

Position of the Oxygen Overlayer on Al(111)

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The energy bands, work function, Al $2p$ chemical shift, and oxygen binding energy have been calculated self-consistently for six-layer Al(111) films with oxygen overlayers at $Z = 0.55, 0.60,$ and 0.70 \AA above the Al surface plane. Because the work function is extremely sensitive to Z , it has been estimated with very small uncertainty, $Z = 0.578 \pm 0.032 \text{ \AA}$. This value is in excellent agreement with the values obtained from the chemical shift and binding energy as well as Stöhr *et al.*'s experimental value.

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The height of the 1×1 oxygen monolayer above the Al(111) surface plane is still a matter of some controversy. Three low-energy electron diffraction (LEED)¹⁻³ determinations place the O atom in the threefold hollow site at distances $Z = 1.46, 1.33,$ and 1.54 \AA above the Al plane. The extended x-ray absorption fine structure (EXAFS) measurements of Stöhr *et al.*⁴ yielded $Z = 0.70 \text{ \AA}$. We⁵ previously reported a self-consistent linear combination of Gaussian orbitals (SCLCGO) energy-band and binding-energy calculation for oxygen overlayers at $Z = 1.4, 1.0,$ and 0.70 \AA above a six-layer Al(111) film. We found for the LEED separation of 1.4 \AA that the calculated work function was 5.5 eV too large, the Al $2p$ chemical shift had the wrong sign, and the O binding energy was negative. For $Z = 0.7 \text{ \AA}$ our calculated results were in only fair agreement with experiment and, because we felt our computational accuracy was better than that agreement, we suggested that perhaps the oxygen monolayer should lie under the surface. Wang, Freeman, and Krakauer,⁶ with calculated results very similar to ours, thought that the agreement with experiment for $Z = 0.7 \text{ \AA}$ was sufficiently good to conclude that that was the correct spacing. It is difficult to compare the accuracy of their calculation with ours; however, we note that for clean Al(111) they obtained⁷ a work function of 4.7 eV whereas both here and in our original calculation⁸ we come well within 0.1 eV of the experimental value of 4.26 eV .

Since our work appeared, Bachrach, Hansson, and Bauer,⁹ using EXAFS, found that at low pressure O_2 chemisorbs while at high pressure O chemisorbs with $Z = 0.98 \text{ \AA}$. Soria *et al.*,¹⁰ using LEED and Auger spectroscopy, reported a 1×1 O underlayer and $Z = 0.73$ and 0.80 \AA overlayer for O_2 exposures of 30, 100, and 150 L, respectively ($1 \text{ L} = 10^{-6} \text{ Torr sec}$). Norman *et al.*¹¹ have refined their EXAFS measurements to ob-

tain $Z = 0.60 \pm 0.10 \text{ \AA}$ (corresponding to an O-Al bond length $R = 1.76 \pm 0.03 \text{ \AA}$) for the overlayer associated with a 1.4-eV Al $2p$ chemical shift. They also find an ordered underlayer with $R = 1.75 \pm 0.03 \text{ \AA}$, implying a tetrahedral O site. This phase, which occurs upon heating to $200 \text{ }^\circ\text{C}$, has a 2.7-eV chemical shift. Both phases occur simultaneously with O_2 exposure greater than 50 L. This is consistent with the vibrating-capacitor work-function measurements¹² which find that φ decreases by 200 meV under the first 50 L O_2 exposure and then increases by 80 meV under the next 200 L. Photoemission measurements¹³⁻¹⁵ of $\Delta\varphi$ give varying results but all agree that for small to moderate O_2 exposures, $\Delta\varphi < 200 \text{ meV}$. We here repeat our calculation of Ref. 5 for $Z = 0.70, 0.60,$ and 0.55 \AA and confirm Norman *et al.*'s result with even smaller uncertainty than theirs, due to extreme sensitivity of the work function to Z .

We used the same 128 orbital basis set for the six-Al, two-O layer film that was used in Ref. 5 and used the same triangle integration scheme between 73 points in the $\frac{1}{12}$ th irreducible two-dimensional Brillouin zone to calculate the Fermi level, charge density, and Kohn-Sham-Wigner exchange-correlation potential. We fit the exchange-correlation potential with 26 spherical Gaussians on each Al and 23 on each O atom¹⁶ but rather than using plane-wave Gaussians of the form $\exp[-\alpha(z-z_0)^2 + i\vec{G} \cdot \vec{r}]$ we used 245 symmetrized combinations¹⁷ of three-dimensional plane waves with k_z chosen to give periodicity over 9 Al interplanar spacings. The charge density was fit with the Laplacian of these functions together with two charge-containing Gaussians on each atom. The fit was made at 3100 points in the $\frac{1}{6}$ th irreducible wedge of the unit cell of the half film out to 4.5 interplanar spacings. The two schemes give fits of equal quality but the three-dimensional plane waves have technical advantages to be discussed

TABLE I. Oxygen binding energy E_B , work function ϕ , Al $2p$ chemical shift Δ , and $\bar{\Gamma}_3$ surface-state energy [$E_F - \bar{\Gamma}_3(ss)$] for three interplanar spacings Z and Al-O bond lengths R .

Z (Å)	R (Å)	E_B (eV)	ϕ (eV)	Δ (eV)	$E_F - \bar{\Gamma}_3(ss)$ (eV)
0.7014	1.796	10.589	5.668	-0.70	4.54
0.5962	1.758	10.722	4.446	-1.17	5.63
0.5495	1.742	10.576	3.857	-1.40	6.13

elsewhere.¹⁸ The largest numerical errors in the SCLCGO method undoubtedly arise from the charge density and potential fits and we note here changes which occurred when we changed to the new fitting functions. For the clean Al film ϕ changed from 4.276 to 4.196 eV and the total energy E_T [see Eq. (1) of Ref. 5]¹⁹ from -2893.174 to -2893.212 Ry whereas for the $Z=0.70$ Å O overlayer film ϕ changed from 5.632 to 5.668 eV and E_T from -3192.469 to -3192.298 Ry. The energy bands and Al $2p$ chemical shifts²⁰ are nearly identical with the two fits.

The binding energy is obtained by subtracting the E_T of the overlayered film from that of the clean film, dividing by two, and adding the calculated E_T for a spin-polarized O atom.²¹ A quadratic fit to the values of E_B listed in Table I gives maximum binding for $Z=0.627$ Å. Because the

very small percentage errors in the core energy (due to fitting the potential) are large compared to the calculated differences in E_B , we have less faith in this estimate of Z than in those that follow. The chemical shifts in Table I represent the Al $2p$ surface eigenvalue minus that from the layer below²² (which is 0.20 eV larger than the average of the bulk Al $2p$ bands). The experimental value of^{4,9,11,23} -1.4 eV suggests $Z=0.55$ Å or even less if the difference between the bulk and subsurface layer is considered. On the other hand, Erskine²⁴ has measured the localized phonon modes and determined that O exists in the subsurface layer even when its Al $2p$ chemical shift is not resolved. These subsurface O probably skew the very broad surface Al $2p$ peak to lower energy than it would otherwise have.

The clean Al(111) work function is²⁵ 4.24 ± 0.02 eV or²⁶ 4.26 ± 0.03 eV. Experimental deviations¹²⁻¹⁵ of +0.1 to -0.2 eV from the clean Al work function are obtained with ordered oxygen layers. From the agreement of our clean Al work function with experiment and the deviations obtained with different fitting procedures, we estimate that our calculated ϕ is accurate to ± 0.10 eV except for added uncertainties in the Kohn-Sham approximation when applied to diatomic systems. Thus we double our estimate to ± 0.20 eV. Therefore, for the correct Z our calculated work function ought to lie between 3.83 and 4.59 eV. Drawing a

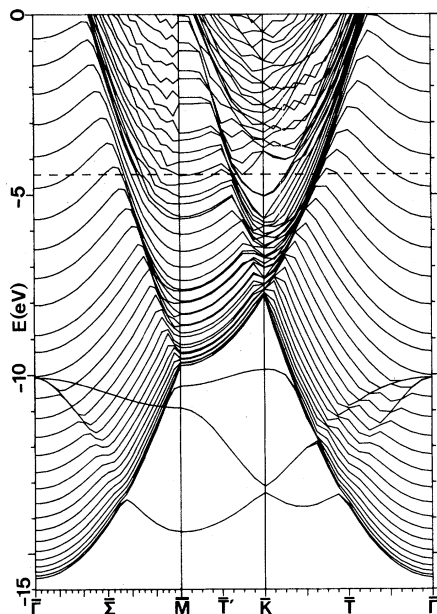


FIG. 1. Energy bands of eighteen-layer Al(111) film with 1×1 oxygen overlayers at $Z = 0.5962$ Å.

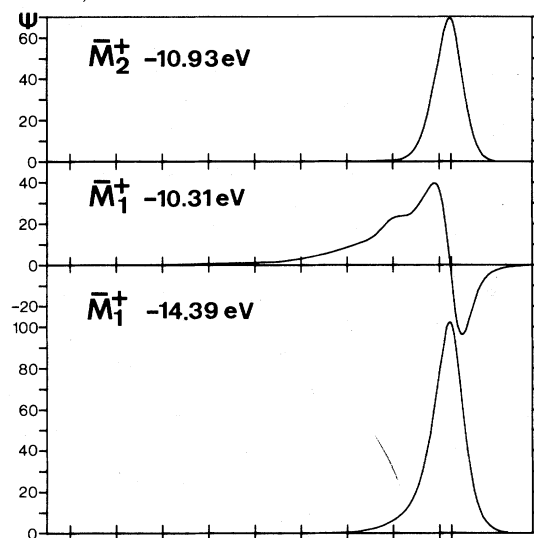


FIG. 2. Oxygen surface-state wave functions at \bar{M} plotted along r_{\perp} for $\bar{r} = a(\frac{1}{6}, -\frac{1}{6}, 0)$ in units of bohr^{-3/2}. The marks along the abscissa represent the nine Al planes and the O plane at $Z = 0.5962$ Å in the half film.

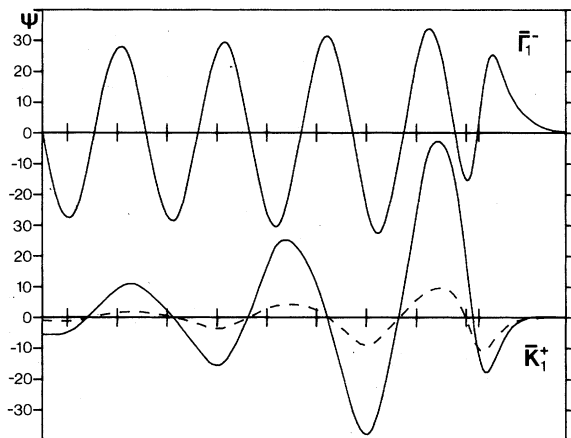


FIG. 3. The $\bar{\Gamma}_1^-$ surface resonance wave function at -9.373 eV and the real and imaginary parts of the \bar{K}_1^+ surface-state wave function at -5.056 eV plotted as in Fig. 2.

smooth curve through our three φ vs Z points, we find $Z = 0.578 \pm 0.032$ Å.

The $\bar{\Gamma}_3$ surface state (ss) has been found experimentally^{14,27,28} to lie between 6.8 and 7.3 eV below E_F . Self-interaction corrections²⁹ to the Kohn-Sham potential could easily lower the partially localized O $2p$ states relative to the nearly-free-electron Al states by 1 or 2 eV. Thus the values of $E_F - \bar{\Gamma}_3$ (ss) in Table I are not inconsistent with $Z = 0.60$ or 0.55 Å. In order to better study the surface-state bands we stretched³⁰ the $Z = 0.60$ -Å film to 18 Al layers and present the bands in Fig. 1. The ss \bar{K}_1 at -13.03 eV, \bar{K}_2 at -13.12 and -9.85 eV, and $\bar{\Gamma}_3$ at -10.08 eV are very similar to those plotted previously⁵ for $Z = 0.70$ Å. We plot the \bar{M} ss in Fig. 2 along the line passing equally far from the atoms in each plane. The upper \bar{M}_1 ss was not pulled out of the continuum for $Z = 0.70$ Å. There is a weak surface resonance in the $\bar{\Gamma}_1^+$ and $\bar{\Gamma}_1^-$ states at -8.90 and -9.37 eV which, as seen in Fig. 3, peaks near the second Al layer. This resonance extends a short distance along $\bar{\Sigma}$ and not at all along \bar{T} . It is not seen^{27,28} along \bar{T} but has been observed^{14,27} to extend all the way to the upper $\bar{\Sigma}_1$ ss band which runs into \bar{M}_1 . The $\bar{\Sigma}_3$ ss band and the $\bar{\Sigma}_1$ resonance emanating from $\bar{\Gamma}_3$ are observed^{14,27} as well as^{27,28} the two resonances along \bar{T} emanating from $\bar{\Gamma}_3$. Aside from the top of the O $2p$ ss bands being about 1 eV too high and the weakness of the $\bar{\Gamma}_1$ resonance and its failure to extend all the way along $\bar{\Sigma}$, all of which might be corrected with the stronger oxygen exchange potential needed to ac-

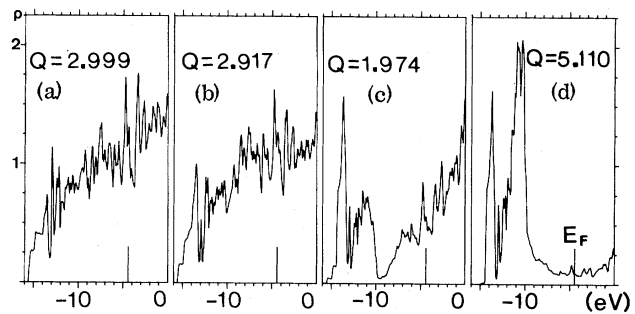


FIG. 4. Three times the projected density of states (electrons/atom-eV) on the three Al planes [(a), center, (b), center plus 1; (c) center plus 2] and (d) the oxygen density of states for the six-layer Al(111) film with O overlayers at $Z = 0.5962$ Å. Q (electrons/atom) is the projected density of states integrated up to E_F .

count for the self-interaction corrections, the O $2p$ bands are in good agreement with experiment.

It is interesting to note that the O overlayer has destroyed the \bar{K}_2 ss obtained⁸ in the gap around E_F in the clean film and induced a \bar{K}_1 ss in its place (see Fig. 3) at -5.05 eV. In Fig. 4 we display planar densities of states for the six-Al, two-O layer film obtained from Löwdin³¹ projection on the atomic orbitals. The contribution of the floating orbitals outside the crystal ($Q = 0.450$) are included with the O density of states in spite of the fact that half of these orbitals lie directly above surface Al atoms and are closer to them than to O atoms. If the excess 1.11 electrons projected on the O and floating orbitals formed a double layer 0.6 Å wide it would increase φ by 17 eV. One can look at the fact that φ is essentially unchanged by O adsorption in two ways. Either one can say that the O is so close to the Al that much of the Al charge is expanded in O orbitals but still belongs to the Al or one can say that the O ion is so strongly polarized that the ionic double layer is canceled. In any case, when the Al-O bond is this short, the bonding is more covalent than ionic.

In conclusion, not only have we shown that Norman *et al.*'s most recent¹¹ value of Z is correct but we have been able to obtain it with less uncertainty because φ is a rapid function of Z whereas the Al-O bond length they measure is only weakly dependent on Z when $Z = 0.6$ Å.

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¹⁶The longest-range spherical Gaussians used with the plane-wave Gaussians caused numerical instabilities when used with the three-dimensional plane waves and thus were discarded.

¹⁷From the first five stars of two-dimensional plane waves there are five even symmetrized combinations which combine with 31 different $\cos k_z z$ and three odd combinations which combine with 30 $\sin k_z z$.

¹⁸A. Euceda, D. M. Bylander, and L. Kleinman, unpublished.

¹⁹Note that because the kinetic energy contribution to E_T does not depend on the fit, there is no variational principle to indicate which is the better fit. The 1.7-eV-smaller O binding energy obtained with the current

fit seems the more reasonable of the two.

²⁰Two chemical shifts were incorrectly reported in Ref. 5. For $Z = 0.70 \text{ \AA}$, the Al $2p$ shift should have been -0.61 eV and for $Z = 1.40 \text{ \AA}$ it should have been $+0.37 \text{ eV}$. In Ref. 5, the chemical shifts were with respect to the average E_{2p} on the interior planes. Thus -0.61 eV there is equivalent to -0.70 eV here.

²¹There was a mistake in the atomic spin-polarized correlation potential used in Ref. 5. $E_T^{OX} = 148.7646 \text{ Ry}$ rather than the 148.7407 Ry reported there.

²²We averaged the $\bar{\Gamma}_1$ and $\bar{\Gamma}_3$ Al $2p$ chemical shifts which differ by about 0.02 eV .

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³⁰This was done by inserting six layers on either side of the central layer and translating the potential in steps of $(a/2, a/2, 0)$ from the central layer into these additional twelve layers. We fit the potential of the eighteen-Al, two-O layer film with the same set of Gaussians on each atom that we used for the thin film with the requirement that the coefficients of the same Gaussian on each of the twelve central planes be identical. The largest k_z (chosen to give periodicity over 21 Al interplanar spacings) for each two-dimensional symmetrized combination was taken to be twice as large as the largest k_z in the thin film which had a coefficient greater than 4×10^{-5} for that symmetrized combination. The basis set for the thick film corresponds to that for the thin film and contains 284 orbitals.

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