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Observation of a low-binding-energy peak in the 2*p* core-level photoemission from oxidized Al(111)

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High-resolution photoemission studies of oxidation of the Al(111) surface have been performed. The appearance of a component at lower binding energy than the metallic bulk Al emission in the Al 2*p* spectrum at oxygen exposures above ~50 langmuir (1 L = 10^{-6} Torr s) is argued to be due to Al atoms which do not bond directly to oxygen atoms at the oxide-metal interface. Low-energy electron diffraction initially shows a 1×1 structure, which subsequently fades away at higher oxygen exposures, $\gtrsim 400$ L.

Oxidation of aluminum has been a subject of considerable interest for several decades due to the thin passivating oxide layer that forms on Al in air. The first comprehensive description of the low-temperature oxidation of Al was forwarded by Cabrera and Mott[1] in 1948. Since then, several models of oxidation kinetics have been presented that refine the original ideas.[2] The growth modes of an oxide film may be quite complicated. An oxide film that is grown at room temperature or below is normally amorphous. Aluminum oxide forms a glassy network, in which growth by anion migration predominates.[2] In recent years, surface science experiments have yielded information on the initial stages of the oxidation of Al surfaces.[3-12] In particular, photoemission has shown that four different chemically shifted Al 2*p* peaks are present in the initial stages of oxidation of Al(111).[5] The interpretation of these four oxide peaks is based on different local Al-O coordination in the thin oxide film.[5]

In this work we present high-resolution core-level photoelectron spectroscopy measurements of the initial oxidation stages of Al(111). In addition to the previously observed four chemically shifted Al 2*p* peaks, a new peak is observed at the lower binding energy side of the bulk metallic emission. This peak is identified as due to those Al atoms in the metal/oxide interface which do not directly bond to oxygen atoms.

These experiments were performed at Beamline 22 at MAX-lab at Lund University, Sweden. Using a modified Zeiss SX700 plane grating monochromator in conjunction with a large hemispherical electron energy analyzer[13] a total experimental resolution of about 50 meV was obtained at a photon energy of 110 eV. The Al(111) surface was cleaned by Ar sputtering (cycles of 20 min at 300 K, 10 min at 600 K) and subsequent annealing (3 min at 750 K). Surface cleanliness was verified by core-level photoemission. The sample was mounted on a liquid-nitrogen cryostat, and was cooled to ~100 K during measurements to decrease phonon broadening. The base pressure in the measurement chamber was $\sim 5 \times 10^{-11}$ Torr.

The evolution of the Al 2*p* emission with oxygen exposure at room temperature of the Al(111) sample is shown in Fig. 1. Low-energy electron diffraction (LEED) patterns initially showed a 1×1 structure that got weaker for increasing exposures, and that eventually disappeared above 800 L (1 L = 10^{-6} Torr s) exposure. This is in accordance with the expectation that Al should form an amorphous oxide at room temperature.[2] The average ox-

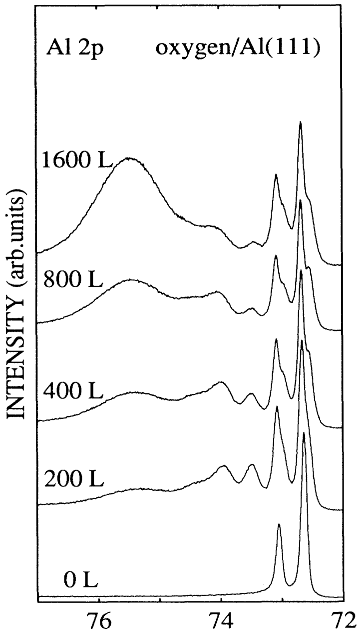

FIG. 1. Al 2*p* photoelectron spectra from Al(111) that has been exposed to oxygen at room temperature as indicated. The photon energy was 110 eV.

ide thickness was estimated, from core-level intensities, to be ~8 Å after an oxygen dose of 1600 L. The Al 2*p* spectrum from an oxidized Al(111) surface may be decomposed into six contributions as shown in Fig. 2. Four oxide components (labeled *c* to *f* in Fig. 2) and two metallic components (labeled *a* and *b* in Fig. 2) reproduce the overall spectrum quite well. The oxide component *c* had to be included to maintain the proper spin-orbit branching ratio of the metallic emission, but could not be directly observed due to a strong overlap with features *a* and *d*. A similar feature was previously invoked to decompose lower resolution data.[5]

The spectra were fitted, after an initial subtraction of a Shirley-type background, by using a convolution of a Doniach-Šunjič[14] function and a Gaussian function. The total spectrum was obtained by adding six spin-orbit-split components manually to reach a visually satisfactory fit to the data. The spin-orbit splitting (0.41 eV), branching ratio (2.4), and asymmetry parameter (0.06) were determined from fits to the clean Al(111) spectrum. Asymmetry parameters from 0.03 (suboxides) to 0 (bulk oxide) were used for the oxide contributions. Lorentzian and Gaussian widths were estimated from the goodness of the fit in a consistent way throughout the oxidation series. The fitting parameters merely indicate a consistent way of reproducing the data, and should not be taken too literally, since small variations in the different parameters may result in visually equally good fits to the data. The details of the fitting procedure will be accounted for elsewhere.[15] The following peak positions, relative to the bulk emission *a*, were obtained for the 800-L sample: *b*, −0.14 eV; *c*, 0.37 eV; *d*, 0.84 eV; *e*, 1.37 eV; and *f*, 2.63 eV. The bulk oxide peak *f* was observed to increase in binding energy from 2.54 eV for the 200-L sample to 2.66 eV for the 1600-L sample. Only small changes (<0.03 eV) in the other peak positions were observed in all the Al 2*p* spectra at oxygen exposures ranging from 200 to 1600 L. The features *c*, *d*, and *e* have previously been assigned to aluminum atoms bonding to one, two, and three oxygen atoms, respectively, in the chemisorption phase.[5] These three peaks were found in Ref. 5 to have binding energies that, within experimental error, were integer multiples of the separation between peaks *a* and *c*. Our higher-resolution measurements contradict these previous findings in that we observe that the separation between these peaks increases slightly with binding energy. Thus, the chemical shift is not exactly proportional to the oxidation number of the Al ion.

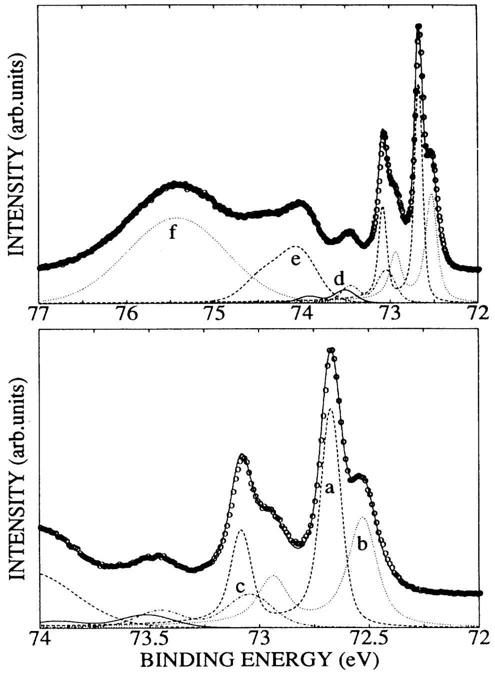

FIG. 2. Al 2*p* spectra from Al(111) that has been exposed to 800 L of oxygen at room temperature ($T=300$ K). The photon energy is 110 eV. The method of decomposition has been performed as described in the text.

The main result in this paper is the observation of a peak at the low binding energy side of the 2*p* emission from the bulk metal (peak *b* in Fig. 2). It seems clear from the binding energy that the atoms which give rise to this peak are not in the immediate vicinity of oxygen atoms; they must be situated in a metallic environment. Low-temperature (room temperature and below) oxidation of Al results in formation of a glassy network.[2] The oxide/metal interface may be envisioned in two dimensions as schematically shown in Fig. 3. The low binding energy peak may result from the Al atoms at the interface which are not oxygen coordinated. These atoms are labeled interface atoms in Fig. 3.

Further evidence for this assignment of peak *b* may be obtained from the variation of the intensity with oxygen exposure of the various components in the Al 2*p* spectrum, which are shown in Fig. 4. The normalization is so that the total intensity at any given oxygen dose adds up to unity. The order of occurrence of the suboxide peaks *c* to *e* as well as the evolution of their intensities with oxygen exposure can be accounted for by the model suggested in Ref. 5, i.e., they are due to Al atoms bonded to one *c*, two *d*, and three *e* chemisorbed oxygen atoms. Recent scanning tunnelling microscopy (STM) data[9] support this interpretation. Peak *b* is not present for low oxygen exposures but appears together with peak *f* which is as-

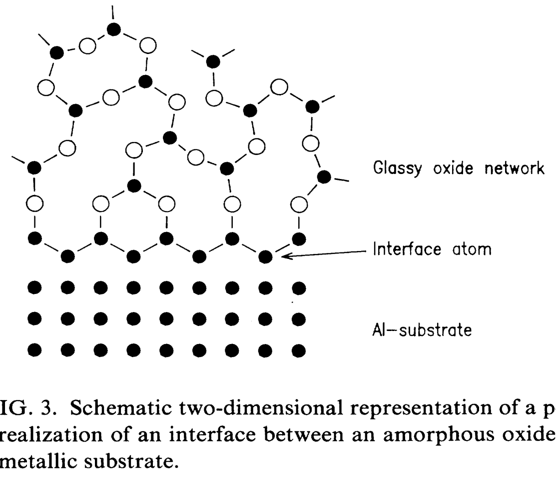

FIG. 3. Schematic two-dimensional representation of a possible realization of an interface between an amorphous oxide and the metallic substrate.

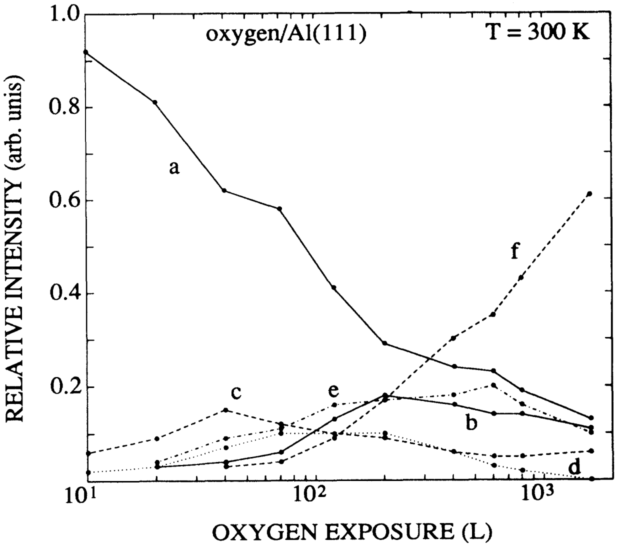

FIG. 4. Relative intensity of the various components of the Al 2p spectrum (as labeled in Fig. 2), as functions of oxygen dose. The total Al 2p intensity is normalized to unity.

cribed to the formation of bulk Al oxide. These two peaks show a very similar intensity increase up to an oxygen exposure of about 200 L after which peak b saturates in intensity. For higher exposures peak b even starts to decrease in intensity, eventually showing an intensity variation which is largely similar to that of the bulk metal emission, peak a. After an oxygen exposure of 1600 L the intensity of peak b is approximately 80% of the bulk metal emission, peak a. This intensity variation of peak b is exactly what would be expected if the peak as suggested is due to Al atoms at the interface between the Al oxide and the underlying Al metal which do not bond directly to oxygen. From the STM measurements[9] it is evident that the initial oxide growth occurs in patches, and therefore a homogeneous film does not form. It also seems clear from STM,[9] as well as LEED,[5] that the 1×1 structure is maintained for the unoxidized areas of the Al(111) surface, and therefore the low binding energy peak cannot be caused by a reconstruction of the Al surface between oxide islands.

Peak b shows that the interface between the Al oxide and the underlying Al substrate contains metallic Al atoms which have their electronic structure modified despite the fact that they do not bond directly to oxygen atoms. To shed some light on the Al 2p core-level shifts which may result from changes in the surroundings of the atoms it may be instructive to consider a number of systems where core-level shifts of similar magnitude are seen. One such example is the core-level shifts between the atoms at the surface and in the bulk of Al metal. The bulk photoemission peak is always at the same binding energy irrespective of the orientation of the surface. However, the position of the surface peak varies from surface to surface. No surface shift (<15 meV) is observed for Al(111), for Al(100) the shift is -96 meV,[16] and for Al(110) the shift is about -130 meV.[17] The trend is that the surface-to-bulk shift is larger the more open the surface, as expected. A different example is interface systems between the Al(111) surface and alkali metals[18] where Al 2p core-level shifts of about -100 meV are induced by the alkali-metal overlayer. Even though the surface and alkali-metal-induced shifts are of similar magnitude as the present one, it is clear, in light of the obvious differences between these systems, that no direct comparison should be done.

Information on the interface segregation energy of Si impurities in the Al(111)-oxide system may be obtained from the present data. It has been shown for metallic systems that the core-level binding energy shifts between atoms at an interface and atoms in the bulk may provide information on the segregation energetics of the overlayer-substrate system.[18,19] As peak b is metallically screened this framework may actually be applied in the present case. In this way, by using the $Z+1$ approximation, we find from the core-level binding energy shift between the Al interface atoms not bonding to oxygen atoms and the bulk Al atoms, that a Si impurity in the Al bulk will segregate to the Al(111)/Al-oxide interface, with a segregation energy of 140 meV, i.e., the shift between peaks a and b.

Finally, we note that total-energy calculations based on the local-density approximation have shown that the group-III metal Al may from an sp^2-bonded (graphite-like) surface layer under certain conditions.[20] This results in the formation of a more open structure. It is conceivable that this occurs in the present interface system.

In Fig. 5 is shown the Al 2p photoemission spectrum

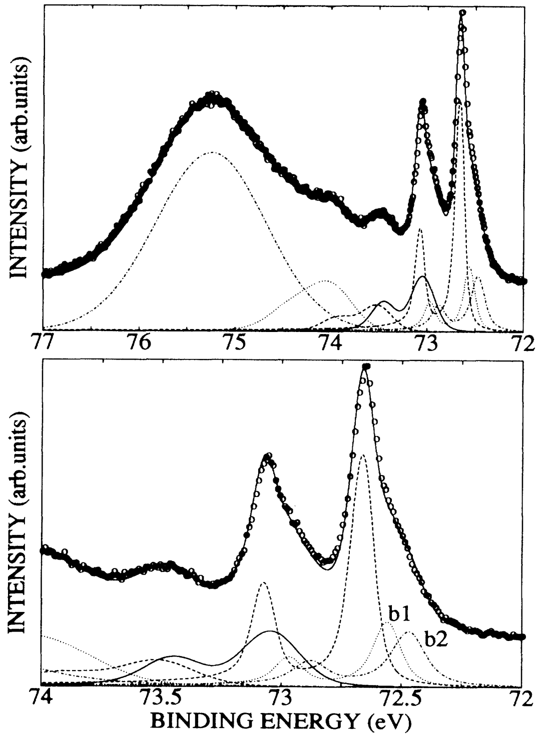

FIG. 5. Al 2p spectra from Al(111) that has been exposed to 400-L oxygen at liquid-nitrogen temperature (~100 K). The photon energy is 110 eV. The low binding energy shoulder has been fitted by use of the two peaks $b1$ and $b2$.

for the Al(111) crystal, which has been exposed to 400-L oxygen at a temperature of ~100 K. The bulk oxide emission is larger than for the corresponding room-temperature oxidation. This is due to an increased sticking at the lower temperature. Instead of a distinct peak, a low binding energy shoulder is observed. This shoulder can be fitted quite well by using two peaks (labeled *b*1 and *b*2 in the lower panel of Fig. 5). The absence of a distinct low binding energy peak in this case may be understood in terms of larger degree of disorder at the oxide/metal interface as compared to the sample that was oxidized at room temperature. This is due to the temperature being too low for the atoms to reach equilibration positions by thermally activated processes like, e.g., site interchange. Thus, at a temperature of ~100 K, at least two different metallic interface configurations seem to exist for the Al atoms.

In conclusion, a peak at lower binding energy relative to the metallic bulk Al 2*p* emission has been found for an oxidized Al(111) crystal. The peak has been ascribed to Al atoms which do not bond directly to oxygen atoms in the interface between the Al oxide and the underlying metallic Al. This low binding energy peak appears at oxygen exposures of ~50 L, but gets more pronounced for exposures above 200 L. Most probably, formation of a more open interface structure, as compared to the dense (111) surface, is taking place. In short, we have presented a study where high-resolution photoemission has given information on the oxide/metal interface, which is of consequence for a comprehensive understanding of the initial stages of oxide growth on Al.

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