

Ordered Oxygen Overlayer Associated with Chemisorption State on Al(111)

S. A. Flodström and C. W. B. Martinsson

Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

and

R. Z. Bachrach, S. B. M. Hagström, and R. S. Bauer

Xerox Palo Alto Research Center, Palo Alto, California 94304

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We present experimental evidence of a unique, ordered chemisorption phase in the initial interaction of oxygen with the Al(111) surface. At high oxygen exposure or high temperature, this phase is shown to transform irreversibly to a bulklike aluminum oxide. The measured temperature dependence, as well as the low-energy electron diffraction, suggests a threefold, centered bonding site. A comparison between calculated and experimental valence-band density of states for the oxygen-covered Al(111) surface is made for the estimated oxygen-atom-substrate-surface distance.

Experimental evidence is presented showing that the initial interaction of oxygen with the (111) crystal face of aluminum is a two-step process. Oxygen atoms are shown to chemisorb first at equivalent sites on the surface in an ordered overlayer. Upon increasing the oxygen exposure or the temperature above 170°C, the chemisorbed oxygen is irreversibly transformed into a bulklike oxide film. The chemisorption phase in the aluminum-oxygen interaction was first observed for "polycrystalline" films.¹ The present work shows that the two-step oxidation process is unique to the closepacked (111) face of aluminum and reveals for the first time the presence of an ordered overlayer with oxygen on a simple fcc metal. The other two faces investigated, (100) and (110), form bulklike oxide films for the lowest observable coverages.²

The existence of a well-defined chemisorption phase on a free-electron-like metal such as aluminum is of great interest since a number of theoretical calculations using different techniques treat chemisorption of oxygen atoms on aluminum as a model system.³⁻⁵ Because of the relatively simple bulk electronic structure of this system, calculations have been made self-consistent and have been performed for different adsorbate-substrate distances. Some calculations explicitly assume a specific adsorption site, but comparisons of the calculated valence-band density of states with experimental valence-band photoemission spectra have been hindered by uncertainty about the actual Al-O configurations. In the present work we deduce a specific position and estimate an adsorbate-substrate distance for oxygen atoms on the (111) surface of aluminum. Valence-band spectra obtained for the oxygen-exposed surfaces

are compared with a theoretical calculation.^{3,6} Discussion of the valence-band spectra for the clean faces is presented elsewhere.⁷

The experiments reported were performed using the monochromatized radiation from the 4° beam line at Stanford Synchrotron Radiation Laboratory (SSRL) as the excitation source. Photons at two energies were used to excite electrons: 50-eV photons to excite the valence-band region and 130-eV photons to excite the 2*p* core of aluminum. Incoming light illuminated the sample at 5°–10° away from grazing incidence. The photoelectrons were energy analyzed in a double-pass, cylindrical mirror analyzer having its optical axis 5°–10° off the sample surface normal; the joint energy resolution (photon plus electron) was 0.4 and 0.15 eV for the 50- and 130-eV photons, respectively. The samples were electrolytically polished single crystals of aluminum. The (111) crystal was extremely specular to the eye and also showed a surface almost free from defects when investigated with transmission electron microscopy. The crystals were cleaved *in situ* by repeated argon-ion bombardment and annealing cycles (0.5 h at 400°C). Cleanliness was checked by AES (Auger electron spectroscopy).⁸ LEED (low-energy electron diffraction) analysis showed good surface order after the final annealing.

Figure 1 shows the evolution of the spectrum from the Al 2*p* core region as a function of oxygen exposure. The appearance of two chemically shifted, oxygen-derived peaks is clearly seen. One is shifted 1.4 eV to higher binding energy relative to the clean Al 2*p* peak. The 1.4-eV-shifted peak is associated with the aluminum substrate interacting with chemisorbed oxygen atoms.

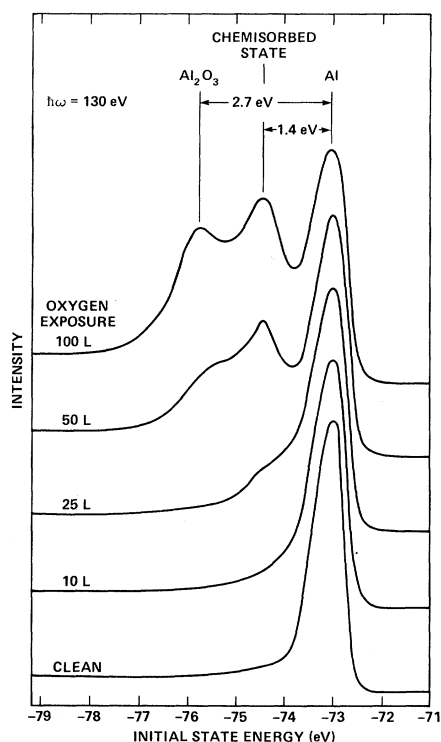


FIG. 1. Al 2*p* region spectra for different oxygen exposures.

The other oxygen-derived peak, shifted 2.7 eV to higher binding energy as compared to the clean Al 2*p* peak, is characteristic of the Al 2*p* level in aluminum oxide (Al₂O₃).⁹ For oxygen exposures above 150 L (1 L = 10⁻⁶ Torr sec), the 2.7-eV peak begins to dominate the spectrum. At about 1000 L, it is the only oxygen-derived feature in the Al 2*p* region spectrum. The initial fast oxygen uptake is correlated with the growth of the "chemisorbed" 1.4-eV peak. This first step is followed by a slower oxygen uptake and a transformation from the chemisorption phase to the oxide phase.

A LEED study has been performed on the clean and oxygen-exposed surface. For a 150-L exposure, which corresponds approximately to a monolayer, a LEED pattern of the same symmetry as for the clean (111) surface is observed. This would not be the case if the aluminum surface had reconstructed. Figure 2 shows the intensity versus incident electron energy curves (LEED spectra) for two nonequivalent spots in the pattern for the clean surface shown by the solid curve and the 150-L exposure shown by the dashed curve.

Drastic changes in the low-energy part of the

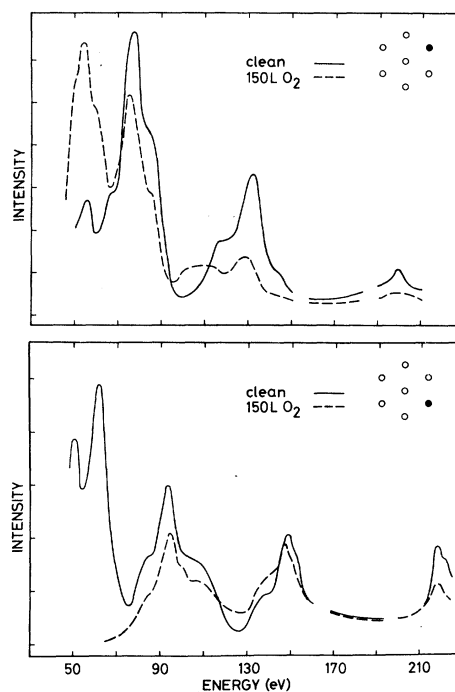


FIG. 2. LEED intensity vs incident electron energy for two nonequivalent beams for the sixfold symmetrical pattern for the clean and monolayer-oxygen-covered Al(111) surface.

LEED spectra are seen upon oxygen adsorption. The observation of a LEED pattern with the original symmetry but with changed intensity versus voltage curves after monolayer adsorption suggests that the oxygen atoms are *chemisorbed*, and chemisorbed in such a way that the clean surface symmetry is preserved. Above a monolayer, LEED spectra show no major changes upon further oxidation. The spots slowly fade away at a uniform rate, and at 1000 L they are not visible. A complete analysis of the LEED spectra is necessary to discriminate among all alternative oxygen-atom positions available which maintain symmetry and change LEED spectra in accord with experiment.

The chemisorption phase on the Al(111) surface was investigated as a function of temperature. Figure 3 displays the temperature dependence of the 1.4-eV-shifted chemisorption peak. In the temperature range 160–200°C, this peak disappears, and at the same time the intensity in the oxide-related 2.7-eV-shifted peak increases. By increasing the sample temperature, the activation energy necessary to go from chemisorption to the bulk oxide phase is supplied. An estimate of the activation energy can be obtained from

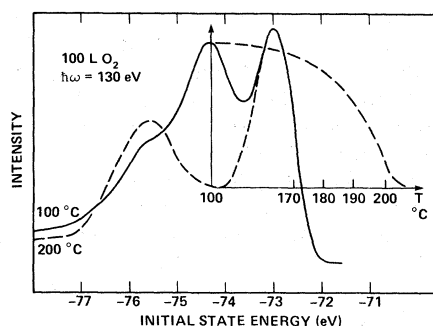


FIG. 3. Temperature dependence of the Al 2*p* region spectra for 100 and 200°C. The superimposed inset shows the abrupt onset with increasing temperature for a constant heating rate.

these data. A simplified analysis yields an activation energy of 1 eV.

The temperature behavior suggests that the oxygen atoms gain the energy necessary to penetrate the surface and interact with aluminum atoms to form an oxide in the octahedral hole right below its chemisorbed site. A surface penetration is consistent with the fact that increasing the substrate temperature increases the amplitudes of the lattice vibrations, making the surface more open and easier for the oxygen atoms to pass through. Thus the measured temperature dependence of the intensities in the oxygen-related Al 2*p* peak is due to an activated transformation from the chemisorption to the oxide phase. This change of state involves a transport of oxygen atoms through the aluminum surface with the penetration taking place at the threefold, centered sites having no aluminum atom immediately below in the second layer.

Further information is obtained by comparing O 2*p* spectra for oxygen-covered Al(111), shown in Fig. 4, with the calculated density of states for the same system.^{3,6} Figure 4 shows the changes in the O 2*p* line shape as a function of exposure with the Al valence band removed. The spectra normalized to a common peak height show a steady increase in strength on the high binding side. Above 150 L, the peak height does not increase as a function of exposure, and all further uptake is reflected in an increasing width. The broadening is due to an increased oxygen-oxygen interaction consistent with the calculation which has the π orbitals higher in binding energy. By contrast, the (100) and (110) faces show an approximately constant line shape with increasing strength as a function of exposure.

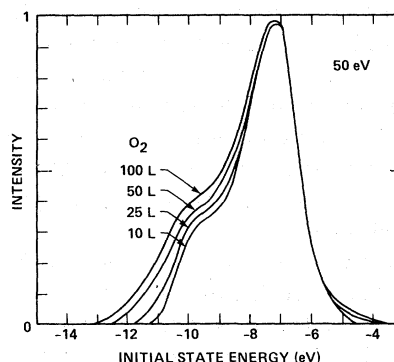


FIG. 4. Al valence-band region for different oxygen exposures having change in line shape.

In discussing the above data, an unknown parameter is the distance (D) above the surface of the chemisorbed oxygen atom in the threefold, centered site on the Al(111) surface. Aluminum-oxygen bond lengths can be used to make an estimate. 1.90 Å is the ionic bond length for Al-O and a good first choice as a minimum bond length in chemisorption. It yields a $D = 0.9$ Å outside the first layer.¹⁰ An upper limit on the chemisorption Al-O bond length is given by the "jellium" calculation. For the threefold, centered site in the (111) surface, the modified "jellium" calculation³ gives an Al-O bond length of 2.10 Å.

Calculation of the valence density of states is very sensitive to the oxygen-substrate distance. The O 2*p* resonance moves deeper down in the band as the oxygen-atom-substrate-surface distance decreases. The asymmetric O 2*p* consists of two peaks due to O 2*p* orbitals perpendicular (σ) and parallel (π) to the surface with calculated binding energies of 5.5 and 7.0 eV, respectively.³ The experimental O 2*p* resonance also has an asymmetric shape (Fig. 4) and can be resolved into two peaks 7.1 and 9.8 eV below E_F . The experimental structures are deeper in the band and their splitting is larger than the calculated values. The position $D = 0.5$ Å gives a better fit between experimental and calculated density of states, but this corresponds to an Al-O bond length shorter than that observed in Al₂O₃ and would be impossible without surface reconstruction. The oxygen-atom-surface distances, therefore, probably lie between 0.9 and 0.5 Å. This estimate is shorter than the distance obtained for the theoretical calculation of the total system minimum energy,³ which gives $D = 1.30$ Å. In that calculation,³ the discrete character of the aluminum surface has

been simulated by using a substrate lattice of pseudopotentials, but no account has been taken of electron-density dimples in the surface. A calculation including electron-density variations in the surface would place the centered equilibrium position further in, and give an O $2p$ resonance at higher binding energies, in agreement with experiment.⁶

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⁸Detection limit on O_{K II} in the AES spectra was less than 1-L oxygen exposure.

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¹⁰Compared to Ref. 3, $D = d + 2.2$ a.u. (1.16 Å).