Sapphire (0001) Surface, Clean and with *d*-Metal Overlayers

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We present local density-functional results for structural and electronic properties of $Al_2O_3(0001)$, clean and with Pt and Ag adsorption. Significant surface relaxations penetrate to the third oxygen layer, 5.2 Å below the surface. The dominant mechanism of metal adhesion is polarization and is relatively weak ($\simeq$0.4 and 0.6 eV/atom for Ag and Pt, respectively); however, isolated metal atoms bind up to 5× as strongly with an ionic bond induced by the surface Madelung potential. [S0031-9007(98)08174-5]

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The nature of the binding of metals to oxides is not definitively established [1–4]. While some authors assumed dispersive forces, Stoneham proposed an electrostatic origin, namely, metal image polarization to oxide surface ions [5]; this and further work [6] estimated that adhesion would be several times stronger than van der Waals interactions alone. In contrast, for α-Al_2O_3, a material of central importance to ceramics, thin-film technologies, catalysis, and as electrical and corrosion barriers [7,8], first principles, though unrelaxed, cluster studies have found charge transfer (i.e., covalency) between the metal and oxide surface [9]. However, slab calculations using both Hartree-Fock [10] and the local density approximation (LDA) [11] found strikingly large surface relaxations in the Al sublattice, which thus prevents reliable quantitative results from the clusters of [9] or from these thin (three O-layer) slabs [10,11]. Also, another unrelaxed cluster study of the clean material [12] discovered an Al-derived surface state near the bottom of the band gap—obviously, saying whether such a state actually participates in the binding of metal overlayers is only possible given an accurate description of the surface, including appropriate relaxations with the metal present.

Major experimental advances have recently occurred due to (1) progress in growing high quality thin oxide films on conducting substrates [13], and (2) the development of microcalorimetry to measure the heat of adsorption of metal vapor on oxide films [3]. The first permits use of scanning tunneling microscopy (STM) and other surface science probes without charging problems. For example, with Pt deposition on an Al_2O_3 film, "dewetting" leading to nanoisland formation is seen, while other STM features suggest small isolated entities, perhaps Pt adatoms, in the presence of the islands [14]. The second advance has provided coverage-dependent heats of adsorption which invite theoretical comparisons. These examples show the necessity of a basic knowledge of the oxide-metal interaction for understanding metal film growth, the metal ceramic interface, and, in the future, the roles of defects and impurities.

In this Letter, we report the first LDA thick slab calculations (up to 18 oxygen layers) for the clean α-$Al_2O_3(0001)$ (sapphire) Al-terminated surface (energetically favored because it is closest to neutrality [12]). We find significant surface-induced relaxations to the third oxygen layer (5.2 Å) in depth. We also report on Pt and Ag adsorption at 1 and 1/3 geometric monolayer (ML). (A "geometric" ML has one metal atom per surface oxygen.) We find that both Pt and Ag 1 ML overlayers prefer atop-Al sites, which results in buckling. At this coverage, local densities of states (LDOS's) show no evidence of significant charge transfer between the metal overlayer and the oxide; i.e., the binding is dominated by polarization, though the thinness of the overlayer produces differences from the classical "image" form [5,6]. In contrast, at 1/3 ML coverage, at which the metal atoms have no nearest neighbor metal-metal bonds, the binding to the surface is about 3 to 5 times as strong and largely ionic. According to our total energy results, no surface wetting occurs with Pt, in agreement with experimental findings [14], and the equilibrium metal growth on the oxide surface would be three dimensional in the absence of kinetic factors. Finally, we use our computed energies to discuss Pt dimer formation, relevant to island nucleation.

With semiempirical approaches, large inaccuracies can result if calibrations are not available from experiment or *ab initio* theory [15–17]. The only first principles theoretical work on the interaction of metals with sapphire (0001) involved substituting atomic Nb for Al on the surface, and a layered Al_2O_3-Nb metal structure [18]: The strength and nature of Nb metal interactions [19] with the oxide was reported for the O-terminated surface [18] but not for the Al-terminated one (nor for the multilayer Nb-Al_2O_3 interface), and oxide slabs with only three O layers were used. Finally, the cluster calculations of Ref. [9] could not allow the surface to relax and/or were not embedded in a point-ion array (and thus could not possibly have had the high degree of ionicity relevant to the extended material). Thus the accurate theory presented here is clearly indicated.

Our electronic structure calculations were performed using the Gaussian-based density-functional pseudopotential code QUEST [20], expressly written for massively parallel computers. While excited state properties may need a treatment of correlations beyond LDA, the latter [21] generally yields excellent geometries and relative energies for metallic and ionic systems. We use the Ceperley-Alder exchange-correlation potential [22,23], and employ generalized norm-conserving pseudopotentials [24]. The atomic basis sets were of the "double zeta" plus polarization function type [25]. To achieve near-linear scaling, QUEST employs an algorithm due to Feibelman [26]. Geometric relaxation is done through an iterative Broyden scheme [27], using accurate forces [28].

For reference, we initially studied bulk α-Al_2O_3 electronic structure [29,30], finding interatomic distances in excellent agreement with experiment (within 0.2%) and other recent computational studies [31]. The electronic density of states is also in good agreement with experimental and theoretical data in the literature. As is typical of LDA calculations, the insulating gap (6.22 eV at the Γ point) is smaller than experiment, here by $\sim$30%, but agrees with an earlier result of 6.31 eV [30].

We then studied α-$Al_2O_3(0001)$ slabs of several thicknesses to determine sufficient depth for reliable quantitative results. The relaxed geometry for two of these structures is summarized in Table I. In the middle column, we display the relaxation in Å from an 18 O-layer slab (90 atoms per unit cell), which reduces the energy by 0.13 eV/Å^2, followed by percentage relaxation values for 18- and 9-oxygen layer slabs. In the bulk, between the staggered Al atoms, the intralayer Al-Al and the Al-O distances are 0.5 and 0.83 Å, respectively. Significant vertical relaxations occur deep within the slab due to displacements of the Al ions: only beyond the 7th and 8th layers are relaxations in the noise. Table I also shows the frustrated character of the relaxations in Refs. [10,12], where the electrostatics is confined within three O layers (actually two due to slab symmetry). While the distance between O planes changes negligibly ($<1\%$), appreciable in-plane oxygen relaxation ($<5\%$) occurs at the surface, due to the competing Al-O (now almost coplanar) and O-O interactions. These results are basically due to the open character of the Al sublattice, with atoms arranged in the …*Al*-*Al*-void … sequence along [0001], and to high ionicity [32], which causes small radius ($\sim$0.5 Å) Al^{+3} ions, which relax notably to the electric fields produced by the surface. The 18- and 9-layer slab results compare well for layers with significant relaxation; i.e., the 9-layer slab is sufficient for metal overlayer work.

TABLE I. Atomic relaxations for the (0001) surface for 18- and 9- O-layer slabs vs a 3-layer slab.

	18-layer (Å)	18-layer (%)	9-layer (%)	Ref. [10] (%)
Al-O	−0.728	−87.4	−86.4	−86
O-Al	+0.026	+3.1	+2.9	+3
Al-Al	−0.208	−41.7	−41.7	−54
Al-O	+0.157	+18.9	+18.3	+25
O-Al	+0.050	+6.0	+5.6	⋯
Al-Al	−0.041	−8.2	−8.3	⋯
Al-O	+0.016	+2.0	+1.1	⋯
O-Al	−0.010	−1.2	−0.5	⋯
Al-Al	+0.026	+5.2	+6.4	⋯
Al-O	−0.010	−1.1	−0.6	⋯
O-Al	−0.002	−0.4	+0.5	⋯
Next layers	≤±0.002	≤±1.1%	≤±1.1%	⋯

Incidentally, LDOS's for the clean surface (not shown) indicate that the Al surface state, reported just above the Fermi energy E_f in Ref. [12], moves >4 eV higher in energy upon relaxing the geometry. Even with the metal overlayers, this state remains well above E_f, preventing surface chemical activity involving the ion. This supports our assertion of the importance of an accurate description of surface relaxations in sapphire, and explains part of our disagreement with previous cluster results [9].

We now consider 1 ML commensurate overlayers of the metals, appropriate because of the small lattice mismatches ($<5\%$ based on the average O-O distance at the surface). Information on the relaxed geometries can be found in Table II, with coding explained in the right-hand panels of Fig. 1. At 1 ML, three inequivalent positions exist, indicated in Fig. 1 as *O* (atop the O atoms), *H* (atop the hollows), and *Al* (atop the Al atoms). Actually, the *Al* overlayer subsumes three distinct sites, *Al*1, *Al*2, and *Al*3, atop the deepest, shallowest, and middle Al atoms near the surface, respectively. We also show the surface unit cell (with unit vector length 4.74 Å). For both Ag and Pt, the total energy in the relaxed geometry shows that the *Al* position is preferred (for Ag, for example, *Al* is favored by 0.07 eV/atom over *O*, which in turn is favored also by 0.03 eV/atom over *H*). This is consistent with electrostatic binding, as may be seen by examining the local environment of the *Al*, *O*, and *H* sites. A first observation is that, in both cases, Al relaxes significantly outwards with respect to the clean surface (in line with general arguments concerning the potentials produced by metal polarization [5,6]). The average metal-O distance is 2.60 and 2.62 Å for Ag and Pt, respectively. Despite this similarity, the buckling in the metal overlayers (Table II) is more pronounced for Ag than for Pt. This can be understood in terms of stronger lateral binding for Pt than Ag, and the greater in-plane stiffness of the Pt metal layer. On the other hand, due to the onset of bulklike metal bonding, negligible ($<2\%$) buckling is found when a second layer of Ag (Pt) is added to the first, and the metal bilayer is farther ($\sim$10%) from the surface than in the 1 ML case. From analysis of the charge densities and integrated LDOS (seen in Fig. 2), no evidence (<0.05 electron) for significant charge transfer or covalency (<0.1 electron, obtained from the integrated interatomic LDOS, not shown) between Ag or Pt metals and the oxide is found,

TABLE II. Structure and adhesion for Ag and Pt; adhesion energies (E_a) are in eV and distances [see Fig. 1, (a)–(f)] in Å.

	1 ML, site *Al*					1/3 ML			
	E_a	(a)	(b)	(c)	(d)	E_a	Site	(e)	(f)
Ag	0.36	0.46	0.38	2.61	0.42	1.1	*Al*1	1.96	1.46
Pt	0.57	0.26	0.27	2.39	0.50	2.9	*O*	1.98	1.42

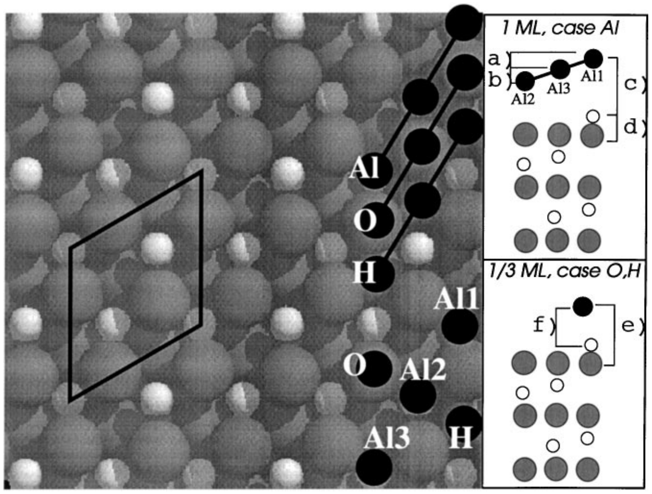

FIG. 1. The (0001) surface, top view: The surface unit cell is shown, together with the possible choices for the commensurate metal overlayer at 1 ML (Al, O, H) and 1/3 ML ($Al1$–$Al3$, O, H) coverages. On the right, a schematic side view which codifies the symbols in Table II is shown. Adsorbed Pt, Ag atoms are denoted by filled black circles.

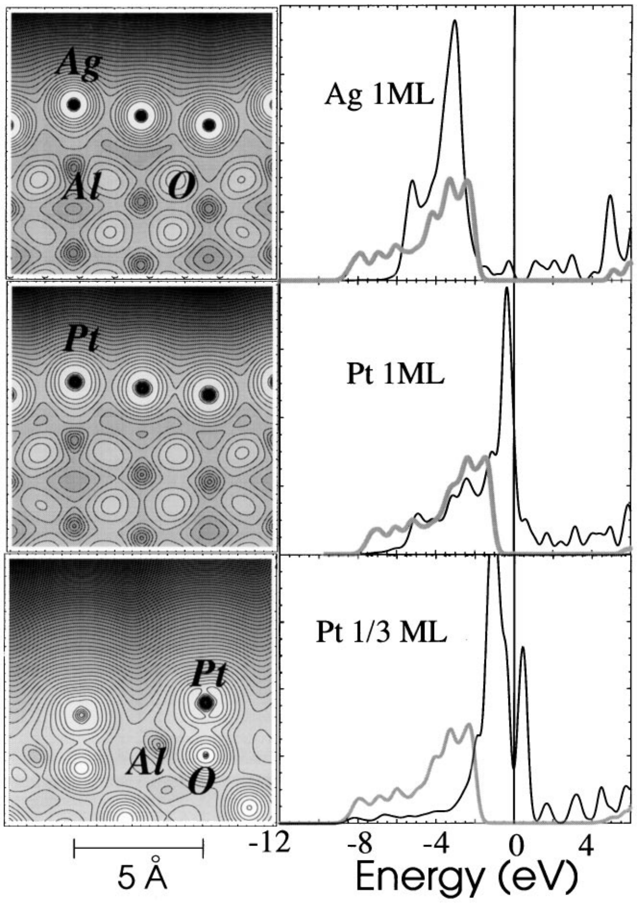

FIG. 2. Ag and Pt charge densities and local densities of states (LDOS's) at different coverages. At 1 ML coverage, the charge density plane is across the three metal atoms in the surface unit cell; at 1/3 ML, with the plane is across the metal, with the O atom beneath it and the closest top Al atoms. In the right panels, the metal LDOS (thin solid curves) is shown, together with the bulk oxygen LDOS (thick grey curves), and the Fermi energy (vertical lines) for reference. Oscillations due to finite k sampling are seen in the gap region.

and thus the relatively weak binding (0.36 eV/Ag atom and 0.57 eV/Pt atom) is largely caused by metal polarization to the Al_2O_3 surface electrostatic field, with Pt being more strongly bound than Ag because of the open d shell, which allows intrashell rehybridization and more mixing with the s band than in the case of Ag.

At 1/3 ML coverage, $Al1$, $Al2$, and $Al3$ constitute separate possibilities and, together with O and H, produce five possible sites, as seen in Fig. 1. For Pt, our relaxed total energies show $E_O < E_H \ll E_{Al1,2,3}$, with the Pt atom now much closer to the surface (see Table II and Fig. 1). However, for Ag, the $Al1$ site is preferred. A completely different type of binding is now found, with much larger "adhesion" energies of 2.9 and 1.1 eV for Pt and Ag, respectively. For example, as seen in the Pt electron density plot of Fig. 2, there is a visible structure from the reduction of d_{z^2} charge (if we take d_{z^2} along the Pt-O axis), allowing for a smaller Pt-O distance. Coverage dependence also affects the LDOS: In Fig. 2, right panels, Ag and Pt at 1 ML show a typical metallic form (small differences from the bulk metal being due to the 2D character). At 1/3 ML, there is a significant splitting of the Pt d levels. The LDOS's of the individual d-shell orbitals (not shown) show all are nearly full except for d_{z^2}, which is about half full. Thus total d-shell occupancy is not substantially changed from 1 to 1/3 ML, suggesting s-orbital density is taken up by oxide surface ions. The Madelung potential at the height of the Pt ion above the surface is 25 V (assuming fractional charges of $Al^{+2.7}O^{-1.8}$ [32]), more than sufficient for multiple ionization. Of course, lateral electrostatic interactions reduce the tendency to ionize, but calculations done at 1/12 ML coverage [33] find similar Pt binding, suggesting that the 1/3 ML results closely mimic isolated adatoms. Thus, at 1/3 ML, lateral metal-metal bonding is negligible, and the near-isolated Pt and Ag atoms respond to the surface Madelung potential.

The atop-O (O) site preference for 1/3 ML Pt is not large. We believe O is preferred only because the $Pt^{\sim +1}$ is relatively large and cannot sink very deeply into the electrostatically preferred Al1 hollow, as can $Ag^{\sim +1}$. Further evidence that this is true was provided by calculations of 1/3 ML Cu: the smaller Cu ions also prefer $Al1$ over O.

A detailed understanding of the kinetics and dynamics of metal deposition is important to technologies involving metal film growth on oxides. Useful information on growth mode(s) can be obtained from thermodynamic quantities (free energy) or, at zero temperature, in terms of total energy (E_t) and Born-Haber cycles. For Pt, we find that $E_t(1\text{ ML Pt} + Al_2O_3) + 2E_t(Al_2O_3) < 3E_t(1/3\text{ ML Pt} + Al_2O_3)$, and that $E_t(2\text{ ML Pt} + Al_2O_3) + E_t(Al_2O_3) < 2E_t(1\text{ ML Pt} + Al_2O_3)$; i.e., our total energy calculations predict no wetting and, except for kinetic factors, that 3D growth would prevail over flat island growth even at less-than-monolayer coverages.

It is likely that surface defects are necessary to nucleate metal island growth: While Pt dimers bind strongly in the gas phase (3.3 eV [34]), our LDA results predict two atoms would rather adsorb separately, yielding 6 eV total. If a dimer adsorbs by polarization as does the 1 ML metal, it would bind weaker than the monolayer (<0.6 eV/atom) due to increased electronic stiffness from the stronger pair bond in the dimer. If the dimer were to transfer 6*s* electron density to the surface, as the adatom does, this would strengthen adsorption but weaken the covalent dimer bond. While a definitive answer must await the difficult calculation of an isolated dimer, a second factor is the activation barrier for dimer formation: Positively charged metal adatoms suggest a high barrier, so dimers might not form under experimental conditions even if they were energetically favored. In contrast, trimers and anything larger should be stable against edge atom evaporation on the surface due to the strong Pt-Pt bonds ($\sim$2.7 eV/pair based on our 1 ML film LDA calculations). Indeed, some thin-film experimental evidence exists that shows that defect site nucleation occurs for Pt [14].

Finally, we examine recent results obtained in the generalized gradient approximation (GGA) for Pt and Ag adsorption on the nine O-layer Al_2O_3 slab [33]. Although it has been reported that GGA does not improve Al_2O_3 geometries and is apparently unimportant for its energetics [17,29], others have concluded that, on MgO(001), it is important for metal adatom energies [35]. Here, no change in adsorbate site preference was found using GGA, and, while a weakening of adsorbate binding and some lengthening ($\sim$0.1 Å) of interatomic distances are noted [36], our fundamental conclusions are robust.

Our study of sapphire (0001) with *d*-metal overlayers provides the first accurate *ab initio* description of the fundamental nature of the interfacial bonds [37], which have been debated in the literature. Surface relaxations must be included for a correct description. Extending these investigations to other sapphire surfaces and to other metal overlayers, where large relaxations are also expected, can lay a foundation for understanding film growth and perhaps the ability to tailor wetting and adhesion.

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[1] *The Surface Science of Metal Oxides,* edited by V. E. Henrich and P. A. Cox (Cambridge University Press, Cambridge, England, 1994).

[2] M. W. Finnis, J. Phys. Cond. Matter **8**, 5811 (1996).

[3] C. T. Campbell, Surf. Sci. Rep. **27**, 1 (1997); J. T. Stuckless *et al.,* J. Chem. Phys. **107**, 5547 (1997).

[4] C. Noguera and G. Bordier, J. Phys. III (France) **4**, 1851 (1994).

[5] A. M. Stoneham, Appl. Surf. Sci. **14**, 249 (1983).

[6] M. W. Finnis, A. M. Stoneham, and P. W. Tasker, in *Metal Ceramic Interfaces,* edited by M. Rühle, A. G. Evans, M. F. Ashby, and J. P. Hirth, (Oxford:Pergamon, New York, 1990), p. 35.

[7] Special issue of J. Am. Ceram. Soc. **77** (1994).

[8] M. L. Bortz *et al.,* Phys. Scr. **41**, 537 (1990).

[9] Ni: G. Pacchioni and N. Rösch, Surf. Sci. **306**, 169 (1994); Fe, Ni, Cu, Ag: K. H. Johnson and S. V. Pepper, J. Appl. Phys. **53**, 6634 (1982).

[10] C. Pisani *et al.,* Prog. Surf. Sci. **25**, 119 (1987); M. Caus *et al.,* Surf. Sci. **215**, 259 (1989); V. E. Puchin *et al.,* Surf. Sci. **370**, 190 (1997).

[11] I. Manassidis, A. De Vita, and M. J. Gillan, Surf. Sci. Lett. **285**, L517 (1993); Philos. Mag. B **69**, 879 (1994).

[12] J. Guo, D. E. Ellis, and D. J. Lam, Phys. Rev. B **45**, 3204 (1992).

[13] H.-J. Freund, H. Kuhlenbeck, and V. Staemmler, Rep. Prog. Phys. **59**, 283 (1996).

[14] T. H. Bertrams *et al.,* Surf. Sci. **331**, 1515 (1995).

[15] N. L. Allan and W. C. Mackrodt, Philos. Mag. B **69**, 871 (1994).

[16] M. Wilson *et al.,* Phys. Rev. B. **54**, 15 683 (1996).

[17] Y. Yourdshayan *et al.,* Phys. Rev. B **55**, 8721 (1997).

[18] C. Kruse *et al.,* Philos. Mag. Lett. **73**, 377 (1996).

[19] Recently, very strong metal/ceramic adhesion was experimentally observed for Nb/Al_2O_3 by Song *et al.* [Phys. Rev. Lett. **79**, 5062 (1997)].

[20] QUEST, QUantum Electronic STructure, written and developed by M. P. Sears and P. A. Schultz at Sandia National Laboratories, Albuquerque, New Mexico 87185-1111.

[21] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[22] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[23] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[24] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[25] P. A. Schultz, paschul@cs.sandia.gov.

[26] P. J. Feibelman, Phys. Rev. B **33**, 719 (1986); *ibid.* **35**, 2626 (1987); *ibid.* **38**, 1849 (1988).

[27] D. D. Johnson, Phys. Rev. B **38**, 12 807 (1988).

[28] P. Pulay, Mol. Phys. **17**, 197 (1969).

[29] I. Frank, D. Marx, and M. Parrinello, J. Chem. Phys. **104**, 8143 (1996).

[30] W. Y. Ching and Y. N. Xu, in Ref. [7], p. 404.

[31] J. C. Boettger, Phys. Rev. B **55**, 750 (1997).

[32] C. Sousa, F. Illas, and G. Pacchioni, J. Chem. Phys. **99**, 6818 (1993).

[33] A. Bogicevic and D. R. Jennison (to be published).

[34] S. H. Yang *et al.,* J. Phys. Condens. Matter **9**, L39 (1997).

[35] I. Yudanov *et al.,* J. Phys. Chem. B **101**, 2786 (1997).

[36] GGA predicts 0.4 (2.0) and 0.12 (0.5) at 1 (1/3) ML for Pt and Ag, respectively; see Ref. [33].

[37] From an experimental perspective, conclusions similar to ours had been anticipated in Ref. [3].