

Atomic Scale Characterization of Oxygen Adsorbates on Al(111) by Scanning Tunneling Microscopy

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Abstract. We present atomic scale STM pictures of clean and oxygen containing Al(111) surfaces. Little influence of the surface oxygen on the topography of the surfaces is found. Three different oxygen species can be distinguished. One of them is associated with adsorbed oxygen and found to grow in small islands upon adsorption at 300 K. Characteristic hexagonal nuclei, created upon annealing of a dilute oxygen adlayer, represent the second one. By comparison with existing spectroscopic data these are assigned to nuclei of a surface oxide.

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Oxygen adsorption on aluminum surfaces, though extensively studied due to the interest in aluminum corrosion, is in many fundamental aspects still little understood [1]. This situation results mainly from the fact that, in most cases, a complex sequence of different, partly coexisting oxygen species is found, whose relative concentration strongly depends on the respective adsorption parameters such as sample temperature, oxygen pressure and presumably also on the crystallographic and chemical state of the surface.

In this communication we report first results of an atomic scale Scanning Tunneling Microscopy (STM) study on the adsorption characteristics of oxygen on Al(111). Because of its potential effects on the adsorption behaviour we will devote special attention to the defect structure of the clean and oxygen covered Al(111) substrate and to the implications of incomplete removal of the adsorbed oxygen on the surface topography.

The experiments were performed in a standard UHV system with facilities for sample cleaning (Ar ion gun) and characterization (Low Energy Electron

Diffraction=LEED, Auger Spectroscopy=AES). During preparation the sample was held in a standard manipulator with indirect heating which allowed access to these techniques. For STM measurements the sample was transferred into the very rigid, pocket size type microscope [2]. Sample preparation was carried out by repeated cycles of ion bombardment (500 eV, 1 μ A) at 300 K and annealing to 800 K, until no further contamination could be detected by AES on the surface and the LEED pattern showed bright spots with little background.

The clean Al(111) sample, as defined by the above standards, initially exhibited a rather irregular topography with many narrow terraces. After prolonged heating/annealing cycles a large fraction of the surface, however, was characterized by a structure as shown in Fig. 1a. Extended terraces of several hundred Angstroms width are separated by monatomic steps. Only in the far left side of the image appears a larger slope which is composed of a sequence of monatomic and biatomic steps. But also here individual terraces of 30–50 Å width are resolved. For a correct impression of the steepness of this “slope” one should not forget the strongly enhanced scale in the vertical direction, which renders this an increase of 6 atomic layers over a distance of ca. 300 Å. The step density on this surface is

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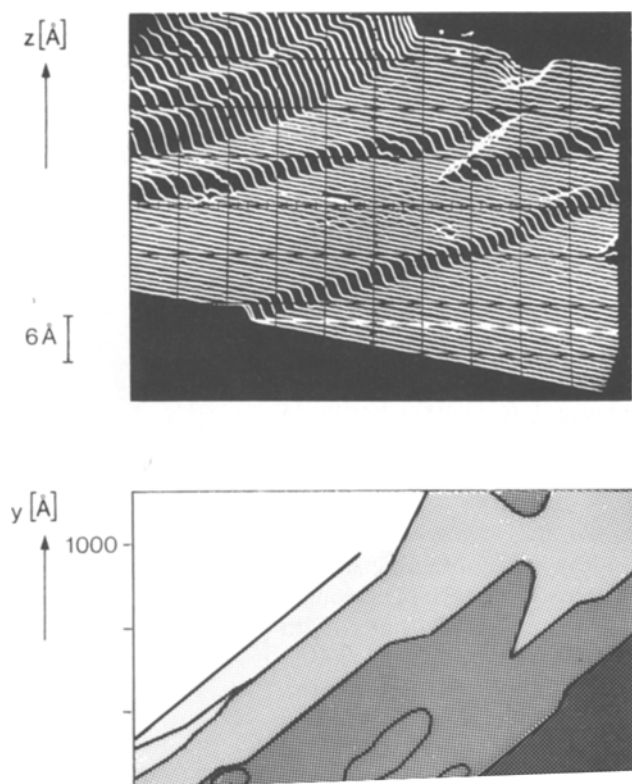


Fig. 1. (a) Line scan representation of an STM image of a clean Al(111) surface, $1200 \text{ \AA} \times 1200 \text{ \AA}$, $V_t = -330 \text{ mV}$, $I_t = 63 \text{ nA}$; (b) projection of the STM scans in (a) indicating the step/terrace distribution over this area, except for the part of the left side slope. Circled areas exhibit additional structure in the STM scans

in good agreement with results from He diffraction reported by Lock et al. [3], who determined a very low defect density on a similarly prepared surface from the specular intensity of the reflected He beam. A projection of these STM scans, shown in Fig. 1b, reveals that the steps mostly proceed in one lattice direction and that the concentration of kink sites, i.e. locations at which the step changes its direction, is rather low. The steps mostly proceed linearly over distances of several hundred Angstroms.

A more thorough inspection of this image yields further information on the (defect-)structure of this area. The terraces are in general imaged as flat and structureless, with basically no noise on the STM scans. There are, however, a few areas which exhibit additional structures. They appear repeatedly in

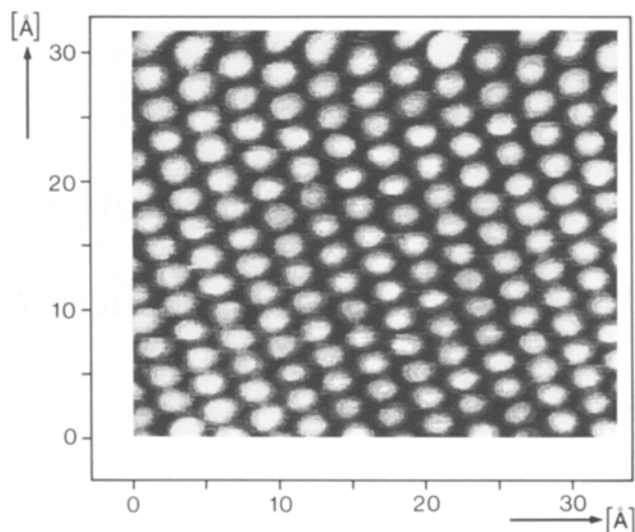


Fig. 2. Grey scale representation of a high resolution STM image of a clean Al(111) surface (low levels are shaded dark), maximum corrugation 0.3 \AA , $V_t = -50 \text{ mV}$, $I_t = 6.3 \text{ nA}$

several scans and can therefore unequivocally be attributed to surface features rather than to instabilities in the STM signal. These locations are indicated in Fig. 1b. Similarly the steps are mostly smooth and structureless except for one place where extra structures appear in the terrace edge. These extra structures are randomly distributed over the surface with no preference e.g. for step sites. The largest such feature extends over an area of at least 200 \AA , for the smaller ones the size can hardly be determined on this scale.

We have recently reported that under certain conditions, i.e. after a specific tip preparation, individual atoms of the close packed Al(111) surface could be resolved by STM [4]. In average a corrugation of 0.3 \AA was found. A grey scale STM image of this surface is reproduced in Fig. 2 (dark shades correspond to low levels). While details of the imaging process and the correlation between STM image and electronic structure are discussed in [4], we will focus here on the information concerning the defect structure of that surface. The periodic arrangement of the Al atoms, indicated by white spots, is neither disturbed nor altered over the entire area imaged, i.e. all of the ca. 170 atoms appear similar and are located on their correct sites. The distortion in the topmost part of the image is an experimental artefact and is caused by a hysteresis of the piezo elements.

Similar patterns of a defect free surface were reproducibly obtained. The periodic part of the surface can thus be characterized by a very low density of defects, most of which are associated with step and kink sites rather than with missing atoms, adatoms on a flat terrace, foreign atoms or with grain boundaries.

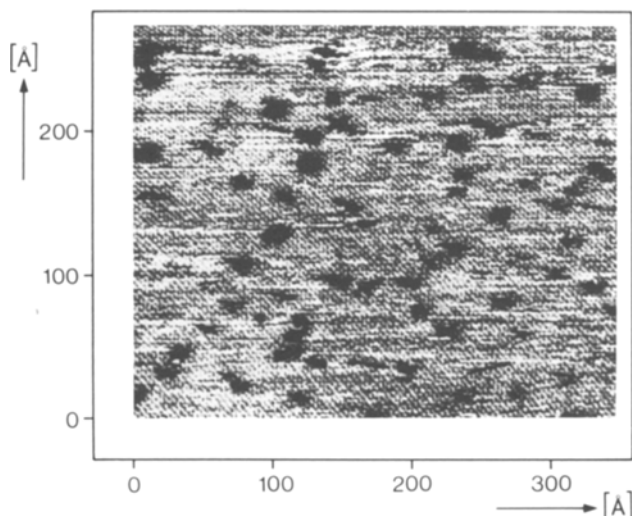


Fig. 3. Grey scale representation of a $350 \text{ \AA} \times 270 \text{ \AA}$ STM image of an Al(111) surface after exposure to oxygen (4L, 300 K), height distribution ca. 0.7 \AA , $V_t = -110 \text{ mV}$, $I_t = 6.3 \text{ nA}$

The STM image reproduced in Fig. 3 shows a surface which after preparation was exposed to 4L ($1\text{L} = 10^{-6} \text{ Torr s}$) oxygen at 300 K ($p_{\text{O}_2} = 1 \times 10^{-7} \text{ Torr}$), leading to an oxygen coverage of 5% of a monolayer (ML) of O_{ad} . The step-terrace structure does not appear to be affected, extended terraces are regularly found. While most of the surface still exhibits the atomic corrugation of the clean surface, there are additional, characteristic depressions of $10\text{--}20 \text{ \AA}$ diameter and ca. -0.7 \AA depth. These depressions are clearly associated with *adsorbed* oxygen, they can be understood from the physical background of an STM image. STM scans follow lines of constant tunnel current, the STM image thus does not reflect the exact geometry of the surface but gives a picture of the electron distribution in front of the surface. By affecting that quantity the adsorbed oxygen can therefore lead to a reduction in tunnel current and thus to a depression in the STM image [5]. Spectroscopic STM measurements gave further evidence of this assignment [6].

The arrangement of the O_{ad} in small islands and the basically random distribution of these islands over the surface was found to be characteristic for oxygen adlayers at low and medium coverages of O_{ad} . This image thus directly supports the assignment of an island growth mode for the distribution of the adsorbed oxygen atoms which was already concluded from other experimental data [1, 3]. In addition we found these islands to be distributed over the terrace area, with no special preference e.g. for step sites.

An entirely different impression of the surface originates from Fig. 4. It displays an STM image of a

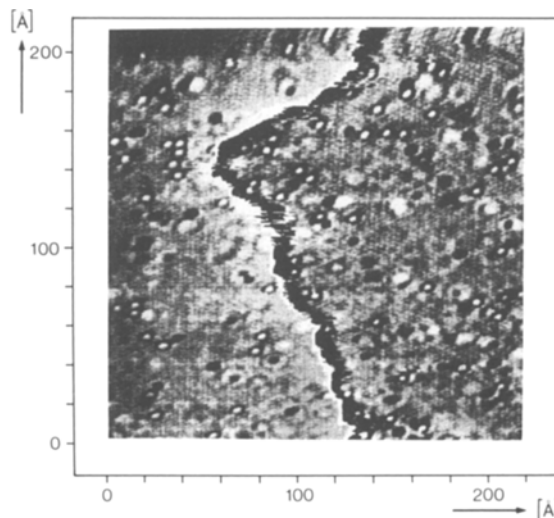


Fig. 4. Grey scale representation of a $210 \text{ \AA} \times 230 \text{ \AA}$ STM image of an Al(111) surface which after ion sputtering and annealing to 800 K still contained traces of surface oxygen (5% of a ML), $V_t = -500 \text{ mV}$, $I_t = 1 \text{ nA}$

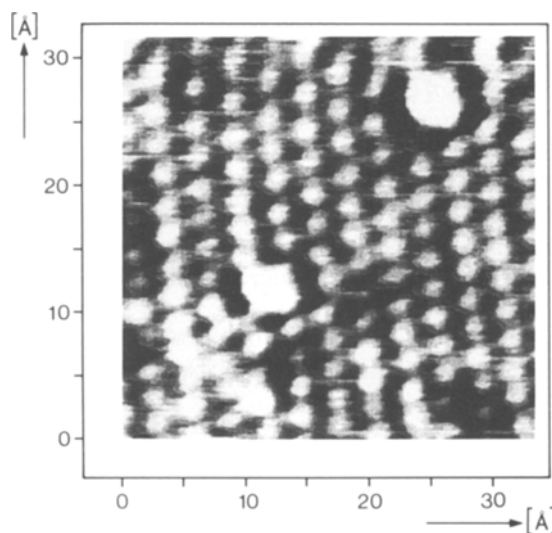


Fig. 5. Grey scale representation of a high resolution STM image showing two "oxidic nuclei" on Al(111), surface conditions as in Fig. 4, $V_t = -40 \text{ mV}$, $I_t = 16 \text{ nA}$

formerly oxygen covered surface that after ion bombardment at 300 K and subsequent annealing to 800 K still contained small amounts of oxygen. Auger spectra of this surface indicated a coverage of again 5% of a ML. On this image, which covers a surface area of $210 \text{ \AA} \times 230 \text{ \AA}$, two flat terraces exist, separated by a monostep. The traces of oxygen apparently do not inhibit the formation of extended terraces on this surface upon annealing. In contrast to the long straight steps found on clean surfaces this one is highly structured and exhibits a large number of kink sites.

Although hardly visible on this scale the atomic corrugation of the Al atoms is resolved again over wide areas of the flat terraces, reflecting a clean Al(111) surface. Most characteristic of this surface, however, is a number of small features which are irregularly distributed over the surface. They exhibit a hat-like shape, a central protrusion is surrounded by a ring of depressed area. The diameter of the entire feature is $\sim 8 \text{ \AA}$, the height difference with respect to the average level of the surrounding Al surface is $\pm 0.4 \text{ \AA}$. In a few cases the depression zone is more extended in one direction.

A more detailed picture of these features, as presented in Fig. 5, reveals that the rings actually consist of six individual hollows arranged in a regular hexagon. Since the Al atoms are clearly visible on this image, also the relative positions of these dips with respect to the underlying Al lattice can be determined. All of them coincide with the center of three neighbouring atoms of the topmost Al layer, which is also the predicted site for adsorbed or subsurface oxygen atoms [7]. The seventh threefold site, in the center of the hexagon, lies within the central protrusion.

Often these hexagons are grouped together into small ensembles of 2–6 individuals. In these cases they apparently arrange into an ordered structure, the distances and directions between individual nuclei are limited to certain values.

Further structures on this surface, in addition to the above nuclei, include local, mostly round depressions of ca. 10–20 \AA diameter and 0.7 \AA depth as well as a few elevated areas. The first ones are comparable to the islands created by oxygen after adsorption at 300 K and are likewise assigned to islands of adsorbed oxygen. For the latter species, which clearly is also related to some kind of surface oxygen, no pertinent model exists at present.

The total number of the hexagonal nuclei is too large to associate them with an incidental feature. Also the reproducibility of their shape indicates them to represent a configuration which is especially stable under these conditions (i.e. after annealing of the sample covered with low amounts of oxygen). HREELS measurements in the low coverage region display characteristic changes of the loss peaks upon annealing [8] and an increasing similarity to the

spectra which were attributed to an oxidic species formed by high coverages of oxygen at 300 K [10]. We therefore assign these features to oxidic nuclei, which apparently are especially stable but whose formation is kinetically limited.

Based on this interpretation of the STM image in Fig. 4, there are two or three electronically different species of surface oxygen on this surface. This is in very good agreement with the results of [8, 9], where upon annealing only part of the O_{ad} was found to be converted into the surface oxide, while the remaining part coexisted with that phase. This gave rise to complex multi-peak spectra. By comparison of differently prepared surfaces could the individual peaks be related to specific states of the substrate/adsorbate layer. In the STM images, in contrast, the states are clearly distinguishable, but cannot be easily interpreted in common terms such as "adsorbed", "subsurface" or "oxidic" oxygen.

Further, more controlled work on the growth conditions and stability of these different features will be necessary. But clearly these and similar STM images provide state and position sensitive information on the adsorbate and thus give valuable insight into the process of surface corrosion.

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