Computational study of subsurface binding sites of oxygen on Al(111)

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Using the same self-consistent linear combination of Gaussian orbitals technique that we previously employed to determine the above-surface initial binding site of oxygen on Al(111), we calculate the energy bands, work function, oxygen binding energy, and Al $2p$ chemical shift of Al(111) films with oxygen underlayers at several sites. The centered octahedral site with a 0.57-Å surface Al relaxation has 1.38 eV greater binding energy than the tetrahedral site suggested by Norman *et al.* The octahedral site also has a work function and chemical shifts closer to the experimental values than the tetrahedral site. We suggest an alternate interpretation of the experimental data of Norman *et al.* which is consistent with the octahedral binding site.

Although the plethora of experimental data[1–20] on the early stages of oxidation of Al(111) has resulted in several contradictory interpretations, most workers[4,5,7] now agree that the initial binding occurs in the threefold hollow site about 0.6 or 0.7 Å above the surface Al plane. We[21] recently made a self-consistent linear combination of Gaussian orbitals calculation of the energy bands, Al $2p$ chemical shift, work function, and oxygen binding energy of Al(111) films as a function of Z, the Al-O interplanar separation. From a comparison of the work function with experiment, we obtained $Z=0.579\pm0.032$ Å. The binding energy was maximized at $Z=0.627$ Å and the experimental chemical shift obtained for $Z=0.55$ Å. The latter two estimates are not believed to be as accurate as the former[22]; however, all three lie well within the uncertainty in what we believe to be the best experimental determination of Z, the extended x-ray absorption fine-structure (EXAFS) measurements of Norman *et al.*[7] We note that these results are also consistent with earlier calculations.[23,24]

With 100 L O_2 exposure [1 langmuir (L)$\equiv 10^{-6}$ Torr sec] or less, Norman *et al.* found a chemical shift of -1.4 eV and Al—O bond length $R=1.76\pm0.03$ Å, which is equivalent to $Z=0.60\pm0.10$ Å for the above-surface site. With greater exposure both -1.4 and -2.7 eV chemical shifts were obtained. With 50-L exposure after heating at 200 °C for 10 min, they found only the -2.7-eV chemical shift and measured R to be 1.75 ± 0.03 Å. With large (1000 L) O_2 exposures and heating to 200 °C, $R=1.88\pm0.03$ Å was found together with the -2.7-eV chemical shift. This value of R lies between the two Al_2O_3 bond lengths and is slightly less than 1.915 Å, the average Al_2O_3 bond length which is obtained from EXAFS. Thus they picture three stages of oxidation—an above-surface initial site, then incorporation in a below-surface site, and finally oxide formation. Although their data give no information concerning the below-surface site location, they suggest it is the tetrahedral site (hereafter called Ti) $\frac{1}{4}Z_{\mathrm{Al}}$ below the surface plane (Z_{Al} is the Al interplanar spacing). Because the Al(111) interplanar spacing is $a/\sqrt{3}$, this yields $R=\sqrt{3}a/4=1.75$ Å for the tetrahedral site in perfect agreement with their experimental value, providing the oxygen does not cause the surface Al plane to relax. From the EXAFS data there is no reason to exclude the other tetrahedral site (hereafter Tii) $\frac{1}{4}Z_{\mathrm{Al}}$ above the subsurface Al plane. They excluded the octahedral site because without relaxation it gives $R=a/2=2.02$ Å.

Erskine and Strong[9] studied the electron-energy-loss spectroscopy (EELS) of the Al(111)-O system, and parametrized force-constant lattice-dynamics calculations were performed by Strong *et al.*[10] At exposures of 200 L or less, loss peaks were observed at 105, 80, and 40 meV. EELS spectra taken after exposing Al(111) at 500 K to 3000 L oxygen were entirely different from the low-exposure spectra and had a primary loss peak at 110 meV corresponding to the 940 cm^{-1} (118 meV) reflectance minimum observed in Al_2O_3. The 105-meV loss peak was associated with a mode[25] in which the O underlayer (at Ti) and Al subsurface layer had large amplitudes 180° out of phase; the 80-meV loss peak involved a similar motion of the O overlayer and surface Al plane; the 40-meV loss peak was associated with a mode in which the O overlayer and Al surface layer moved together but 180° out of phase with the subsurface O and Al planes. Although we do not believe their two-parameter calculation[10] is sophisticated enough to determine the underlayer site, it, together with their experimental results,[9] convincingly demonstrates the existence of such sites. With either 2- or 20-L O_2 exposure the loss peak at 80 meV was about twice as strong as the 105-meV peak and the 40-meV combination mode loss peak was very weak. With 200-L exposure the two primary peaks were of equal strength and the combination mode peak not quite so weak. After heating to 500 K or waiting for two hours at 300 K the 105-meV peak became twice as strong as the 80-meV peak and the 40-meV peak, while still weak, became somewhat stronger. Thus the EXAFS and EELS data interpretations are in complete agreement as to the existence of above- and below-surface oxygen binding sites but completely disagree as to (1) whether or not one can (at room temperature) occupy the above-surface sites without having a large fraction of the O diffuse immediately to the below-surface sites and (2) whether by heating one can drive *all* the above-surface oxygen to below-surface sites. We propose the following explanations of these discrepancies. (1) The EXAFS samples were electropolished before ion bombardment and annealing whereas the EELS samples were not, causing the surfaces of the EXAFS samples to be more resistant to oxygen penetration. Because the Thomas-Fermi screening length in Al is 0.5 Å, those oxygen atoms that do penetrate the electropolished surface do not cause a chemical shift. Only when islands with high density of O in below-surface sites are formed does linear screening break down and the −2.7-eV chemical shift appear. (2) Oxygen underlayers never occur; only overlayers and double layers consisting of oxygen atoms in both above- and below-surface sites occur. The −2.7-eV chemical shift is due to double layer rather than underlayer formation, and the EXAFS and EELS samples actually behaved identically with heating.

We are unable to explain the discrepancies in the measured work function changes, $\Delta\phi$, with oxygen exposure. Either[13] $\Delta\phi = -37$ meV with 54-L exposure decreasing to $\Delta\phi = -250$ meV at 180-L exposure, or[12] $\Delta\phi = -200$ meV with 50-L exposure increasing to −120 meV at 200 L, or[11] $\Delta\phi = 0$ with 25-L exposure increasing to 130 meV at 100 L. In any event, because there is no evidence that ordered underlayers are ever formed, comparison of experimental $\Delta\phi$'s with those calculated for an ordered underlayer will not be nearly so useful as it was for ordered overlayers. On the other hand, in-plane O—O bonds should make only a small nearly site-independent contribution to the binding energy, and therefore that site which maximizes the binding energy in an ordered 1×1 underlayer is almost certain to be the correct subsurface binding site.

Our calculations are identical to those in Ref. 21, to which the reader is referred for details. In the first three rows of Table I are displayed the work function, oxygen binding energy, and surface and subsurface Al $2p$ chemical shifts (relative to the central layers) for 1×1 oxygen layers in the two tetrahedral sites, separately and together. It is interesting to note that the calculated work functions for the two sites (which we believe accurate[21] to within 0.1 eV) when compared with the clean Al(111) work function[21,26] of 4.26 eV yield $\Delta\phi$'s large compared with experiment and of opposite sign and that occupancy of both sites yields a $\Delta\phi$ nowhere near the sum or the average of the other two. Note that there is some O—O bonding between the two sites, as the binding energy is greater for both sites than the sum of that for each site individually. It is not, however, twice as great as that for the Ti site, which must be considered to be the most likely of the three tetrahedral possibilities especially since $\Delta_s = -2.00$ eV is reasonably close[22] to the experimental −2.7 eV and $\Delta_{s-1} = -0.38$ eV

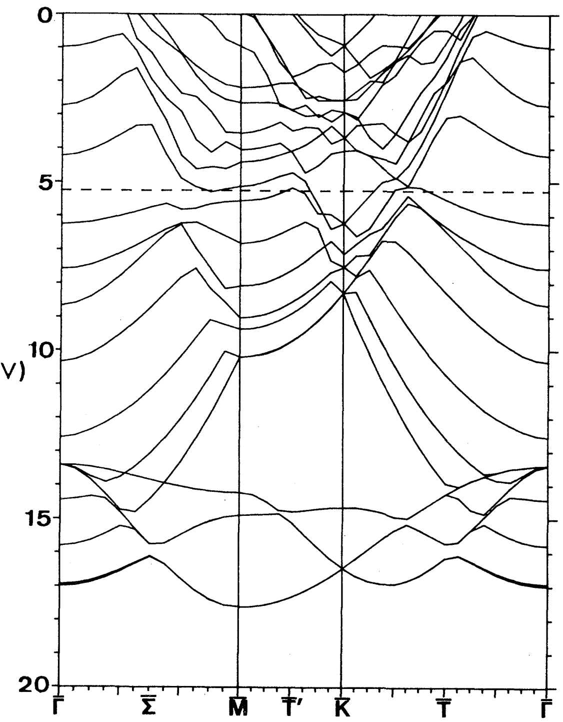

FIG. 1. Energy bands of a six-layer Al(111) film with oxygen underlayers in the tetrahedral sites closest to the surface.

TABLE I. Shortest Al—O bond length, work function, oxygen binding energy, and surface and subsurface Al $2p$ chemical shifts as a function of surface and subsurface Al interplanar spacing Z_{Al} for different oxygen sites. Ti and Tii are the tetrahedral sites $\frac{1}{4}Z_{\mathrm{Al}}$ and $\frac{3}{4}Z_{\mathrm{Al}}$ below the surface plane. The oxygen lies 0.6009 Å above the subsurface Al plane in the displaced octahedral site and midway between Al planes in the centered octahedral site. The centered octahedral equilibrium values were obtained by interpolation.

	Z_{Al} (Å)	R (Å)	ϕ (eV)	E_B (eV)	Δ_s (eV)	Δ_{s-1} (eV)
Ti	2.3381	1.754	5.262	8.62	−2.00	−0.38
Tii	2.3381	1.754	3.471	7.44	−0.87	−2.46
Ti + Tii	2.3381	1.754	5.025	17.10	−1.41	−1.39
dO	1.9407	1.759	4.040	5.49	−1.40	−2.33
dO	1.7069	1.759	4.383	6.34	−1.71	−2.39
dO	1.5128	1.759	4.759	7.08	−1.87	−2.36
cO	1.3561	1.787	4.951	7.54	−2.46	−2.21
cO	1.5198	1.820	5.001	9.06	−2.31	−2.11
cO	1.8471	1.894	4.947	9.91	−2.16	−1.96
cO	2.0108	1.935	4.848	9.08	−2.03	−1.89
*cO*eq	1.7726	1.876	4.97	10.00	−2.21	−1.99

is probably too small to be observed. The energy bands of a six-layer Al(111) film with oxygen in the Ti sites below both surfaces are shown in Fig. 1 and will be discussed later.

Because our calculated binding energy for oxygen in the above-surface site[21] is 10.75 eV, we suspected that there would be a subsurface site with greater binding energy than we obtained for the Ti site. In order to have an Al—O nearest-neighbor bond length close to the experimental value we put the oxygen in the octahedral cage but displaced it downward so that it was only 0.601 Å from the subsurface Al plane. The second three rows of Table I list the calculated results for different surface Al relaxations. The binding energy is too small for any value of Z_{Al} for this site to merit further consideration. In the next four rows of Table I we list our results for different Al surface relaxations in the centered octahedral site. There are six nearest-neighbor Al—O bonds of the length shown in the second column for this site. The last row shows the results of a cubic fit to $E_B(Z_{\text{Al}})$. We note that ϕ is quite insensitive to Z_{Al} as long as the oxygen is kept midway between the two Al planes. The equilibrium Al—O bond length is only slightly greater than the shorter of the two Al_2O_3 near-neighbor bond lengths. The surface and subsurface Al $2p$ chemical shifts are sufficiently close to each other that only a weighted average would be expected to be observed experimentally and that average is in satisfactory agreement with experiment. The 10.00-eV equilibrium binding energy is sufficiently[27] larger than the value obtained for the Ti site that we believe the Ti site can be discarded. It is sufficiently smaller than the binding energy at the above-surface site to make the existence of isolated underlayers unlikely, but sufficiently close to that overlayer binding energy to make it likely that the energy of a double layer would be greater than twice that of the overlayer. Thus, upon heating an Al sample with an O overlayer in vacuum, islands of double layer would be formed. If we assume that this picture is correct and that the Al—O EXAFS bond length ascribed to the Ti site is actually the bond length between an above-surface oxygen and the surface Al in a double layer, then the EXAFS and EELS data are consistent with each other and with theory. Unfortunately, the bond lengths in a double layer need not be equal to those in the single layers and many calculations for different positions of the surface Al plane as well as both oxygen planes will have to be performed to determine the equilibrium positions (it is likely that the surface

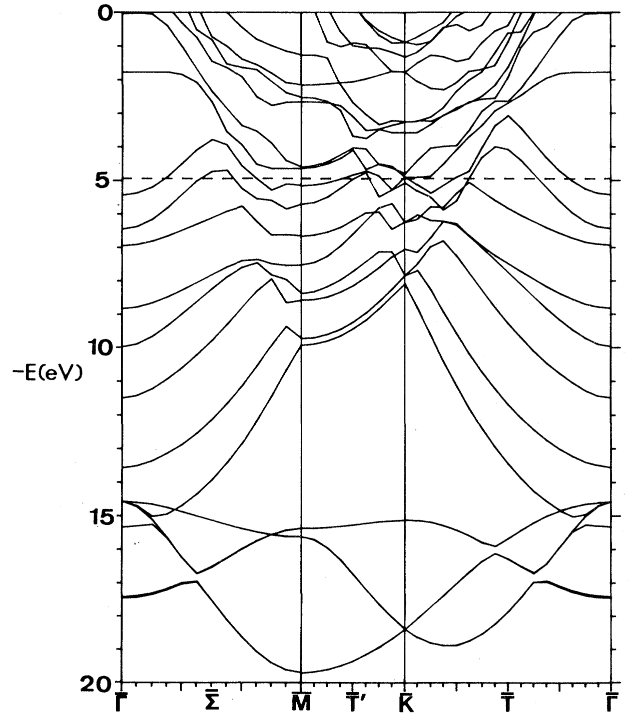

FIG. 2. Energy bands of a six-layer Al(111) film with oxygen underlayers at the centered octahedral site and a surface Al interplanar spacing of 1.8471 Å.

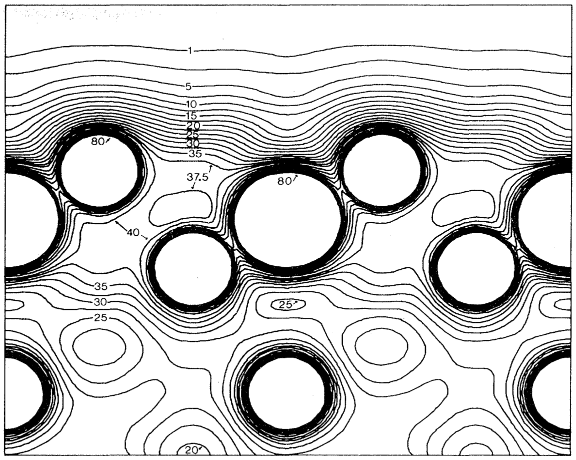

FIG. 3. Contour plot of the total charge density in the ($\bar{1}10$) plane of a six-layer Al film with oxygen underlayers at the centered octahedral site and a surface Al interplanar spacing of 1.8471 Å. Except for the unit contour, all contours below 40 are 2.5 times an integer number of millielectrons per cubic bohr; the step size is doubled above 40.

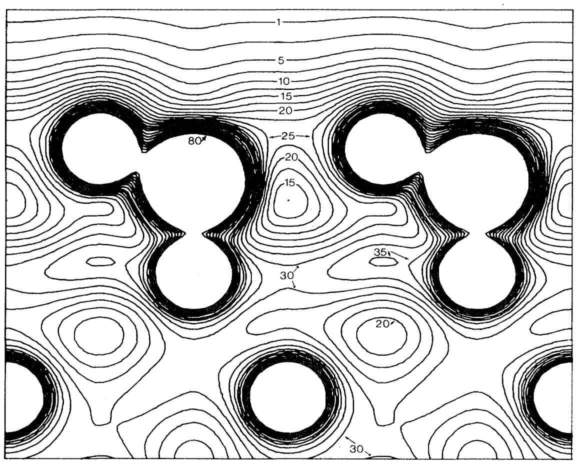

FIG. 4. Contour plot as in Fig. 3 but for Al(111) film with oxygen underlayers in the tetrahedral sites closest to the surface.

O will pull the subsurface O out of the center of the octahedron). We are just beginning these calculations and will report them in a later publication.

Figure 2 is the energy bands for the centered octahedral site with $Z_{\text{Al}} = 1.8471$ Å. The oxygen bands are similar to those in Fig. 1 for the Ti site except they are somewhat lower in energy and somewhat more dispersive. There is a $\bar{\Gamma}_3$ surface state (SS) at -14.586 eV (in Fig. 2) and a $\bar{\Gamma}_1$ SS at about -17.44 eV. A slight splitting in the degeneracy of $\bar{\Gamma}_1$ SS on opposite sides of the film due to their overlap can be seen (the O planes in the six-layer Al film are only 8.86 Å apart). The twofold-degenerate $\bar{\Gamma}_3$ SS splits into a $\bar{\Sigma}_3$ SS band and a $\bar{\Sigma}_1$ surface resonance band which quickly moves through the bottom of the Al bands and becomes a SS band which is then repelled by the $\bar{\Sigma}_1$ SS band emanating from $\bar{\Gamma}_1$. The $\bar{\Sigma}_1$ bands terminate as $\bar{M}_1$ SS and the $\bar{\Sigma}_2$ band as a $\bar{M}_2$ SS. Note that the $\bar{\Sigma}_1$-$\bar{\Sigma}_2$ crossing in Fig. 2 makes the $\bar{M}$ ordering different than in Fig. 1. In the $\bar{T}$ direction all SS pairs (on opposite sides of the film) have $\bar{T}_1$ and $\bar{T}_2$ symmetry. Therefore, both bands emanating from $\bar{\Gamma}_3$ are resonances until they break through the bottom of the Al bands and no bands can cross. The two transverse O $2p$ functions are nearly degenerate at $\bar{K}$ (at -18.395 eV). This degeneracy which would be exact in bulk octahedral or tetrahedral sites is well split in the above-surface site. The symmetry labeling at $\bar{K}$ is meaningless without further discussion.[28,29] The $\bar{\Gamma}_3$ (octahedral) SS is 4.5 eV below the same SS calculated[21] for the above-surface site and about 3.2 eV below its measured[14–16] energy. The lower $\bar{M}_1$ SS is 5.3 eV below both the calculated and measured energies for the same above-surface SS. Just above the above-surface $\bar{\Gamma}_3$ SS is a very broad $\bar{\Gamma}_1$ surface resonance which is replaced by the $\bar{\Gamma}_1$ SS at -17.44 eV in the octahedral case. Thus photoemission should be able to distinguish easily the underlayer (which has not yet been observed) from the overlayer. If, as we have suggested, double layers rather than underlayers exist, the repulsion between the $2p$ bands on the above- and below-surface O should make them even easier to distinguish. If the double layer is always disordered then the broadness of these bands would smear out the O $2p$ photoemission but the O $2s$ levels (whose bands are about 1.3 eV wide) at -25.82, -29.28, and -30.32 eV in the above-surface, Ti, and octahedral sites, respectively, might still be distinguishable.

In Figs. 3 and 4 are displayed contour plots of the electronic charge density in the $(\bar{1}10)$ plane for octahedral and Ti site occupation, respectively. It is interesting to note that a comparison with a clean Al(111) contour plot[30] shows that when O is in the octahedral site, the charge in the Ti site is increased, but when O is in the Ti site charge is removed from the octahedral site.

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[27] In Ref. 21 we pointed out that discrepancies as large as 2 eV in the binding energy were obtained using two different schemes for fitting the charge density. We believe but cannot prove that our current fitting scheme is accurate to better than 1 eV with even smaller relative errors.

[28] Our six-layer Al film is ordered *CABCAB* where the threefold rotation axis goes through atoms in the *A* plane. Thus the Ti oxygen planes on both sides of the film are *A* planes but the octahedral O planes are *B* and *C*. The longitudinal O $2p$ func-

tions on A planes are $\bar{K}_1$ and transverse are $\bar{K}_2$. On B and C planes the longitudinal p functions are $\bar{K}_2$ and the transverse in proper combination are $\bar{K}_1$ and $\bar{K}_2$.

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