

***Ab initio* structural predictions for ultrathin aluminum oxide films on metallic substrates**

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On several metallic substrates, first-principles density-functional calculations of Al_2O_3 5–7 Å films predict a structure, stabilized by interfacial electrostatics, which has no bulk counterpart. In two and three O-layer films, Al ions prefer distorted *tetrahedral* sites, over the normal octahedral sites. The film/substrate interface is found to consist of strongly chemisorbed oxygen and is the determining factor in geometry; these oxygens are only weakly perturbed by the presence of Al_2O_3 overlayers. In an experimentally relevant film (two O layers, as on NiAl), Al ions are nearly coplanar with surface O ions; thus observing “oxygen termination” does not indicate a polar surface. As a test case, we find Pt overlayers bind similarly as to $\alpha\text{-Al}_2\text{O}_3$, suggesting these films may indeed be useful models for thicker materials. [S0163-1829(99)50524-9]

Aluminum oxide films grow naturally on the Ni_3Al class of “superalloys,” giving corrosion protection in high-temperature environments,¹ such as jet engines. In addition, high-quality laboratory films grown on NiAl(110) (Ref. 2) and Ni_3Al (111) (Ref. 3) are experimental models for the study of corrosion, adhesion,⁴ and metal island formation relevant to heterogeneous catalysis.⁵ On these materials, film thickness is self-limited to 5 Å (two oxygen layers),^{2,3} but structural details are unknown. In contrast, thicker films can be grown in an O ambient by Al deposition. If the substrate is a refractory metal, annealing produces films with few surface defects,^{6,7} yet still sufficiently thin (~20–40 Å) to avoid charging problems, which were problematic in older oxide research.⁸ In spite of increased use in microelectronics,⁹ and rapid progress in oxide surface science,⁵ Al_2O_3 is not well understood microscopically. For these reasons, we desire an atomic-scale knowledge of Al_2O_3 film structure and growth, the oxide-metal interface, and adsorption properties.

In this paper, we report surprising first-principles density-functional results on the structure of ultrathin films (5–7 Å, 2–3 O layers). A different Al_2O_3 structure is predicted, which has no bulk counterpart, and is energetically favored on all metals studied. We show this geometry to be a natural consequence of previously unappreciated interfacial structure and electrostatics. In addition, this structure accounts for several unexplained experimental observations, such as the seemingly anomalous polar surfaces and the sharp “ γ -like” phonon signatures observed by ion scattering spectroscopy (ISS) and high resolution electron energy loss spectroscopy (HREELS), respectively, from films on NiAl(110).²

Because the Al ions occupy distorted tetrahedral site positions in the O sublattice, we refer to the structure as “ τ ”- Al_2O_3 . Whether this is a true phase is not known, because many hypothetical larger unit cells would have to be studied. However, the surprising result is the reversal in the films of the normal preference of Al ions for octahedral sites. We propose that this reversal will have morphological consequences in real films.

The preferred films have one full monolayer (ML) of chemisorbed oxygen on the metal substrate, with Al ions sitting atop, fourfold coordinated to the one below, and the three oxygen atoms above in the next layer (see Fig. 1).

While “oxygen terminated,”² a polar surface not favored in bulk-truncated materials,¹⁰ the film surface is actually neutral, as Al ions are almost coplanar with the O ions, which shadow the former from the ISS beam. This pattern persists in three O-layer films, though some stability and surface neutrality is lost (see below), possibly producing the self-limitation observed in Ni-Al alloy oxidation.^{2,3}

A critical question concerning the use of the Ni-Al oxide films as experimental models is whether adsorption properties are affected by the 5-Å thinness. Surprisingly, we find Pt adsorption on the two O-layer films compares very well with previous bulk sapphire, $\alpha\text{-Al}_2\text{O}_3$ (0001).¹¹ We ascribe this result to similar surface polarities (near neutrality) and close packing (low-energy electron diffraction² shows the film surface is close packed).

Lattice mismatches result in computationally prohibitive large unit cell for films on the Ni-Al substrates.² However, since no Ni is incorporated into the film nor has direct contact with oxygen atoms,² Al(111) is a valid model substrate for a theoretical study of these systems, and is, of course, of interest in itself. For comparison, we also study Mo(110) (Ref. 6) and Ru(001) (Ref. 7) substrates, used in the studies of deposited films.

Our electronic structure calculations used the massively parallel Gaussian-based code QUEST (QUantum Electronic

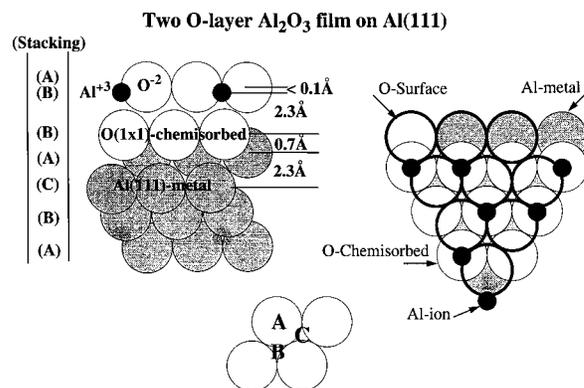


FIG. 1. Side and top views of the most favored geometry, with tetrahedral Al ions atop oxygens in the fcc hollows of the Al(111) surface, with a stacking fault at the second oxygen layer.

TABLE I. Stackings of the three metastable two oxygen layer (O₂) films. Site labels are shown in Fig. 1; *t* (*o*) has tetrahedral (octahedral) Al ions; and st denotes a stacking fault.

Atoms/structures	O2- <i>t</i> -st	O2- <i>t</i>	O2- <i>o</i> -st
Surface O	A	C	A
Al ions	B	B	C
Chemisorbed O	B	B	B
Al-metal layer #1	A	A	A
Al-metal layer #2	C	C	C

Structure)¹² and density-functional theory in the local-density approximation (LDA).¹³ The Perdew/Zunger parametrization¹⁴ of the Ceperley/Alder quantum Monte Carlo results¹⁵ was employed, with core electrons removed by the generalized norm-conserving pseudopotentials of Hamann.¹⁶ The atomic basic sets are of the “double zeta plus polarization” type.¹⁷ In order to achieve near-linear scaling, QUEST employs an algorithm due to Feibelman.¹⁸ Geometric relaxation is done through the iterative Broyden scheme developed by Johnson,¹⁹ using accurate computed interatomic forces.²⁰

Successful tests of computational accuracy were reported in our previous study of substitutional La in bulk α -Al₂O₃,²¹ which made comparisons to the LDA results of others.²² The computed lattice constant is within 0.3% of experiment. Further satisfactory tests were reported in a recent study of bulk-truncated α -Al₂O₃(0001) with metal overlayers.¹¹

Aluminum oxide consists of a close-packed oxygen sublattice. In the more important phases, this sublattice is somewhat distorted from hcp in α -Al₂O₃ (sapphire) and fcc in a γ phase, due to the symmetry of the Al sublattice. In γ , a small number of Al ions are thought to occupy tetrahedral sites (the exact percentage depends on the temperature history of the material²³), while in α -Al₂O₃ all are octahedrally coordinated. We write layering perpendicular to [001] as . . . O₃-Al₂-O₃ . . . , showing the number of atoms in the unit cell.

Our slabs had four layers of substrate metal (twelve atoms per unit cell), with an oxide layer on one side. The bottom two metallic layers are frozen at the LDA spacing, while all other atoms are geometrically free to relax. Because Al₂O₃ films on Al(111), Mo(110), and Ru(001) have lattice mismatches of only 2%, 1%, and 3%, respectively, we assume registry between the film and the substrate. Conceptually, one could construct an Al₂O₃ film on such a surface by mating the metal slab to a thin neutral oxide film. In the case of only two oxygen layers, the latter could be sequenced (from the vacuum down) Al₂-O₃-Al₂-O₃, Al₁-O₃-Al₂-O₃-Al₁, or O₃-Al₂-O₃-Al₂. However, the latter two arrangements produce vacancies at the interface, and tests show they are higher in energy than the first ordering and are unstable in that geometric relaxation changes the layering. [The first choice is equivalent to 2/3 ML of a metal (Al) on the oxygen-terminated film of interest.]

A different conceptual starting point notes that the lowest-energy interface is without vacancies and involves chemisorbed oxygen. Indeed, O(1×1)/Al(111) has been extensively studied experimentally²⁴ and theoretically,²⁵ and the binding energy of O to Al(111) is very large (5 eV at 1

TABLE II. Relative energies in eV per unit cell of the metastable films (stackings in parentheses).

Substrate	O2- <i>t</i> -st (A-B-B-A)	O2- <i>t</i> (A-B-B-C)	O2- <i>o</i> -st (A-B-C-A)
Al(111)	0.00	+0.20	+0.34
Mo(110)	0.00	+0.69	+0.80
Ru(001)	0.00	+0.07	+0.16

ML).²⁵ A neutral oxide overlayer of O₃-Al₂ then produces a 5-Å O-terminated film with two oxygen layers.

We first discuss two O-layer films on Al(111). Chemisorbed oxygen prefers fcc (vs hcp) hollow sites, and thus avoids sitting above the atoms in the second Al layer.²⁵ We encode possible stackings using the labels of Fig. 1, inset. Proceeding upwards from the topmost metal layer, which we take as A, and denoting the fcc site occupied by chemisorbed oxygen as B, due to permutations there are nine stacking possibilities for the next layers of Al ions and oxygens: A-A, A-B, A-C, B-A, etc.

Our calculations show that oxide geometries with Al ions directly above the somewhat positive Al metal-surface atoms (i.e., films of types A-A, A-B, and A-C) are both high in energy and unstable. Furthermore, the same is true if the Al ions are directly below the surface oxygens (types A-A, B-B, and C-C), as then the film surface is maximally polar. Thus, there are only three independent low-energy choices, and all are found to be stable after geometry relaxation (see Table I).

In Table II, we find the relative energies in eV of the three stable structures, and the favored one is shown in Fig. 1. We see a clear preference for tetrahedral-site Al ions, and a similar preference for a “stacking fault,” in that the fcc order is not preserved through the interface and into the film. In Table III, we see layer separations in the energetically favored system, averaged over the buckling produced by Al-sublattice asymmetry. (Only 2/3 of similar sites are occupied by Al ions, resulting in bucklings of up to 0.3 Å in the surface O layer and 0.2 Å at the interface.)

These results may be understood by basic electrostatics. Note first (Table III) that chemisorbed oxygen sits deep within the hollows of Al(111), and the metal-surface Al atoms are somewhat positive. The Al-O interplanar distance (0.7 Å) is the same as has been found for the O(1×1)/Al(111) system,²⁵ showing the presence of the oxide overlayer does not substantially perturb the strong chemisorption

TABLE III. Average interlayer spacings in Å for two O-layer Al₂O₃(001) films on Al(111), Mo(110), and Ru(0001), averaged over the buckling (see the text).

Layer pair/ spacing (Å)	Al(111)	Mo(110)	Ru(0001)
O-Al	0.05	0.29	0.07
Al-O	2.36	2.02	2.88
O-M	0.71	1.25	1.24
M-M	2.27	2.26	2.22
M-M	2.17	2.25	2.13
M-M (bulk)	2.29	2.16	2.15

TABLE IV. Adhesion energy (per atom) to the O_x-t -st films vs bulk sapphire(0001) (Ref. 11).

Pt overlayer	1 ML	2/3 ML	1/3 ML
α - Al_2O_3 (eV)	0.6	0.5	2.9
O2- t -st (eV)	0.7	0.8	3.0
O3- t -st (eV)	1.0	1.2	4.5

bond. Furthermore, the small vertical displacement reduces the net electrostatic interactions of these two layers with the ions above, and helps the overlayer Al ions sit high (2.4 Å) off the chemisorbed oxygens where they are nearly coplanar (within <0.1 Å) with the surface oxygens. The effect of this near coplanarity is to *neutralize* the surface oxide layer. Now the reason for tetrahedral site occupancy becomes clear, as electrostatics predicts atop site preference at any given height above a close-packed plane of opposite charges—the only time hollow sites are preferred is when the ion sits lower in the hollow site than in the top site. Here, however, achieving near layer-by-layer neutrality prevents significant lowering of the Al ions in the sapphiralike O2- o -st geometry.

In order to test the generality of the above argument, two O-layer films were similarly constructed on Mo(110), where chemisorbed oxygen prefers threefold hollow surface sites, and on Ru(001), where they prefer the hcp hollow. In both cases, atop tetrahedral-site Al-ions are preferred over octahedral (Table II), but only by 0.1–0.2 eV in the case of Ru(001); the basic geometries are also similar to Al(111) (Table III).

Calculations were also done for hypothetical films on Al(111) with three O layers. It was found that continuing the preferred tetrahedral order *did not* produce film metastability unless the Al metal atoms were frozen in place. These results seem consistent with the observation that stable oxygen-terminated films are not known on Al(111),²⁴ but do occur on NiAl where the substrate atoms are more rigidly bound. Furthermore, since no phase of Al_2O_3 is known with only fourfold-coordinated Al, instability must arise with increasing thickness as the energies of the film “bulk” and the interface compete.

In Table IV, the adhesion energies for 1, 2/3, and 1/3 ML “geometric” overlayers of Pt (i.e., 1 ML means one Pt atom per surface O atom) are presented for two and three-O layer films. The Pt/O2 energies are very similar to those found for sapphire(0001),¹¹ while those for Pt/O3 are 50% larger. This shows that the thinness of the real films being made on NiAl and Ni₃Al(O₂) and “oxygen termination” do not necessarily alter the binding. We ascribe the similarity of sapphire and O2 to the near coplanarity in the latter of Al ions with surface oxygens, neutralizing the surface polarity. However, with the hypothetical O3 the surface is much more polar, as we find the Al ions are fully 0.3 Å below the oxygen plane (vs <0.1 Å with O2). This suggests a loss of stability and is perhaps why the O3 films are not observed to grow on the Ni-Al materials.

Local densities of states (LDOS) for the clean two O-layer film are seen in Fig. 2. There are substantial differences between the surface (“O1”) and the chemisorbed (“O2”) oxygens; however, both are highly ionic as the areas are about the same and O1 closely resembles the LDOS from

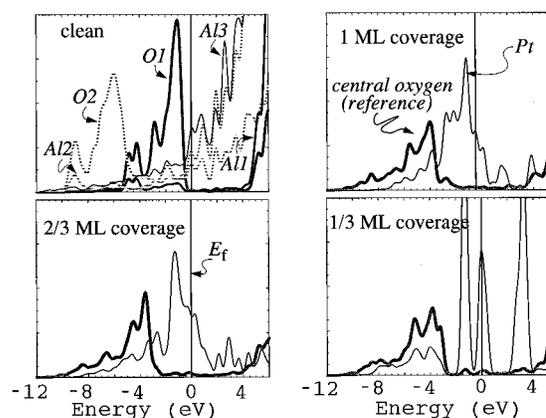


FIG. 2. Local densities of states for the clean two O-layer film on Al(111), and the three O-layer film with varying coverages of Pt (cf. Ref. 11), where the central O is shown for the position of the film band gap. Oscillations above E_f are due to finite k -point sampling. Surface atoms are O1 and Al1, interface atoms are O2 and Al2, and Al3 is at the metal slab center.

sapphire(0001), shown in Ref. 11. In addition, Al ions coplanar with the surface oxygens (“Al1”) also closely resemble sapphire, and the relative areas of O1 and Al1 show the high ionicity of the film. The Al atoms on the metallic surface (“Al2”) are clearly metallic in their resemblance to bulk Al (“Al3”), but the somewhat reduced area shows a fractionally positive charge. The Pt LDOSs for O2 adsorption closely resemble those for sapphire¹¹ and are not repeated. Here we show the Pt results for the more polar O3 surface, which also display the large differences between metallic Pt at 1 ML, and ionic (i.e., oxidized to Pt^{+1} , $\sim 6s^05d^9$) at 1/3 ML, where there are no nearest-neighbor Pt-Pt interactions. We also find Pt is metallic at 2/3 ML, where there are half the number of Pt-Pt bonds as in the case of 1 ML. There is no evidence of significant charge transfer to or from Pt at 1 or 2/3 ML, in that the areas of the LDOSs do not significantly change upon bringing the Pt layer into contact with the film. Instead, as with sapphire,¹¹ at these coverages the binding is dominated by Pt polarization to the ions at the oxide surface, similar to a mechanism proposed originally by Stoneham.²⁶ Furthermore, the reported dimer instability and trimer stability will also be the same.¹¹

In the case of NiAl(110) oxidation,² the HREELS “gamalike” phonon spectrum has three peaks between 400 and 900 cm^{-1} .²⁷ Furthermore, simulations reported in Ref. 2 showed this could indicate the presence of tetrahedral Al ions, which we confirm here. However, unlike γ - Al_2O_3 , with more octahedral than tetragonal ions (exact ratios depending on temperature²³), here octahedral site occupancy represents “defects” in the τ - Al_2O_3 structure, and numbers may again depend on temperature and substrate. On Mo(110), an “ α -like” spectrum (two peaks²⁷) is seen in the thinnest films, but with greater thicknesses (~ 20 Å) they are γ -like (all films were annealed at 1200 K).⁶ However, the reported extreme thinness of the Mo(110) film (4.4 Å) raises questions of uniformity, the bcc(110) face results in some symmetry breaking (from the near-hexagonal oxygen layer on the Al and Ru basal planes), and Table III shows greater surface polarity which could result in a different termination in the experimental situation; thus, this film needs to be studied separately.

Finally, one may ask whether use of the generalized gradient approximation (GGA) would alter our results, although prior work indicated it does not improve geometries and is apparently energetically unimportant for either the oxide²⁸ or for chemisorbed O/Al(111).²⁵ Recent GGA results support this, for while small changes occur in geometry and in the relative energies of Table II,²⁹ the new structure is still favored.

In conclusion, the structure of ultrathin (5 Å) Al₂O₃ films on metallic substrates is found to be contrary to that expected based on a knowledge of bulk phases. Morphological consequences may occur in films under ~10–20 Å, where the

ultrathin film energetics competes with that expected in thicker films. In spite of extreme thinness, the experimentally relevant 5 Å film is found to adsorb Pt very similarly to the bulk-truncated close-packed surface.

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