Layer intermixing during metal/metal oxide adsorption: Ti/sapphire(0001)C. Verdozzi,¹ P.A. Schultz,² Ruqian Wu,^{1,3} A.H. Edwards,⁴ and Nicholas Kioussis¹¹*Department of Physics, California State University Northridge, Northridge California 91330*²*Sandia National Laboratories, Albuquerque, New Mexico 87185-1413*³*Department of Physics and Astronomy, University of California, Irvine California 92697-4575*⁴*Air Force Research Laboratory, Kirtland AFB, New Mexico 87117-5776*

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First principles density functional calculations for adsorption of Ti on $\text{Al}_2\text{O}_3(0001)$ indicate that $\text{Ti}:\text{Al}_2\text{O}_3(0001)$ interfaces become intermixed. Substitutional Ti replaces a surface Al atom rather than a subsurface Al, and the Al-terminated surface is unstable under Ti adsorption. Adsorbed Ti displaces the surface Al, resulting in a mixed Ti/Al interfacial layer instead of a sharp $\text{Ti}:\text{Al}_2\text{O}_3$ interface. Our results provide a coherent picture of the structural and electronic properties of this interface and are consistent with available experimental data.

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Metal/metal oxide interfaces are crucial to electronics devices, and aluminum (Al_2O_3) and titanium (TiO_2) oxides play pivotal roles.¹ The $\text{Ti}:\text{sapphire}$ interface at low Ti coverage has notable applications in high power laser² and optoelectronics waveguide³ technologies. More generally, Ti/Al oxide interfaces occur in several applications. These include, for example, Ti/Al alloys for aerospace/automotive applications, when an Al_2O_3 coat evolves into $\text{Al}_2\text{O}_3 + \text{TiO}_2$,⁴ or nanolayered sandwich structures, such as $\text{Cu, Ag/Ti/Al}_2\text{O}_3$, where Ti prewetting improves Cu and Ag adhesion.^{5,6}

While an extensive literature exists in general for clean oxide surfaces and metal- or oxide-oxide interfaces, much less effort has been devoted to understanding the specific $\text{Ti}:\text{sapphire}$ interface. Although crucial to the technological applications mentioned above, many aspects of such interface are currently uncertain. Furthermore, the current microscopic understanding of the $\text{Ti}:\text{sapphire}$ interface derives exclusively from experiment,^{5–10} with temperatures in these studies varying from 300 K (Ref. 8) to above 1100 K.^{7,9} In some cases, experimental evidence is inconclusive: for example, RHEED and ion scattering results⁹ for low-dosage, shallow-implant Ti, indicate that Ti is in the surface layer atop the (subsurface) Al atoms, even though the actual site preference of the substitution is uncertain. Also, this leads to commensurate growth of crystalline Ti.⁹ Moreover, XPS (Ref. 7) and Auger⁸ data show clearly that at elevated temperatures the metallic Al $2p$ signal is present and the shape of the valence bands, which have primarily oxygen character, are broadened. Furthermore, the Ti $2p$ signal is shifted. All of this is consistent with the formation of an oxidized Ti layer and concomitant partial Al_2O_3 reduction.

In this paper we report the first *ab initio* density functional results to elucidate the nature the $\text{Ti}:\text{sapphire}$ interface. We find that: (i) substitutional Ti prefers to replace the terminating Al rather than the subsurface Al and, additionally, little deformation of the surface occurs in the latter case; (ii) a single Ti adatom on sapphire displaces the terminating Al rather than adsorbing atop the surface; and (iii) a mixed Ti_2Al adlayer on a Ti-terminated oxide surface is preferred over a sharp $\text{Ti}_3:\text{Al}_2\text{O}_3$ interface. These results indicate that

the Al-terminated surface is unstable to Ti adsorption, and predict a mixed Al/Ti interfacial layer.

The calculations were performed using density functional theory in the local density approximation,^{11,12} which yields excellent structural energetics for many oxides and specifically for Al_2O_3 . We used SEQUEST,¹³ a Gaussian-based linear combination of atomic orbitals method. Standard (non-local) norm-conserving pseudopotentials were used for O (Ref. 14) and Al.¹⁵ For Ti, the pseudopotential¹⁵ placed the six $3p$ (together with the $3d$ and $4s$) electrons in the valence space, leaving the $3s$ electrons in the core, and invoked a nonlinear core correction.¹⁶ The basis sets were high-quality, optimized “double zeta plus polarization” contracted Gaussian functions.¹⁷

Our calculations involved 1×1 and $\sqrt{3} \times \sqrt{3}$ surface unit cells (SUC) of sapphire (0001), $a = 4.757 \text{ \AA}$, with slabs nine O-layers thick: $1 \times 1 = 45$, $45 + 1$, and $45 + 3$ atoms/cell, and $\sqrt{3} \times \sqrt{3} = 135$ atoms/cell. Several theoretical^{18–32} and experimental³³ studies of the sapphire (0001) surface are in broad agreement, showing large Al relaxations deep below the surface and predicting a Al-terminated clean sapphire (0001) surface for UHV environments. This is the surface termination used as a starting point in our calculations. Selected results for the 1×1 systems were compared to and found consistent with 18 layer slabs. Ti atoms were adsorbed on only one side, and artificial interslab dipole interactions were exactly removed with the local moment counter charge method.³⁴ A converged Brillouin zone (BZ) sampling used a hexagonal k -grid with 32 (8) points in half of the BZ for the 1×1 ($\sqrt{3} \times \sqrt{3}$) super-cell, reduced to 12 (4) special k -points in the irreducible BZ when threefold symmetry was available. The entire slab geometry was relaxed until the maximum force was $< 0.01 \text{ eV/\AA}$.

Figure 1 summarizes the structures investigated. Let Al₁ represent the bare, Al-terminated, sapphire (0001) surface, depicted in the side and top views in Figs. 1(a) and 1(b,c) respectively. The three different aluminum sites are denoted by Al1–Al3, and the two oxygen sites O1–O2 (in order of increasing depth). A Ti-terminated surface in which the terminating Al is replaced by a Ti is denoted Ti₁. At

FIG. 1. Side (a) and top (b,c) views of the sapphire (0001) surface. White (gray) circles denote Al (O) atoms. The 1×1 SUC is shown in (b), and the three in-registry (three-atom) adlayer conformations are depicted in (c).

higher metal coverage (+3 atoms), there are three “in-registry” conformations, denoted M1–M3 in Fig. 1(c). For M1(M2), all three adatoms start at equivalent O1(O2) sites. The M3 conformation occupies the three inequivalent Al sites, leading to three distinct permutations of atoms for the Ti_2Al M3 adlayer considered later. In all cases, the adatoms can relax off of these nonsymmetry sites.

Substitutional Ti at and below the surface. Because the substitutional surface is crucial to understanding the physics of Ti coverage and intermixing, we first studied whether Ti preferred to substitute for the surface (Al1) or subsurface (Al2 or Al3) aluminum atoms.

We used a $\sqrt{3} \times \sqrt{3}$ SUC, replacing one of the three surface (Al1) or subsurface (Al2) atoms in the SUC with a Ti. The threefold symmetry that exists for these configurations was retained. The Ti–Ti separation of 8.24 Å in this cell is reasonably sufficient to simulate single impurity doping.³⁵ Ti substituting for Al1 induces only small changes in the host; displacements of neighboring O and Al are negligible. The Ti sits 0.58 Å above the O1-plane, 0.48 Å higher than the Al it replaces in Al_t , due to its larger size. The minimal structural changes suggest that Ti primarily compensates the local polarity of the replaced Al. As expected, the subsurface (Al2) substitution causes somewhat larger host modifications, but the relaxations are still minor and limited to adjacent Al and O atoms. This points to a surface “resiliency” as found in experiments.¹⁰ The O1-layer rumples with deviations of the O z -coordinate from the average by less than 0.09 Å, with similar small in-plane displacements. The average O1–O2 layer spacing (2.13 Å for Al_t) increases by <0.07 Å, and the Al1–O layer spacing also increases, by <0.05 Å. Total-energy results favor Ti replacing the surface Al1 over subsurface Al2 (consistent with experiment⁹) by 0.92 eV. Removing the Al1 atom and placing Ti above Al3 is not a viable alternative; the energy is 1.8 eV higher.

Additional insight can be gleaned from the local density of states (LDOS) projected onto Löwdin orbitals. In Fig. 2(a) [2(b)] we show the LDOS for the surface (subsurface) Ti impurity, and for the neighboring O atoms.

The integrated LDOS, Löwdin populations (LP), of the next-nearest neighbor O atoms (6.66 e) already resembles that in clean Al_t (6.68 e) (for neutral O, LP=6.0). The Ti impurity LDOS has a peak at E_F , which is larger and narrower for the subsurface Ti [Fig. 2(b)] than for the Ti in the

FIG. 2. LDOS for Ti impurities in (a) surface-Al1 and (b) subsurface-Al2 sites. Dotted (dashed) curves, magnified four times, are LDOS for the nearest-neighbor (next nearest) O to the Ti. In both panels, solid curves refer to Ti, and $E_F=0$.

terminating surface site. The surface Ti d -states are strongly split, with an excess of 0.4 electrons of $3z^2-r^2$ character. In contrast, the subsurface Ti has a more localized, compact electron population with more nearly constant d -LP’s in response to the more isotropic Madelung field.

Isolated Al (Ti) atom on the Ti_t (Al_t) surface. Having established that a substitutional Ti prefers to replace the terminating Al, we next examine whether a single Ti adatom added to a clean Al_t surface adsorbs atop the surface ($\text{Ti}:\text{Al}_t$), or displaces a surface Al, forming $\text{Al}:\text{Ti}_t$. The 0 K calculations reported here should give insight into the interface formation³⁶ and diffusion barriers. However, a comprehensive theoretical description would require the inclusion of kinetic effects and explicit calculations of transition barrier energies, beyond the scope of this work.

The ground state configuration is found within those associated with $\text{Al}:\text{Ti}_t$, with Al relaxing into an adatom site between O1 and O2 [Fig. 1(a)]. The Al relaxes to this site from either the O1 or O2 starting point. Total energies, referenced to this state, of five distinct adatom sites [i.e., Al1–3 and O1–2, Fig. 1(a)] for both $\text{Al}:\text{Ti}_t$ and $\text{Ti}:\text{Al}_t$ are listed in Table I. The ground state is favored by 0.40 eV over the next most stable configuration: $\text{Ti}:\text{Al}_t$ with Ti atop the Al3 site. In the presence of the Ti adatom at the Al3 site the surface Al atom moves 0.77 Å outwards from its clean surface position [Al1 in Fig. 1(b)]. Concomitant with this relaxation, the Al LP changes from 1.87 e on the clean surface to 2.41 e , closer to the neutral value of 3.0 e . The O ionicity remains nearly constant, leading to a smaller Coulombic attraction between the surface aluminum and its neighboring O ions. This is consistent with the fact that Ti is less electronegative than Al. Although the difference is small, the net change in ionicity may result from a feedback wherein the Al atom loses more charge by separating further from its neighbors. We expect similar behavior whenever the metallic adatom has a smaller electronegativity than Al.³⁷

When comparing $\text{Al}:\text{Ti}_t$ to $\text{Ti}:\text{Al}_t$ we see the same qualitative trend; even though the partial s -, p -, d -LPs for the surface atoms are rather different, the total LP for the Ti and surface O are virtually identical, while the LP difference for

TABLE I. Relative energies (in eV) for relaxed surface configurations started from different initial starting points, for the $\text{Al}:\text{Ti}_t$ and $\text{Ti}:\text{Al}_t$ single adatom surfaces, and for the three-atom adlayer $\text{Ti}_3:\text{Al}_t$ and $\text{Ti}_2\text{Al}:\text{Ti}_t$ geometries. Energies in bold indicate constrained threefold symmetry and u denotes structurally unstable configurations. Energies marked by an asterisk pertain to extrema (local maxima or saddle points) rather than minima: forces are zero, but a very small perturbation would lead to downhill motion to one of the other configurations. The (normal) distance (in Å) of the terminating metal atom to the O1-plane is given for both the clean Ti_t and Al_t (d_{clean}), and for the minimum energy configuration with adsorbates (d_{adsorb}).

	O1	O2	Al1	Al2	Al3	d_{clean}	d_{adsorb}
$\text{Al}:\text{Ti}_t$	0	0	1.15	0.67*	0.45*	0.58	0.67
$\text{Ti}:\text{Al}_t$	1.20	1.20	4.65	1.20	0.40	0.10	0.87
			M3	M3	M3		
	M1	M2	Al1	Al2	Al3	d_{clean}	d_{adsorb}
$\text{Ti}_2\text{Al}:\text{Ti}_t$	1.27	u	0.35	0.0	u	0.58	0.61
$\text{Ti}_3:\text{Al}_t$	2.44	4.31*	1.46	...	...	0.10	0.77

the surface Al atom differs by only ~ 0.2 electron. The similar LP's and the small total energy difference (0.40 eV), suggest that Ti displacing Al in the surface results from a subtle charge redistribution.

The $\text{Ti}:\text{Al}_t$ configuration assumed in Ref. 9 is partially unsupported by our calculation, since Ti largely prefers Al3 to Al2 adsorption sites. The O1 and O2 adatom sites are not even metastable in $\text{Ti}:\text{Al}_t$: starting from either of these positions, a Ti adatom relaxes to the Al2 site. The Ti position in $\text{Al}:\text{Ti}_t$ is mostly unchanged by the Al adatom. The calculated Ti adsorption energy is ~ 5.0 eV, substantial, but not atypical for sapphire surfaces. Previous results²² for 1/3 ML Pt on the clean surface reported an adsorption energy of 2.9 eV. The LDOS results for $\text{Al}:\text{Ti}_t$ ($\text{Ti}:\text{Al}_t$) are shown in Fig. 3(a) [3(b)]. The three key atoms are the surface Al and Ti, and their nearest neighbor, the intermediate O. The most important feature is the behavior of Ti and Al LDOS close to E_F . In $\text{Ti}:\text{Al}_t$ [Fig. 3(b)], the Ti LDOS exhibits a large peak across E_F , with minimal overlap with the Al LDOS. The situation is quite different in $\text{Al}:\text{Ti}_t$ [Fig. 3(a)]; the change in the local environment reflects into a redistribution of states near E_F ; specifically, a splitting in the Ti LDOS at E_F transfers significant intensity 0.4 eV below E_F that overlaps strongly with the Al LDOS.

Ti_3 (Ti_2Al) onto the Al_t (Ti_t) surface. The final issue we consider is whether higher coverages of Ti on sapphire(0001)

FIG. 3. LDOS for (a) $\text{Al}:\text{Ti}_t$ and (b) $\text{Ti}:\text{Al}_t$. Dotted, dashed, and solid curves refer to Al, O, and Ti, respectively, and $E_F = 0$.

leave an oxidized Ti in the surface (with a mixed metal overlayer), or segregate into a distinct Ti-overlayer. The results are presented in the last two rows of Table I, and show a mixed Ti_2Al overlayer (atop metal sites, Al in the Al2 site) is favored by 1.46 eV over the lowest-energy Ti_3 overlayer configuration (atop Al positions). Both the Ti_3 and the Ti_2Al overlayers exhibit considerable buckling, also found for other metals on sapphire. The Ti_3 adlayer has the same effect on the sapphire substrate that a single Ti adatom has (see above), moving the terminating Al outwards from its clean surface position. This suggests that the same mechanism of electron redistribution and structural rearrangement applies. A discussion of the electronic properties will be presented elsewhere.

Our study is the first *ab initio* description of the $\text{Ti}_x\text{Al}_2\text{O}_3$ interface and provides a theoretical rationalization, consistent with available experiments, of many aspects of the interfacial behavior. These are the surface rigidity of sapphire for dilute shallow Ti impurities; the Ti preference for surface rather than subsurface replacement of Al; the instability of the Al-terminated sapphire surface in the presence of Ti; and the consequent formation of a mixed Al/Ti layer at the onset of interface formation. These results should be germane to other $\text{Ti}_x\text{Al}_y\text{O}_z$ phases of Ti/Al-based technological materials, and informative to the adsorption of other metals on the Al_2O_3 surface.

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