X-ray photoelectron spectroscopy of oxygen adsorbates on Al(111): Theory experiment

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We present the result of polar angle resolved x-ray photoemission spectroscopy on Al(111)/O and cluster calculations of the O(1s) binding energy (BE) for various model situations. In the experimental data two O(1s) peaks are observed, separated by 1.3 eV. The angular behavior (depth-resolution) could indicate that the lower BE peak is associated with an O atom *under* the surface, and the higher BE peak with an O atom *above* the surface. Equally, it could indicate oxygen islands on the surface where the perimeter atoms have a higher O(1s) BE than the interior atoms. The cluster calculations show that the former interpretation cannot be correct, since an O ads *below* the surface has a *higher* calculated O(1s) BE than one above. Cluster calculations simulating oxygen islands are, however, consistent with the experimental data.

I. INTRODUCTION

The Al(111)/O system has been extensively studied in the past[1-4] and until a recent scanning tunnel microscope (STM) study the accepted picture was that two O adsorbate species existed, one *above* and one *below* the surface. The STM study indicated that only small, close-packed (1×1)O islands existed prior to formation of oxide on flat (111) terraces.

In the present work, we report the x-ray photoemission spectroscopy (XPS) O(1s) spectrum in the chemisorption regime at room temperature as a function of electron detection angle, which varies the degree of surface sensitivity. We have also performed *ab initio* electronic structure calculations on Al_{10} clusters with oxygen adatoms and small islands in various configurations. O(1s) BE are derived from these calculations with the framework of Koopmans' theorem.[6]

II. RESULTS AND DISCUSSION

The XPS data were taken on a previously described instrument using a AlKα source.[7] Takeoff angles of 10° and 80° were used to strongly vary the degree of surface sensitivity of the measurement. The sample was a single crystal Al(111) surface oriented to within 0.6°. The oxygen coverage in this work (room temperature exposure) was ~0.3 monolayer, based on relative Al(2p)/O(1s) intensities and theoretical photoionization cross-sections.[8] No oxide species were present, as judged by the lack of any 2.7 eV chemically shifted Al(2p) component [which is known to represent Al_2O_3 (Ref 9.)] even at 10° takeoff angle.

Figure 1 shows the Al(2p) and O(1s) spectra for the clean surface and after oxygen exposure. The main point to notice is that the ratio of the 533.5/532.1 eV peaks increases at low takeoff angle. An obvious explanation for this would be that the 533.5 eV peak represents an oxygen adatom on the surface and the 532.1 eV peak one below the surface. The cluster calculations, however, show that this cannot be the case because it is always found, independent of the size of the Al substrate cluster and the exact site of an O adatom, that an O

adatom beneath the surface has a *significantly higher* O(1s) BE than one above. For example, a Al_{10}O cluster, one of those calculated is shown in Fig. 2 with the O adatom in its calculated equilibrium position 0.66 Å above the surface. The calculated O(1s) BE (Koopmans' theorem value) is 560.6 eV in this position. The equivalent value where the O atom is moved below the plane of the surface to a new equilibrium position (1.17 Å below the surface) is 562.5 eV, 1.9 eV higher. Performing O(1s) hole-state calculations to include final-state screening reduces the absolute numbers by ~25 eV, bringing them close to the experimental O(1s) values, but does not change the ordering; i.e., an O atom below the surface still has a significantly higher O(1s) BE than one above.

Since the idea that the two O(1s) peaks represent O adsorbates above and below the surface was inconsistent with the BE calculations, we redid the calculations for a number of oxygen clusters designed to simulate a small O adsorbate island on an Al(111) surface where perimeter O atoms have
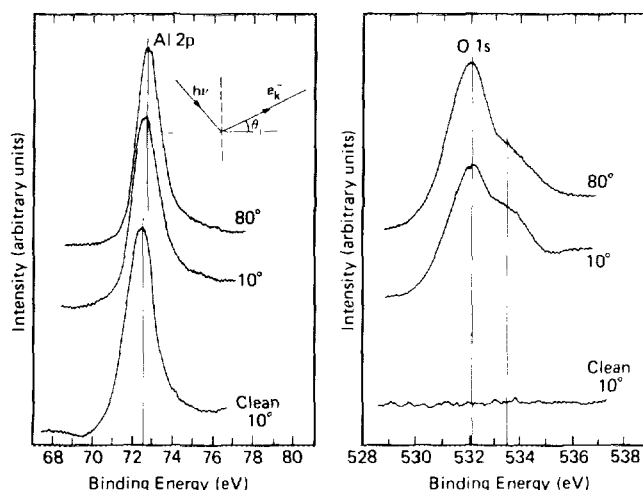

FIG. 1. Al(2p) and O(1s) spectra for a clean Al(111) surface and after adsorption to ~0.3 mL O. Data at two emission angles, 80° (near normal emission) and at 10° (near grazing emission) are shown.
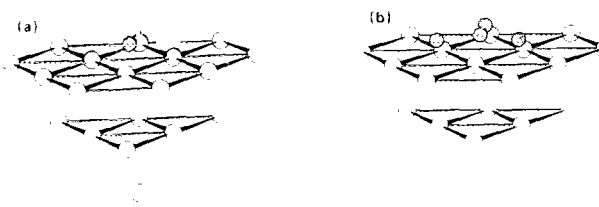
FIG. 2. (a) Sideview of an $Al_{19}O$ cluster. The Al(111) surface is represented by 12 atoms, the second layer by six atoms, and the third by one atom below the central adsorption site of the O adatom. (b) As Fig. 2(a) except for an $Al_{19}O_4$ cluster with the O adatoms in adjacent threefold sites.

a lower number of O atom neighbors than interior O atoms. An O_4 cluster of this type is shown in Fig. 2(b). The central oxygen is in the same position as the O adsorbate of Fig. 2(a), but additional atoms have been added at adjacent threefold adsorption sites. The O–O adsorption distance here is very short (0.6 that found in the STM study)[5] so any differential effect between central and perimeter O atom, due to a change in O atom coordination, might be expected to be maximized. The calculated O(1s) BEs are 557.3 eV (central) and 558.7 eV (perimeter). Thus, there is a 1.4 eV *higher* O(1s) BE for the perimeter O. This separation of BEs is consistent with the experimental BE difference, but an explanation in terms of O islands requires a reason why the O(1s) intensity of the perimeter atoms should increase relative to that of interior atoms as one moves from normal to grazing angle emission. This is in fact, to be expected since, on average, photoelectrons ejected, at grazing emission, from perimeter O atoms will suffer less effect of inelastic scattering with other O atoms than will photoelectrons ejected from interior O atoms. The self-attenuation of the O(1s) signal at grazing angle emission is thus less for perimeter atoms and the O(1s) intensity ratio of perimeter to interior atoms will therefore increase as one moves to grazing angle.

III. CONCLUSIONS

On the basis of the O_4 cluster calculation, then, we are drawn to the conclusion that the *higher* O(1s) BE experimental peak represents perimeter atoms in *small* O islands, in agreement with the STM results. Performing calculations on different O clusters (number of O atoms, O–O spacing) does not change this conclusion, through the calculated BE difference does vary from the 1.4 eV value found for the O_4 cluster.[10] On the basis of the present results we suggests that a reassignment of the vibrational spectra, (obtained by high-resolution electron-energy-loss spectroscopy)[2-4] in terms of oxygen islands be considered. It was largely the interpretation of a particular vibrational frequency that led to the ideas of the coexistence of surface and subsurface O adsorbate species. In addition, the O(1s) spectra during oxygen adsorption on surfaces known to form islands should be reexamined to look for similar effects.

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