PHYSICAL REVIEW B **69**, 193405 (2004)

Mg(0001) surface oxidation: A two-dimensional oxide phase

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(Received 16 March 2004; published 21 May 2004)

First-principles electronic structure calculations and angle-scanned x-ray photoelectron diffraction experiments reveal the geometrical structure of the Mg(0001) surface upon oxidation. In contrast to previous studies of Mg(0001) oxidation and unlike the case of aluminum oxidation we determine a surface oxide structure, consisting of mixed oxygen-magnesium layers on top of an almost unchanged Mg(0001) surface. This unusual, directionally bound, surface oxide is locally formed already at very low dosing, corresponding to total coverages of 0.1 monolayer (ML), and grows laterally with increasing oxygen coverage up to at least 3 ML total coverage.

DOI: 10.1103/PhysRevB.69.193405 PACS number(s): 81.65.Mq, 61.14.Qp, 68.43.−h

Understanding the oxidation pathway of metallic surfaces remains one of the challenges of today's surface science. This important but complicated process[1] proceeds in several stages, beginning with the dissociation of the oxygen molecule above or at the surface and ending with the correctly restructured bulk oxide. One of the most widely exploited oxides in various applications, such as in electronic and microelectronic devices and in catalysis, is magnesium oxide. Ultrathin films of MgO can be fabricated in a controlled manner through the deposition of metal and subsequent oxidation to produce the desired orientation of the MgO crystal of the rocksalt structure. Yet we are still far from a complete understanding of how a clean Mg crystal surface exposed to the ambient atmosphere oxidizes to form MgO of the proper rocksalt structure.

In this Brief Report we show by first-principles density-functional theory (DFT) calculations and angle-scanned x-ray photoelectron diffraction (XPD) experiments in unison that O adsorption on Mg(0001) leads to a rather unanticipated layered, graphitelike (Fig. 1) surface oxide with directional bonds within the planes, as opposed to the ionic rocksalt structure of bulk MgO. Up to recently it was believed that surface oxide structures were identical or closely related to the corresponding bulk oxides.[1] However, recent studies of the Pd(111) (Ref. 2) and Ru(0001) surfaces[3] have shown that *transition-metal* surface oxides may form two-dimensional structures that are nothing like their bulk oxides. There is no *a priori* reason to expect a similarly complex process for *simple*, free-electron-like metals, but this Brief Report documents that a hitherto unknown two-dimensional (2D) surface phase constitutes the first oxide formation on the Mg(0001) surface. We further show that the adsorbed O atoms form clusters that grow at increasing overall oxygen coverage and discuss how this clustering complicates our theory-experiment comparison.

In the complex intermediate stage of metal oxidation the oxygen atoms may adsorb directly onto the surface or into the metal layers immediately below the surface. Earlier calculations of O adsorption both on a transition metal Ru(0001) (Ref. 3) and the free-electron-like Al(111) surface[4] have demonstrated that O will first occupy on-surface sites and only when a full ML is completed the additional O is incorporated. While most of the previous theoretical[5,6] and experimental[7–12] studies devoted to the incipient oxidation of Mg(0001) agree that, immediately after the dissociation of O_2 molecules on the surface, oxygen atoms are incorporated into the substrate, other experiments[13] have to some extent questioned this picture. Recent scanning tunneling microscopy studies[14–16] of the oxidation of Mg(0001) suggest that at low oxygen exposures, up to 2 L (Langmuirs), the incorporated O atoms form a single layer underneath the top layer of Mg. This seems consistent with our results.

The DFT calculations, within the generalized gradient approximation, were performed[17] for coverages 1–3 ML.

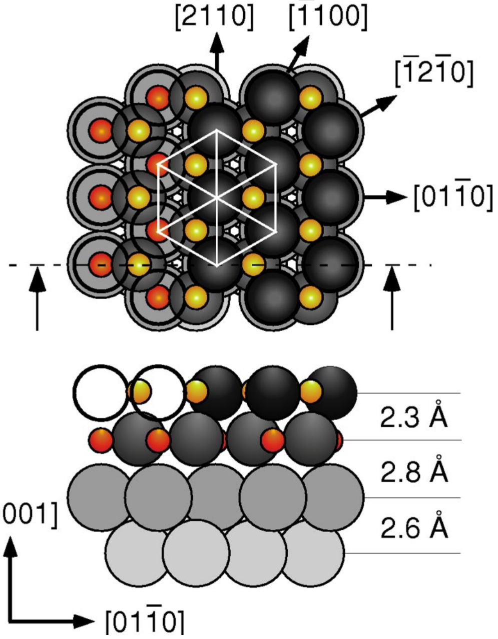

FIG. 1. (Color online) Sketch of the layered Mg-oxide structure at 2 ML local coverage, as determined by combined XPD experiments and DFT calculations.

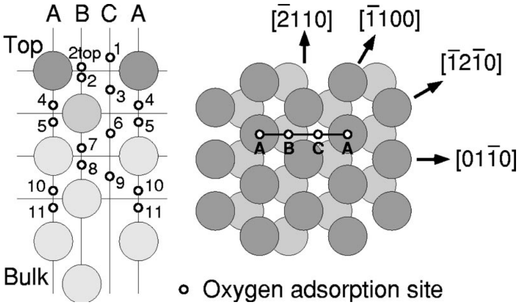

FIG. 2. The geometry of the topmost Mg(0001) atomic layers before oxidation and location of possible O adsorption sites (small open circles). The labeling of the sites refers to their lateral positions, identified by the letters *A*, *B*, and *C*, and the respective number.

In our survey, we included the adsorption sites suggested by earlier studies[6,11,12] along with a number of other positions above and below the surface.[18] Of these, the stable sites are sketched in Fig. 2. The Mg(0001) surface was modeled by periodic slabs. All calculational details are given in Ref. 18.

As discussed further below, the experimental findings show that at the O_2 dosings presently studied the surface organizes in patches (of size >50–100 Å) with a (1×1) structure and thus at least 1 ML local coverage Θ. When comparing our theory findings and experiments the relevant local structure is thus the repeated (1×1) surface cell with one or more O atoms. Theory calculations of small local coverage $(1/16\ \mathrm{ML}\leqslant\Theta\leqslant1\ \mathrm{ML})$ are described elsewhere,[18] and show an increase in binding energy with local coverage. This indicates that subsurface island growth is energetically favored over the formation of a dispersed phase, as also previously seen in the lattice-gas-model calculation.[6]

In the present investigation we systematically analyzed various possible structures with one, two, or three occupied O sites per unit cell (1, 2, and 3 ML local coverage), including structures that required distortions of the lattice of the top few Mg layers. We find that also in the range $1\ \mathrm{ML}\leqslant\Theta\leqslant3\ \mathrm{ML}$ do the binding energies[19] per O atom E_{ads} increase with the local oxygen coverage, up to $E_{\mathrm{ads}}=5.22$ eV (Table I for 2–3 ML structures). Indeed, we extracted three types of structures with approximately equal binding energies which are all energetically favored over the single site and 1 ML geometries discussed in Ref. 18. All these thin surface structures have the correct MgO stoichiometry.

TABLE I. The binding energy E_{ads} per O atom and the experimental XPD reliability factor R_{MP} in different chemisorption sites for 2–3 ML local oxygen coverage Θ. Only structures of high adsorption energy are listed. The multipole *R* factor R_{MP} is not a normalized quantity, and thus only relative differences are significant for structural analysis.

Θ(ML)	Sites	E_{ads} [eV]	R_{MP} (1.4 L)	R_{MP} (9.7 L)
2	$A4+B7$	5.12	0.41	0.50
	$A5+B8$	5.07	0.56	0.45
	$B2+A5$	5.05	0.44	0.33
	Rocksalt 2 ML	4.96	0.54	0.45
	Flat 2 ML	4.93	0.29	0.36
3	$A4+B7+A10$	5.22	0.45	0.50
	$A5+B8+A11$	5.18	0.53	0.43
	$B2+A5+B8$	5.17	0.46	0.35
	Rocksalt 3 ML	5.12	0.55	0.50
	Flat 3 ML	4.99	0.30	0.37
	MgO(111)		0.56	0.52

Of the $\Theta=2$ and 3 ML structures considered, two of the energetically favored configurations give a qualitatively similar structure, which is sketched in Fig. 1. They can be described as a Mg(0001) surface with slightly changed atomic positions to accommodate O atoms within the top layers of Mg atoms, thereby creating an either buckled or flat layered structure. Each layer has a honeycomb structure with O at every second vertex. The layers are stacked with O on top of Mg atoms and *vice versa* at a layer separation of approximately 2.3–2.7 Å. The main difference between the two types of layered structures is the vertical separation of the O and Mg atoms within a layer. In the structures we here term "Flat" this separation is only 0.01–0.06 Å, whereas the other structures, named by the approximate positions of the adsorbed O atoms, have a 0.6 Å vertical O-Mg separation. The $A4+B7(+A10)$ structures are buckled up (O above Mg layer) whereas the $A5+B8(+A11)$ and $B2+A5(+B8)$ are buckled down (O below Mg layer).

A further analysis of the layered phases reveals that the bulk structure of the flat (buckled) layered phase has an in-plane lattice constant of 3.52 Å (3.29 Å) and a separation of planes of 2.13 Å (2.59 Å). When lattice matching the layered phase with the Mg bulk substrate the structure is laterally compressed by 9% (3%) compared with the DFT-calculated lattice constant 3.19 Å.

The third structure of high binding energy is a thin, Mg terminated, rocksalt MgO(111) structure. This surface MgO structure is laterally strained by 6% compared to bulk MgO (DFT calculated lattice constant $2^{1/2}\times3.01$ Å). Despite its close resemblance to the bulk MgO, at 2 ML coverage this surface rocksalt configuration has distinctly lower O binding energy than the buckled layered structure and is only slightly more favored than the flat layered one (Table I). However, at increasing coverage $(\Theta=3\ \mathrm{ML})$ the difference between the binding energies in the buckled layered and rocksalt structures diminishes because the rocksalt configuration binding energy grows more than the binding energies of the buckled layered structure. Our DFT calculations thus predict a layered Mg-oxide structure as the initial structure, possibly changing into a rocksalt structure as the local coverage is further increased.

An analysis of the calculated change in charge density due to the presence of the O atoms shows a distinct difference in the character of bonding in the layered and rocksalt structures. For the layered systems a clear directional bonding between O and nearest-neighbor Mg atoms is found. This is in contrast to the ionic type of bonding observed for the rocksalt configuration with the electron charge distribution spherical around the position of surface ions. The directional bonding character of this layered surface oxide may give

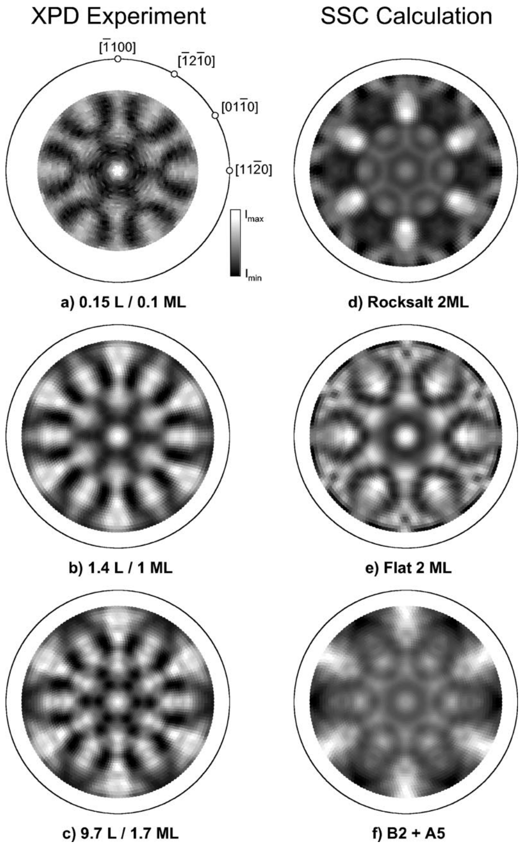

FIG. 3. (a)–(c): Experimental O 1*s* XPD patterns for different oxygen exposures of the Mg(0001) surface. The diffraction patterns are shown in stereographic projection and in a linear gray scale with white corresponding to maximum intensity. Maximum polar emission angles are 70° for 0.15 L, and 80° for 1.4 L and 9.7 L. (d)–(f): SSC calculations for the 2 ML oxide structures.

arguments for an unusual reactivity and special catalytic properties of the oxidized Mg(0001) surface.[3]

The XPD experiments were performed at the University of Fribourg's ESCALAB Mark II photoelectron spectrometer.[20] The Mg(0001) crystal was prepared by sequential Ar^+ sputtering and annealing cycles. After O_2 exposure with the sample at room temperature, the coverage was determined from the relative intensities of the O 1*s* and Mg 2*p* photoelectron peaks. Experimental O 1*s* XPD patterns ($E_{kin} = 723$ eV) were obtained after exposure of the Mg(0001) surface to 0.15, 0.7, 1.4, and 9.7 L of O_2.

The most prominent feature of the 0.15 L pattern [Fig. 3(a)] is a strong intensity maximum at normal emission (center of plot). At 723 eV kinetic energy, the scattering of electrons is strongly anisotropic and dominated by the so-called forward-focusing effect,[21] which in XPD leads to dominant intensity maxima along directions of near-neighbor emitter-scatterer pairs. The central intensity maximum of the 0.15 L pattern thus is a clear and direct evidence for O adsorption directly beneath a top layer Mg atom.

Apart from differences due to counting statistics, the patterns of the 0.15, 0.7, 1.4, and 9.7 L exposures [Figs. 3(a)–3(c)] are strikingly similar, not only regarding the intensity maximum at normal emission but regarding all the prominent diffraction features. Further, low-energy electron diffraction measurements[18] show that as the O_2 dosing is increased the surface pattern stays (1×1), indicating that oxide islands must be larger than 50–100 Å. From these two observations it must therefore be concluded that the local atomic geometry is the same over the entire exposure range. This is in contradiction to most earlier scenarios[7,8] in this exposure range.

Combining experiment and theory. The structures found by our DFT calculations were analyzed with respect to the experimental XPD patterns of the slightly oxidized Mg(0001) surface at doses 1.4 L and 9.7 L. Simulations of the O 1*s* diffraction patterns for the different DFT-determined adsorption geometries were carried out using the single-scattering cluster (SSC) model.[22] In these simulations the atoms were fixed at the positions found by DFT without any further structural optimization. The agreement between the SSC calculations and the experiment was quantified using the reliability factor R_{MP}.[23]

SSC calculations were performed for few atoms up to $\Theta = 1$ ML in the sites sketched in Fig. 2, as well as for all $\Theta = 2$ ML and 3 ML structures. Of the SSC calculations for $\Theta \leqslant 1$ ML none gave satisfactory agreement with experiment. Of the $\Theta = 2$ ML and 3 ML structures identified by the DFT calculations (Table I) the layered surface-oxide structures gave simulated diffraction patterns in significantly better agreement with experiment than the rocksalt structure. This is reflected in the low values R_{MP} (1.4 L) = 0.29 for "Flat 2 ML" [Fig. 3(e)] and R_{MP} (9.7 L) = 0.33 for $B2+A5$ [Fig. 3(f)] compared to values of $R_{MP} \geqslant 0.45$ for the 2 ML rocksalt structure [Fig. 3(d)]. Visually comparing the calculated and experimental patterns at 1.4 L we find that all the dominant features are well reproduced by the SSC calculation of the Flat 2 ML geometry, whereas the other geometries fit poorly to the experiment. For increased O_2 dosing the $B2+A5$ and $B2+A5+B8$ geometries reproduce the dominant features.

An even better agreement is obtained by considering coexistence of the two layered surface-oxide structures Flat 2 ML and $B2+A5$. Comparison to the experimental 9.7 L XPD pattern yields $R_{MP} = 0.23$ for 68% Flat 2 ML and 32% $B2+A5$. For lower global coverages the best fit is obtained when including less of the buckled $B2+A5$ structure, e.g., for 1.4 L we find 79% Flat 2 ML and 21% $B2+A5$ to give the best fit, with $R_{MP} = 0.24$. This indicates that as the patches of the layered surface oxide, and thus the global coverage, grow in size the buckled $B2+A5$ structure becomes more pronounced in the signal. The DFT calculations are carried out with periodic boundary conditions and are thus in effect models of a fully covered surface. The above picture of an increasing amount of O in the $B2+A5$ structure as the clusters are growing therefore fits well with the DFT result of an energy preference for the $B2+A5$ structure.

Interestingly, only the flat (Flat 2 ML or 3 ML) geometry yields a calculated work function drop (-1.14 eV) that agrees with experimental values.[8,13] This provides further evidence for the existence of the layered structure at the initial stage of Mg(0001) oxidation.

The coexistence of the two layered structures can be related to the size of the oxide clusters. Small clusters have small cores and can stay flat even when laterally compressed to match the Mg(0001) structure. Exceeding a certain critical cluster size, however, the relaxations in the cluster lead to buckling. A growing number of large clusters thus increases (decreases) the signal from the buckled (flat) structure. We speculate that this process facilitates the transformation of the buckled $B2+A5$ structure into the rocksalt MgO structure at higher O load.

In conclusion, we find that after the initial O adsorption further O atoms are accommodated as close neighbors within the topmost Mg layers. This leads to the formation of a thin layered and directionally bound surface oxide not previously reported. The layered structure grows laterally with increasing O exposure and represents the characteristic phase for O coverages up to 3–5 ML. The layered surface oxide appears to be metastable, however, and for higher O load increased buckling might eventually facilitate its transformation into the bulk MgO(111) rocksalt structure.

This work was supported in part by the Swedish Foundation for Strategic Research (SSF), the Swedish Research Council (VR), The Swedish Foundation for International Cooperation in Research and Higher Education (STINT), the Royal Swedish Academy of Sciences (KVA), and the Polish Academy of Sciences (KVA–PAS bilateral agreement), and the Polish State Committee for Scientific Research (KBN), Project No. 5 P03B 066 21. R.F. would like to thank P. Aebi for continuous support and help with the XPD experiments. The allocation of computer time at the UNICC facility at Chalmers and Göteborg University is gratefully acknowledged.

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