Polar-Orientated Mg-O Layers on Ag(111): a STM Study*

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We report on a scanning tunneling microscopy (STM) study of Mg-O surfaces obtained from ultra-thin Mg/Ag(111) layers exposed to different doses of oxygen at room temperature. Large scale images of any of the Mg-O surfaces show faintly corrugated alignments of 2-2.5 nm wide elementary dots. For adequate O₂ pressure with respect to the nominal Mg coverage, the dots are aligned along the $\langle 112 \rangle$ directions of silver. A hexagonal array of dots with a 4.5 nm periodicity may even be obtained, which we attribute to an epitaxial Mg-O (111) layer with in-plane spacing equal to 3.0 or 3.2 nm.

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I. INTRODUCTION

Ultra-thin oxide films attract increased interest for the development of new systems in spintronics [1–3] or in catalysis [4, 5]. Unreconstructed, polar-orientated oxide thin films might be promising candidates in both fields. While bulk-truncated polar surfaces are intrinsically unstable due to the divergence of the electrostatic potential [6], leading to surface depolarization mechanisms, the situation may be by far different in the case of a finite system [7]. In particular, reconstruction-free surfaces with high reactivity may be anticipated as well as metal-insulator transition as a function of thickness. MgO/Ag(111) is an attractive model system in this respect. MgO is a simple highly ionic (sp orbitals) oxide with the rock-salt (RS) structure and a wide band gap (7.8 eV). It is expected that the MgO(111) orientation, which results in equidistant charged layers, should be driven by the Ag(111) substrate (3.1% of lattice mismatch), with an abrupt interface. The most recent *ab initio* calculations on MgO(111) films [8] predict several structural configurations as possible in the low thickness regime: uncompensated RS (111), compensated boron-nitride (BN) (0001) and uncompensated zinc-blende (ZB) (111). Unreconstructed MgO(111) thin films have been reported to be grown on Ag(111) [9] and on Mo(110) [10] substrates, by means of alternate deposition of Mg and O₂. However, the structural information relied exclusively on electron diffraction patterns. We report here on a scanning tunnelling microscopy (STM) study of the oxidation process at room temperature of ultra-thin Mg layers preliminary deposited in ultra high vacuum (UHV) on Ag(111), and on the different types of MgO nanostructures that are obtained in this way.

II. EXPERIMENTAL

The Ag(111) substrate was cleaned by repeated cycles of Ar⁺ sputtering and annealing until STM images showed atomically stepped terraces, several hundreds of nanometers wide, free from contaminants. Mg was evaporated at room temperature using either an electron beam cell or an effusion cell, calibrated by means of a quartz microbalance. The oxidation was followed in situ by STM exposing the Mg/Ag(111) films several minutes to an O₂ atmosphere of 2×10^{-8} mbar or of 5×10^{-6} mbar. We used electrochemically etched W tips, tentatively Ag-coated by applying bias pulses prior to Mg deposit.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows a 100×100 nm² image of a sample with a nominal Mg coverage of 1 monolayer (ML). Flat, irregularly shaped islands are observed, whose apparent height is close to the $c/2$ bulk lattice parameter of Mg (260 pm), suggesting the supporting terrace is here of Mg nature. Various sample bias voltages can be used for the Mg/Ag(111) image recording. In order to be ensured of tunnelling conditions throughout the following O₂ exposure, sample voltage was thereafter fixed to -3 V (Fig. 1(b)), a value which has been proven sufficient to image insulating MgO(001) films in the ML range [11–13], while allowing image recording without insurmountable tip/surface damages. The image 1(c) displays the surface 10 min after a first O₂ dosing (3 min to 2×10^{-8} mbar). A uniform population of dots whose lateral size is about 2.5 nm is revealed at the surface of the main island as well as on the supporting terrace. The overall roughness of the surface has significantly increased with respect to 1(b), height variations up to ~ 250 pm being measured when scanning on top of the main island. Figure 1(d) shows the surface 10 min after a second O₂ dosing (6 min to 2×10^{-8} mbar). The density of dots has raised and dot alignments emerge along badly defined directions. The surface was then exposed a third time to oxygen (15 min, 2×10^{-8} mbar). At this stage of oxidation, the island shape together with the dot alignment undergoes some al-

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FIG. 1: (a),(b): $100 \times 100 \text{ nm}^2$ STM images of a $\sim 1.5 \text{ ML}$ Mg/Ag(111) surface [-0.6 V , 50 pA for (a), -3 V , 20 pA for (b)]. (c)-(f): Images (-3 V , 20 pA) of the same film after successive increasing oxygen exposures (from 3 min at $2 \times 10^{-8} \text{ mbar}$ to 8 min at $1 \times 10^{-7} \text{ mbar}$).

terations (Fig. 1(e)). In particular, smaller but straighter dotted segments are constituted. After a fourth O_2 dosing (8 min to $1 \times 10^{-7} \text{ mbar}$), the whole surface has reacted (Fig. 1(f)), the shape of the starting Mg islands being no more recognizable. Close inspection of the image (top left for instance) reveals hexagonal-like arrangements of the dots, with one direction rotated by $\sim 30^\circ$ with respect to the horizontal axis.

To ensure a rapid and full oxidation of the deposited Mg layers, the other experiments were done using an O_2 pressure of $5 \times 10^{-6} \text{ mbar}$ (2 min exposure time). Several Mg/Ag samples were investigated. Figure 2(a) shows the surface of a nominal 3 ML Mg/Ag film. Figures 2(b) and (c) display the surface immediately and 5 min after O_2 exposure. Here again, the Mg layer burst into dots upon O_2 exposure, the dots organizing themselves in the form of lines with preferential directions. Along these lines, the average separation between dots is $\sim 4.5 \text{ nm}$. One dotted line direction is turned by about -30° with respect to the horizontal axis, the latter having been preliminarily identified as a close-packed axis ($\langle 110 \rangle$) of the silver substrate. Angles of 60 or 120° between the lines are clearly recognized in some locations. In Fig. 2(d), we compare the height histogram of a chosen region of image 2(c) to that before oxidation. The height distribution of the oxidized

FIG. 2: (a)-(c): $100 \times 100 \text{ nm}^2$ STM image (0.3 V , 50 pA) of a $\sim 3 \text{ ML}$ Mg/Ag film, before and after oxygen exposure (d): Height distributions from images (a) and (c).

film has increased with respect to that of the Mg film, several components (instead of two) distant by about 120 pm (instead of 260 pm) being extracted from the new profile. The smallest distance between (111) layers in bulk MgO is 121.5 pm , in accordance with the experimental apparent heights. The identification of at least 4 layers in the oxidized film suggests oxygen atoms incorporate below as well as above any exposed Mg layer.

A well ordered array of dots could be obtained oxidizing a uniform, nominally 1 ML , Mg/Ag(111) film (see Figs. 3(a)-(b)). The Fourier Transform (FT) of one of the oxidized terraces is shown in 3(c). It takes the form of a hexagonal pattern turned by 30° with respect to the one obtained from the Ag template (LEED and STM measurements not shown here). The periodicity between dots is found equal to $4.5 \pm 0.2 \text{ nm}$, the dot size is $\sim 2.5 \text{ nm}$. The corrugation along closest-packed dots is $\sim 40 \text{ pm}$. In addition, the STM image reveals a super-periodicity of $\sim 3 \times 4.5 \text{ nm}$ in the dotted arrangement, through triangular topographical contours. Apparent heights of $\sim 120 \text{ pm}$ are measured along a given terrace (see the height histogram in 3(d) as well as the line profile in 3(e)), confirming the previous estimation of the interlayer spacing in our Mg-O/Ag(111) ultra-thin films. For comparison, the interlayer spacing in MgO(001) is 210.5 pm .

All observations are consistent with polar-orientated Mg-O layers akin to RS MgO(111) layers. First, the apparent heights obtained from scans at the surface of an oxidized terrace are half the value that should be measured (at -4 V) in the case of MgO(001) layers [11]. Second, the local hexagonal organization of the dots, observed for Mg films exposed to high doses of O_2 , points towards a hexagonal in-plane atomic structure, at variance with the three (rotated by 120° from each other) (001) domains of quadratic symmetry that could be con-

FIG. 3: (a)-(b): $100 \times 100 \text{ nm}^2$ STM images of a $\sim 1 \text{ ML}$ Mg/Ag film before and after oxidation, using an O_2 pressure of 5×10^{-6} mbar [-4 V , 20 pA for (b)]. (c): The Fourier Transform of image (b). (d),(e): Height histogram and height line profile from (b), respectively.

ceived on Ag(111). Third, the morphological and topographical features of the Mg-O/Ag(111) STM images were obtained using various bias voltages (from -0.7 to -4 V), suggesting a metallic nature of the oxidized films, in accordance with the EELS measurements and the density functional calculations of Ref. [14]. This electronic behaviour is quite distinct from the insulating one reported for MgO(001) layers [11, 15]. Last but not least, the recurrent hexagonal 4.5 nm periodicity may be accounted for, by considering RS MgO(111) layers epitaxial with respect to Ag(111), with azimuthal orientation: $\langle 110 \rangle \text{MgO} // \langle 112 \rangle \text{Ag}$ [16]. Indeed, the closest-packed dot directions are along the $\langle 112 \rangle \text{Ag}$ axes, and a noticeable point is that 4.5 nm correspond to a site-to-site distance in silver (nine $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cells of Ag, exactly). The lattice parameter of the surface (1×1) unit cell of bulk MgO(111) being 0.298 nm , fifteen such (1×1) MgO cells, rotated by 30° with respect to the (1×1) Ag cell, would match at -0.67% with every 4.5 nm Ag site. A

perfect 4.5 nm coincidence between MgO and Ag lattices is obtained assuming a MgO (1×1) lattice parameter either equal to 0.3 nm or 0.321 nm . In the first case (lattice parameter dilated by 0.67% with respect to bulk), 15 MgO cells would be involved, while in the second case (lattice parameter dilated by 7.7%), 14 cells would intervene. The 0.321 nm lattice parameter value is close to that reported on the same system by Kiguchi *et al.* (0.325 nm for a 2 ML film) [9], as well as to that calculated in the case of an unsupported BN MgO layer [17]. On contrary, experiments on submonolayer films are in favor of the surface (1×1) lattice parameter value equal to 0.3 nm [16]. One may emphasize here that the MgO(111)/Ag(111) epitaxy with $\langle 112 \rangle \text{MgO} // \langle 112 \rangle \text{Ag}$, associated with a bulk lattice mismatch of 3.1% , could not explain the observed 4.5 nm hexagonal periodicity. The MgO(001)/Ag(111) epitaxy may be excluded as well. Besides, it is beyond the present experiment to discriminate confidently between the bulk-derived Mg^{2+} , O^{2-} layer (111) stacking and slightly different stackings such as those encountered in ZB (111) or BN (0001), which were considered as metastable [8]. Also, further experiments (in particular, use of chemically sensitive techniques) are needed to investigate the exact stoichiometry of the oxidized films and the nature of the bonding at the MgO-Ag interface, together with the eventual incorporation of Ag atoms in the MgO film.

IV. SUMMARY

The alternate deposit of Mg and O_2 on Ag(111) surface leads to long-range organized Mg-O (111) surfaces that involve elementary dots of $2\text{-}2.5 \text{ nm}$ width. Oxidation of $\sim 1 \text{ ML}$ Mg films results, for O/Mg ratio $>$ or $= 1$, into a hexagonal array of these dots, rotated by 30° with respect to the Ag lattice and in coincidence with it (4.5 nm periodicity). The one-dimensional dot alignments observed with thicker Mg films or with non-completely oxidized films suggest complex stabilization mechanisms.

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