O-terminated [3]. Toofan and Watson found in a tensor LEED experiment both Al- and O-terminated domains in a 2:1 ratio, respectively [3]. Ahn and Rabelais annealed the surface under 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$^\circ$ 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 ($\alpha$-Al$_2$O$_3$) crystallizes in a structure which can be described by a primitive rhombohedral unit cell with two Al$_2$O$_3$ formula units (10 atoms) or by a conventional hexagonal unit cell with six Al$_2$O$_3$ formula units (30 atoms). For the hexagonal unit cell, the atoms are stacked along the (0001) direction according to the sequence $R$-AlAlO$_3$-$\alpha$AlO$_3$-$R$, 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 [3].

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 [3][13] have so far identified only one stable termination stoichiometry for the $\alpha$-Al$_2$O$_3$ (0001) surface: an Al-monolayer indicated by AlO$_3$-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% [13] to -63% [9], whereas the density-functional theory (DFT) pseudopotential calculations predict a relaxation of about -87% [14], and Hartree-Fock gives -40% [9]. Toofan 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 $\alpha$-Al$_2$O$_3$ (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 work 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 ma-
terial and the environment at 0K and 1000K. For a metal oxide such as $\alpha$-Al$_2$O$_3$, the O$_2$ 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, 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 O$_2$, H$_2$, and H$_2$O gases in equilibrium with the surface at different temperatures. We use the full-potential linearized augmented planewave (FP-LAPW) method to solve the Kohn-Sham equations and calculate the total energies, forces, and chemical potentials for all reasonable (1 x 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 O$_2$ 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 x 1) (0001) surface which is observed at annealing temperatures below 1250$^\circ$C, we have generated what we believe are all the possible (1 x 1) Al- and/or O-surface terminations of Al$_2$O$_3$, plus several additional surfaces containing hydroxyl groups. Previous studies which investigated possible (1 x 1) (0001) surface terminations examined only the three types of structures obtained by simply cleaving the unit cell at unique positions [10]: AlO$_3$-Al, O$_2$AlAl- and AlAI0$_3$-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 x 1) surface periodicity. Two additional O-terminated structures can be created by introducing one or two oxygen vacancies per unit cell, indicated by O$_2$AlAl- and O$_1$AlAl- respectively. Hence, there are a total of at least eight possible (1 x 1) geometries of the (0001) surface which we investigate to determine their relative stability.

In our calculations, the (1 x 1) $\alpha$-Al$_2$O$_3$ 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 10Å of vacuum. The slab contains six oxygen O$_3$ 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 of that of the slabs are sufficiently large to ensure that surface-surface interactions through both the vacuum and the slab are negligible. 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] 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 non-symmetry fixed positions of the atoms agree with experimental values to within 0.7%. The calculations give the heat of formation at 0K of the bulk Al$_2$O$_3$, $\Delta H_f^o=17.37$ 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 $\Omega$ of the surface relative to the chemical potential of oxygen. The Gibbs free surface energy $\Omega$ of a slab at temperature $T$ and partial pressure $p$ is given by $\Omega = E_{\text{total}}^o + \Delta G_{\text{vib}}^o - \sum N_i \mu_i(T, p)$, where $E_{\text{total}}^o$ is the scf energy of the slab, $\Delta G_{\text{vib}}^o$ is the vibrational contribution to the Gibbs free energy, $N_i$ 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 the types of the 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 0K 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 0K values for surfaces and for bulk Al and Al$_2$O$_3$ are taken from our...
total energy calculations. For the dissociation energies of the \( \text{H}_2 \), \( \text{O}_2 \), and \( \text{H}_2\text{O} \) molecules, we use experimental values. The \( \Delta \mu(T, p) \) 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: \( 2\mu_{\text{Al}} + 3\mu_{\text{O}} = E^\text{bulk}_{\text{Al}_2\text{O}_3}, \mu_{\text{Al}} < E^\text{bulk}_\text{Al}, \) and \( \mu_{\text{O}} < \frac{1}{2}E^\text{molecule}_{\text{O}_2} \), where \( E^\text{bulk}_{\text{Al}_2\text{O}_3} \) is the total energy per bulk \( \text{Al}_2\text{O}_3 \) 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 \( \text{O}_2 \) molecules at 0K, which corresponds to \( \text{O}_2 \) 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\(_2\)O\(_3\), the minimum \( \mu_{\text{O}} \) occurs when \( \mu_{\text{Al}} \) is at a maximum and \( \mu_{\text{O}} = \frac{1}{3}E^\text{bulk}_{\text{Al}_2\text{O}_3} - \frac{2}{3}E^\text{bulk}_\text{Al} \). 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 \( \mu_{\text{H}} \) in both \( \text{H}_2 \) and \( \text{H}_2\text{O} \), as desorption of hydrogen as either molecular species is possible. The lines for the HO\(_2\)AlAl-R and H\(_3\)O\(_2\)AlAl-R surface energies calculated with respect to \( \mu_{\text{H}} \) in equilibrium with \( \text{H}_2 \) and \( \text{H}_2\text{O} \) cross at \( \mu_{\text{O}} \) equal to -2.7 eV at 0K. Below -2.7 eV, \( \mu_{\text{H}} \) is determined by the equilibrium with \( \text{H}_2 \), and above with \( \text{H}_2\text{O} \). Below these lines either \( \text{H}_2 \) or \( \text{H}_2\text{O} \) would condense on the surface. It should be noted that the only independent variables in our system is \( \mu_{\text{O}} \) in equilibrium with bulk Al\(_2\)O\(_3\), and \( \mu_{\text{H}} \). From these the dependent Al, \( \text{O}_2 \), \( \text{H}_2 \) and \( \text{H}_2\text{O} \) chemical potentials follow.

The results are shown in Fig. 2. The Gibbs free energies per surface area for various \((1 \times 1)\) geometries of the (0001) surface are displayed as a function of \( \mu_{\text{O}} \). The dashed black vertical lines bracket the allowed range of \( \mu_{\text{O}} \). For the systems containing just aluminum and oxygen, there is clearly only one overwhelmingly low energy surface stoichiometry: the Al\(_2\)O\(_3\)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 \( \text{O}_2 \) 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 \(^{20,21}\) indicate that the surface aluminum atom relaxes inward until it is practically coplanar with the oxygen layer, and rehybridizes to an \( sp^2 \) orbital configuation 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 3\( p_z \) 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 3\( p_z \) 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 non-bulk positions indicated in Fig. 1 increases the surface energy dramatically from 133 meV/\( \text{Å}^2 \) to 355, 282, and 228 meV/\( \text{Å}^2 \) for the three sites, respectively.

The \( \text{O}_3 \)-terminated surface has a very unfavorable energy, although this decreases sharply as \( \mu_{\text{O}} \) 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 \( \text{O}_2 \)-terminated surface has a consistently lower free energy than the \( \text{O}_3 \)AlAl-R, and the \( \text{O}_1 \)AlAl-R surface is more stable than \( \text{O}_2 \)AlAl-R, except at the highest range of the oxygen chemical potential. At 1000K the metal-terminated surfaces become the lowest energy sur-
For the oxygen-only terminated surface, theoretical predictions have indicated an inward relaxation of the top layer of 0.05Å. 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 0.12Å. Placing a hydrogen at site 1, however, results in a predicted outward relaxation of 0.11Å, in excellent agreement with experiment. Saturating the surface with hydrogen, the H$_2$O$_3$-structure, increases the predicted relaxation to 0.19Å. 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.

| interlayer | Theory of Ref. this | Experiment of Ref. |
|------------|---------------------|-------------------|
| Al-O$_2$   | −86 −86 −87         | −63 −51 +30       |
| O$_2$-Al   | +6 +3 +3            | −16 +6            |
| Al-3        | −49 −54 −42          | −29 −55           |
| Al-O$_2$   | +22 +25 +19          | +20 −             |
| O$_2$-Al   | +6 − +6             | −                |

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