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Atom resolved evidence for a defective chemisorbed oxygen state at a Mg(0001) surface

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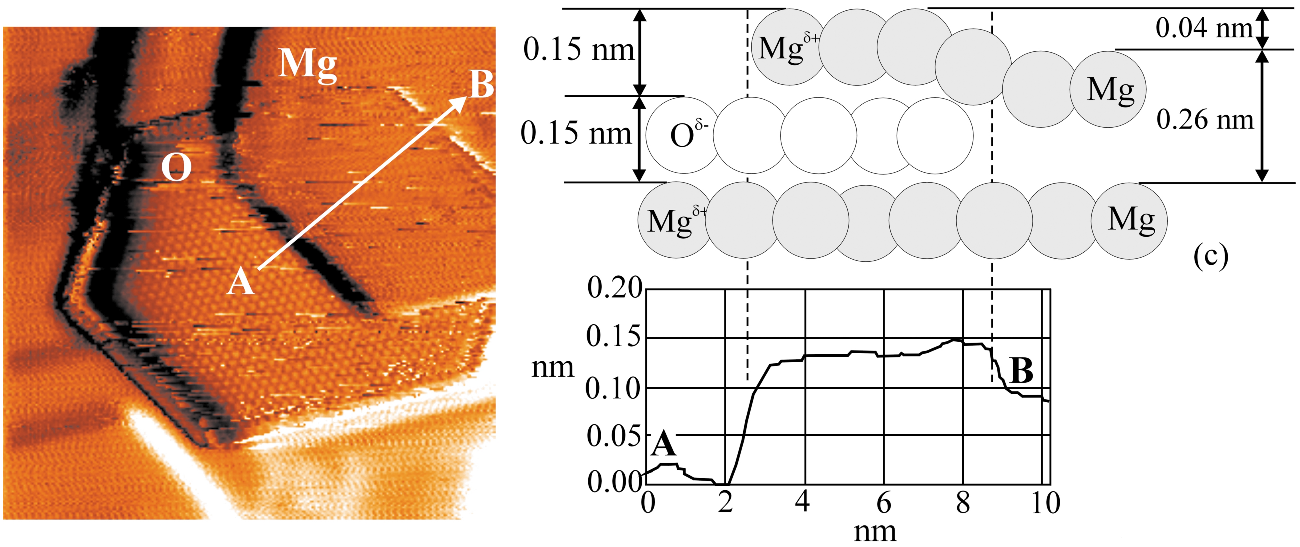
A chemisorbed oxygen state has been revealed for the first time by scanning tunnelling microscopy to be present at the interface between a (1 × 1)-O structure and overlying magnesium atoms; the step-height at the interface is between 0.14 and 0.15 nm and compatible with the presence of $O^{\delta-}$ like states.

Interest in the molecular events involved in the transition from the oxygen chemisorbed state to the oxide overlayer at metal surfaces have been sustained for over 50 years, much of it stimulated by the theory of Cabrera and Mott[1] in 1948. A range of experimental techniques have been brought to bear on this question, including work function,[2] photoemission and photoelectron spectroscopy[3] and structural aspects using low energy electron diffraction,[4] ion-scattering[5] and more recently scanning tunnelling microscopy (STM).[6]

The oxidation of Mg(0001) has been studied previously by various experimental methods; in this paper we report the first atom-resolved evidence for the surface structure at the chemisorption stage. Previous studies using low energy electron diffraction (LEED)[7] and work function changes[8] have provided the basis of models for oxygen chemisoprtion, with incorporated or subsurface oxygen, ionic oxygen states and bulk-like magnesium oxide invoked at various stages. Although our interest in metal oxidation is long standing the present STM study was driven by our observation[9] that oxygen states at Mg(0001) surfaces, which we had designated as $O^{\delta-}$, were active in selective oxidation catalysis at low temperatures whereas the MgO-like surface was inactive. It is the specific nature of these oxygen states that we sought possible evidence from STM.

An atomically clean surface of Mg(0001) was prepared by a sequence of argon-ion bombardment and annealing, with X-ray photoelectron spectroscopy (XPS) confirming the absence of surface contaminants. The STM, with *in situ* XPS facilities, was supplied by Omicron Vacuum Physik.

In experiments where the surface was monitored by STM during oxygen chemisorption at 295 K, hexagonal islands approximately 0.3 nm in height develop consisting of two layers. The latter is evident from the example shown in Fig. 1(a) which was obtained after the Mg(0001) surface had been exposed to oxygen (25 L) at 295 K and when the O 1s intensity in the photoelectron spectrum indicated the presence of 5×10^{14} oxygen adatoms cm^{-2}. Fig. 1(b) shows the profile of the relative height (nm) across the line AB (~ 10 nm) of the surface. The accuracy of the height measurements was checked against monatomic steps on a Cu(110) surfaces. It is clear from the figure that the upper hexagon has slid approximately 10 nm away from the lower, producing a characteristic 0.14–0.15 nm step and an associated 0.05 nm 'step'. This is compatible with the model shown in Fig. 1(c) where a magnesium layer overlaps the (1 × 1)-O island and the 0.05 nm step is due to the difference in height between a magnesium layer above the chemisorbed oxygen and over the magnesium substrate. The atom-resolved adatoms in region A are a hexagonal (1 × 1)-O type structure, epitaxial with the atomically clean Mg(0001) surface. Region B of the surface is composed of magnesium atoms but not atomically resolved.



(a) (b)

Fig. 1 15 × 15 nm STM image (a) observed of a (1 × 1)-O chemisorbed oxygen adlayer at a Mg(0001) surface partially obscured by an overlayer of magnesium atoms. Tunnelling conditions: sample bias +0.30 V, I_T = 1.47 nA. Similar images were also obtained with a negative sample bias. The relative height profile (b) along the line AB reveals a step height at the oxygen/magnesium interface of between 0.14 and 0.15 nm. A model of the step-region is shown (c) illustrating the location of the $Mg^{\delta+}$–$O^{\delta-}$ sites.

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The interatomic Mg–Mg distance in Mg(0001) is 0.26 nm (Fig. 1), and the Mg^{2+}–O^{2-} spacing in MgO is 0.149 nm. Clearly neither the chemisorbed oxygen adatoms nor the magnesium atoms at the step can be considered to be in their fully ionised states (O^{2-} radius 0.138 nm when 4-coordinated, 4-cordinated Mg^{2+} state is 0.049 nm). By comparison the radius of the neutral O-atom is 0.07 nm while the radius of the metallic, Mg^0 atom is 0.16 nm. Furthermore, LEED and ion-scattering data have provided information on bond distances and bond angles for atomic adsorbates chemisorbed at metal surfaces. For metal–oxygen systems the bond lengths summarised by Somorjai and Van Hove[10] are in the range 0.18–0.21 nm.

Chemisorbed oxygen states clearly exist at a Mg(0001) surface that are neither characteristic of the bulk MgO-like structure nor of the (1 × 1)-O chemisorbed layer. They, therefore, provide the first atom-resolved evidence for the presence of special oxygen states at the chemisorption stage which are analogous to those designated as $O^{\delta-}$ (or O^- like) and suggested[9] to be the active centres in the low temperature catalytic oxidation reactions at Mg(0001). The role of special oxygen states in oxidation catalysis has been reviewed recently.[11–13] Step-movement at metal surfaces is frequently observed by STM during oxygen chemisorption and was reported.[14] recently for Mg(0001). Although this has, in some cases, been attributed to the role of the ‘tip’ in STM studies, facile metal atom movement, including faceting, is a fundamental feature of oxygen chemisorption at metal surfaces. In the present system, steps of varying heights have also been observed to undergo rapid movement with evidence for the formation of MgO-like structures; these will be discussed elsewhere.

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