How Growing Conditions and Interfacial Oxygen Affect the Final Morphology of MgO/Ag(100) Films


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Supporting Information

ABSTRACT: In spite of the relevance of ultrathin MgO films for the study of model systems as well as for technological applications, great difficulties have been found so far in the growth of extended, well-ordered, ultrathin films. Combining scanning tunneling microscopy, X-ray photoemission spectroscopy, and high-resolution electron energy loss spectroscopy experiments with ab initio calculations, we demonstrate here that the structure of sub-monolayer MgO films grown on Ag(100) by reactive deposition is strongly affected not only by the growth conditions but also by after-growth treatments. The latter ones allow one to quench the thermodynamically most stable configuration at the deposition temperature or let the system evolve toward the low-temperature equilibrium state. Moreover, we give experimental and theoretical evidence of the accumulation of oxygen atoms at the MgO/Ag interface at the highest deposition temperature, which reduces the stress of the oxide film favoring the formation of extended terraces. The result is the possibility to tune the morphology of the films from small islands with corrugated borders, to perfectly square islands of larger size, to MgO terraces several tens of nanometers wide.

INTRODUCTION

Oxide films are used in several areas such as catalysis, corrosion, microelectronic devices, spintronics, energy applications, and sensor industry.1−3 In particular, wide band gap oxides are inert, and this very property makes them particularly suitable as support for metallic catalysts.1 The electronic and catalytic properties of MgO thin films from single-crystal substrates.3,7,8 MgO (Eg ≈ 7.8 eV) films on Mo(100) or on Ag(100) are one of the most studied among two-dimensional (2D) oxide systems.2,9−15 In fact, the simple structure of the cubic MgO lattice and the small distortion of the MgO layers when grown on Mo(100) or on Ag(100) make ultrathin MgO films a model system for the study of the electronic and catalytic properties of oxide films7 and of oxide-supported metal nanoclusters.16,17 Moreover, MgO is currently employed as interface material, e.g., as high-k dielectric in electronic devices and in magnetic tunnel junctions.18 It is demonstrated that, in the ultrathin limit, the characteristics of MgO layers depend critically on the growth parameters. The stoichiometry is related to the O2 partial pressure and Mg evaporation rate during the reactive deposition process,19 while the morphology of the MgO islands is determined by the growth temperature (Tg).20 In their investigation on the quality of MgO ultrathin layers in the range 373 K ≤ Tg ≤ 673 K, Ouvrard et al.20 showed that island formation occurs at all temperatures and indicated Tg = 543 K as the optimal condition. According to their interpretation, at this Tg the balance between the high mobility of Mg and/or MgO and the still low mobility of Ag atoms leads to islands of more regular shape and average dimensions of ~10 nm. On the other hand, a 3 monolayer thick MgO/Ag(100) film with terraces of more than 20 nm width and very regular borders was reported after growth at Tg = 773 K by Shin et al.13 Discrepancies are present in the literature also for preparations performed under nominally very similar conditions. For 450 K < Tg < 500 K, e.g., either nearly square islands with nonpolar borders (i.e., aligned along the Ag ⟨001⟩ direction)14 or polar borders (in the ⟨011⟩ direction)21,22 were reported. Furthermore, films grown following exactly the same nominal protocol may show very different aging effects and reactivity toward hydroxylation.12,23–25

Some of us have recently demonstrated the possibility to tune the shape of the MgO islands grown on Ag(100) in the monolayer limit by controlling not only the usual growth parameters, but also postdeposition conditions, in particular the cooling rate after growth.26 In such a way, very extended and uniform monolayer MgO terraces could be produced, which are

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a suitable substrate for further deposition of molecules and/or clusters.

In the cited letter we suggested a possible role of extra oxygen accumulated at the MgO/Ag(100) interface in expanding the substrate lattice and thus in reducing the mismatch between oxide film and metal substrate. Our interpretation was entirely based on experimental results. In the present work we further develop and complete the characterization of the MgO/Ag(100) system both by experimental means and computational modeling. X-ray photoemission spectroscopy (XPS) provides information on the chemical composition of the films whereas scanning tunneling microscopy (STM) allows for their morphological analysis. The vibrational spectrum provides additional information relevant for the determination of the film structure. Finally, density functional theory (DFT) models of the investigated system further support this analysis. We confirm the influence of the deposition temperature and of the cooling rate after growth, but we analyze in more detail the role of each pre- and postdeposition treatment. We conclude that the cooling rate after growth is the most effective parameter in determining the final product, and we demonstrate the importance of the accumulation of extra oxygen at the metal/oxide interface in order to obtain highly ordered monolayer films.

**EXPERIMENTAL AND COMPUTATIONAL METHODS**

(a) Experiments. Experiments were carried out in two different ultrahigh-vacuum (UHV) chambers. Both of them are equipped with a Knudsen cell and an O₂ doser for reactive Mg evaporation, with a quartz microbalance (QMB) for Mg flux measurements, with an ion gun plus gas inlet for sample cleaning, and with a quadrupole mass spectrometer for residual gas analysis. Besides that, the former apparatus (STM chamber in the following) hosts a low-temperature STM (LT-STM, by Createc). A commercial high-resolution electron energy loss spectrometer (HREELS, Delta0.5 by SPECS), a X-ray source (DAR400 by Omicron), and hemispherical analyzer (EA125 by Omicron) for XPS, and low-energy electron diffraction optics (LEED) are installed on the other chamber (XPS chamber in the following) hosts a low-temperature STM (LT-STM, by Createc). A commercial high-resolution electron energy loss spectrometer (HREELS, Delta0.5 by SPECS), a X-ray source (DAR400 by Omicron), and hemispherical analyzer (EA125 by Omicron) for XPS, and low-energy electron diffraction optics (LEED) are installed on the other chamber (XPS chamber in the following). Both apparatuses are equipped with a four degrees of freedom manipulator, coolable to liquid nitrogen temperature. In the STM chamber the sample can be resistively heated to 850 K while in the XPS chamber the same temperature can be reached by electron bombardment.

The substrate is an Ag single crystal cut within 0.1° from the (100) plane. Before each experiment it was carefully cleaned by repeated cycles of sputtering and annealing to a temperature of 720 K < T < 850 K, depending on the growth conditions. Surface cleanliness and order were checked either by STM or by XPS and LEED. MgO films were grown by reactive deposition at \( T_g = 773 \text{ K} \) and \( T_g = 450 \text{ K} \). To increase the local pressure and reduce the loading of the experimental chamber, the crystal was exposed to O₂ via a doser placed at ∼2 cm from the Ag(100) surface during Mg evaporation. The temperature of the Mg crucible was set to 593 K, corresponding to an O₂ pressure of 5 × 10⁻⁷ mbar for the preparations at \( T_g = 773 \text{ K} \) and \( T_g = 450 \text{ K} \). It was raised to 7 mbar for the preparations at \( T_g = 500 \text{ K} \).

(b) Preparation and XPS analysis. The top and bottom sections refer to the Mg 1s and O 1s spectral regions, respectively. No data are present for different ultrahigh-vacuum (UHV) chambers. Both of them are equipped with a Knudsen cell and an O₂ doser for reactive Mg evaporation, with a quartz microbalance (QMB) for Mg flux measurements, with an ion gun plus gas inlet for sample cleaning, and with a quadrupole mass spectrometer for residual gas analysis. Besides that, the former apparatus (STM chamber in the following) hosts a low-temperature STM (LT-STM, by Createc). A commercial high-resolution electron energy loss spectrometer (HREELS, Delta0.5 by SPECS), a X-ray source (DAR400 by Omicron), and hemispherical analyzer (EA125 by Omicron) for XPS, and low-energy electron diffraction optics (LEED) are installed on the other chamber (XPS chamber in the following). Both apparatuses are equipped with a four degrees of freedom manipulator, coolable to liquid nitrogen temperature. In the STM chamber the sample can be resistively heated to 850 K while in the XPS chamber the same temperature can be reached by electron bombardment.

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summarizes all the different growth protocols, including the cooling rate discussed later. They are labeled from i to vii, according to the order in which the different preparations are mentioned in the text. The film thickness was evaluated \textit{a priori} from the Mg flux estimated through the quartz microbalance and \textit{a posteriori} by inspection of STM images or by the analysis of the FK modes and of the XPS intensities. The error assigned to the QMB is ±8%, while the Mg evaporation rate measured in different days under identical conditions is stable within 5%.

Samples are cooled immediately after removing the O\textsubscript{2} pressure, i.e., in a vacuum always better than 5 × 10\textsuperscript{-9} mbar. The cooling rate of the sample after film growth is determined by the manipulator and sample holder characteristics. It was carefully controlled since it is a key parameter of our experiments. Both the fast cooling (FC) and the slow cooling (SC) rates from 773 to 300 K (see Figure 1) are set to be very similar for the STM and for the XPS apparatuses, which guarantees the validity of the comparison between microscopic and spectroscopic results. In the FC procedure the sample heating is switched off abruptly immediately after film growth. The SC rate, on the contrary, is chosen \textit{a priori} and it is kept nearly constant by thermoregulating the sample. Two different cooling rates, leading to films with identical spectroscopic signature, are reported in Figure 1 for SC. As it is evident, the time required by the crystal to cool from \(T_g\) to \(T = 450\) K is \(\sim 75\) s for FC and more that \(3000\) s for SC. In the XPS apparatus the SC procedure is stopped at room temperature while in the STM one the sample is brought slowly to 250 K and then frozen to \(T < 200\) K before being inserted into the scanning tunneling microscope.

STM images were recorded with the microscope cooled at liquid nitrogen temperature. Since the instrument is completely shielded by a double cold screen, the vacuum is much better than the one measured in the chamber thanks to the cryopumping action of the screen walls. This allows the sample, transferred into the scanning tunneling microscope directly from the manipulator, to remain uncontaminated for several days. Accurate probing of different sample areas is thus possible. For all MgO experiments we used a Pt/Ir tip cut in air under strain and then reshaped by controlled crashes into the surface, so that tunneling occurs effectively through an Ag tip. The images were acquired in constant current mode, with typical tunneling currents of 0.2 nA and bias voltage \(-4.0\) V < \(V < +4.0\) V. The lateral size of the images and the orientation of the surface are determined from atomically resolved measurements of the clean Ag(100) surface; similarly, heights are calibrated on monatomic Ag steps. STM analysis was performed with the help of WSXM software.

HREEL spectra are recorded in-spectacular, at an angle of incidence of the impinging electrons of 62°, with at a primary electron energy \(E_e = 4.0\) eV and with typical resolution of 4.0 meV. XPS spectra were recorded at normal emission, using a Al K\textalpha\ exciton source. The binding energy was calibrated on the Ag 3d\textsubscript{3/2} line, fixed at \(E_b = 368.25\) eV according to literature.

A careful fitting of the XPS spectra is essential to extract quantitative information. All spectra were normalized to the same electron background before starting the fitting procedure, in order to achieve a full comparability of the results. In order to calculate the total area and to resolve the different peak components, the spectra were fitted with Gaussian curves and a Shirley background, using self-made procedures running within the Igor Pro software v. 6.3.1.2. In Figure 2 we report an example of this analysis. Left panels show the original spectra and the Shirley background; the right ones contain the experimental curves after background subtraction, the best fit to the data, and the different components which are resolved within each peak. 

![Figure 1. Sample temperature vs time during the FC and SC protocols, measured during XPS experiments. Two different cooling rates, leading to films with identical spectroscopic properties, were used for SC experiments. Their average values in the temperature range 773 K > \(T > 450\) K are 3 and 5 K/min, respectively, to be compared with a \(\sim 40\) times faster rate for FC.](image)

![Figure 2. Analysis of the O 1s and Mg 1s photoemission spectra recorded on the 0.7 monolayer film grown at \(T_g = 773\) K, SC. Left panel: Raw experimental data and calculated Shirley background. Right panel: Experimental data (dotted curve) after background subtraction, best fit to the data, and components resolved within each peak.](image)

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The 4 × 4 supercell for the simulations consists of four layers of Ag, whereby the two bottom layers are kept frozen in the bulk positions while the upper two are free to relax, and either one or two layers of MgO. A Γ-centered mesh of 3 × 3 × 1 k-points is adopted. Different concentrations of oxygen at the interface have been considered. The interface oxygen ions occupy Ag hollow sites, situated under the Mg ions. The oxygen ions from the MgO first layer sit on top of the Ag atoms. The MgO/Ag(100) structure has been formerly characterized by means of STM measurements, X-ray absorption experiments, and DFT calculations.

The work function $\Phi$ is estimated as the difference between the vacuum level and the Fermi energy. The O 1s core levels within the initial state approximation are evaluated by solving the Kohn–Sham equations for core electrons inside the PAW sphere, after a full self-consistency with frozen core electrons is achieved.

We have also performed calculations by a supercell with three Ag layers only, with a higher kinetic energy cutoff (40 Ry), and without including the van der Waals contributions obtaining qualitatively similar results. This setup has been used to analyze the stability of additional O atoms at the interface as a function of coverage (see Supporting Information).

## RESULTS

(a). STM Results. Figure 3 shows STM images of MgO films of 0.7 monolayer nominal thickness grown at various $T_g$. Panels a–c correspond to increasing $T_g$ under otherwise identical conditions: no preannealing or postannealing treatments were performed, and the samples were fast cooled below 250 K immediately after growth. In all cases we observe the formation of several nanometers wide MgO islands. At $T_g = 450$ K (film i) and 500 K (film ii) they are of irregular shape and show corrugated borders, while for $T_g = 773$ K (film iii) the islands are regular squares with well-defined borders aligned along the (001) direction. Some islands show an internal structure, appearing as a darker region when imaged under nontopographic conditions ($V < 3.5$ V, i.e., when tunneling occurs through the MgO band gap). Such structure, almost absent for $T_g = 450$ K, has an irregular shape at $T_g = 500$ K and is concentrated at the center of the squared islands for preparation iii. It is possibly related to the MgO/Ag interface structure and composition, as it will be discussed in the
following. From comparison of parts a to c of Figure 3, we have a first indication of the role of the substrate temperature in the growth of ordered islands. Figure 3d shows the outcome of growth at $T_g = 773$ K and SC$^*$ (film iv). The Ag(100) surface was preannealed to 823 K for 60 min in order to generate very large terraces and postannealed at O$_2$ atmosphere at the evaporation temperature. This protocol leads to the formation of extended flat terraces of MgO of monolayer thickness. The result is of utmost interest, since it shows the dependence of the film structure also on pre- and postevaporation conditions and since it paves the way to the possible use of these films as substrates for further deposition of nanoobjects such as clusters or self-assembled organic layers.

For a better understanding of the influence of pre-growth and after-growth parameters on film morphology, we focus our attention on the $T_g = 773$ K preparations. Figure 4 reports STM images of 0.7 monolayer thick MgO films grown at such temperature. If no preannealing and no postannealing of the Ag(100) surface are performed and the film is FC after growth (film iii), MgO organizes in perfectly squared islands with nonpolar borders and average lateral size of $5 \pm 1$ nm (see panel a). Additional preannealing of the Ag(100) surface to 823 K for 60 min and postannealing in O$_2$ atmosphere (film iv, panel b) leads to similar MgO islands, but of larger size ($\sim 10$ nm, measured under identical bias conditions). This difference is related to the postannealing process, which allows for an additional mobility of the MgO units, as discussed in the following. Although the determination of the heights is not straightforward, from the analysis of line profiles of topographic images we can safely assume that most of the squared islands consist of bilayers of MgO. The most interesting condition is, however, the one in which the MgO film is grown on a preannealed substrate, postannealed in O$_2$ atmosphere and then SC to $T < 300$ K (Figures 3d and 4c, growth protocol iv). In this case flat terraces, tens of a nanometer wide, are produced. Since the only difference between the growth protocols v ($773$ K – FC$^*$) and iv ($773$ K – SC$^*$) is the cooling rate, the latter must be the key parameter in the determination of the final morphology of the sub-monolayer MgO films.

Finally, in Figure 5 we compare the structure of MgO films grown following protocol iii ($773$ K – FC) in the monolayer (column a, 0.7 monolayer) and in the multilayer (column b, 3.0 monolayers) regime. As evident, the cubic structure characteristic of the FC procedure persists with increasing MgO coverage, so that the 3 monolayers film consists of several squared islands of similar size merged together. This is best appreciated in the comparison between top and bottom panels of column b: the large topographic island marked by the arrow and visible at $V = 3.0$ V appears indeed as a patchwork of rectangular smaller islands when inspected at $V = 1.0$ V. Also in the multilayer regime the MgO islands present a weak inner structure. We remark that the squared bilayer islands of the 0.7 monolayer film appear larger and of less defined shape when imaged in topographic conditions (see bottom panel). At 3 monolayers, on the contrary, the relative contrast among islands changes but their shape and dimension remain nearly the same. Therefore, although we are not fully able to justify the observed effect, we can correlate it with the presence of MgO units at the border of the islands and in contact with the metal, which are transparent at the lower voltages.

(b). Spectroscopic Results. For a more complete characterization of the sub-monolayer MgO films, we investigated them also by integrated spectroscopies. Figure 6 shows the O 1s and Mg 1s core level spectra corresponding to MgO films of 0.7 monolayer nominal thickness grown following different protocols. The XPS spectra are labeled according to the preparations listed in the first column of Table 1 and coherently with the STM images. The two bottom spectra of each panel were recorded after preparations at $T_g = 450$ K (FC and SC, respectively). The other spectra were recorded after MgO growth at $T_g = 773$ K and different pre-growth and after-growth treatments. The different preparation methods lead to different spectroscopic signatures. In particular, both $E_b$(O 1s) and $E_b$(Mg 1s) are significantly upshifted for preparation iii ($773$ K – FC). In all other cases, $E_b$(O 1s) $\leq$ 530.3 eV and $E_b$(Mg 1s) $\leq$ 1303.7 eV. A simple comparison with the STM images of Figure 3 and of ref 26 evidence that the upshifted spectra correspond to the “3D” morphology of MgO islands, i.e., to the case in which the film organizes mainly in double layers; we can thus draw a correlation between the O 1s and Mg 1s binding energy and the surface morphology. This result goes in the stream of the wide and partially contrasting literature about the characterization of the O 1s binding energy of MgO thin films. Indeed, Altiere et al. measured a significant reduction of the O 1s and Mg 1s binding energy for thinner films and used this parameter to calculate the Coulomb interaction energy associated with the film. This behavior, which was not observed for other oxide films, was also reproduced in previous studies by some of us, where no thickness dependence of the O 1s line and only a small Mg 1s dependence (but with opposite trend) was observed. In the present work and in ref 26 we find that O 1s and Mg 1s binding energies are indeed higher for bilayers, but we demonstrate that the surface morphology can be very different even for films of the same nominal coverage. We can thus rationalize the contrasting results published so far by admitting that those films were grown under only partially controlled conditions, resulting in very different morphologies. The effect may be even more evident in the low-coverage limit.
Figure 7 summarizes the HREEL analysis performed on 0.7 monolayer MgO films grown under identical conditions as for the experiments of Figure 6. The spectra are characterized by three intense losses between 50 and 85 meV, which are best resolved in the green spectrum corresponding to protocol i (450 K − FC). The 53 meV vibration is intense for this film, significantly reduced for film vi (450 K − SC), and almost absent for films grown at higher Tg. We identify it with the microscopic vibration of oxygen atoms at the edges of MgO islands and in contact with the Ag substrate. Indeed, comparison with STM images confirms that film i corresponds to the conditions in which there is the highest density of MgO groups at monolayer island borders. The loss at 64−65 meV is ascribed to the Wallis mode, i.e., to the perpendicular motion of oxygen atoms at the topmost layer, by comparison with previous results on bulk MgO surfaces and MgO films. The loss upshifts by 1 meV when passing from monolayer to bilayer islands. A similar effect was reported also for MnO(100) grown on Pt(111).

The assignment of the high-energy mode is more delicate. In a previous work some of us ascribed it to the macroscopic Fuchs-Kliever mode (i.e., the counterphase vibration of O and Mg sublattices − FK in the following) and observed a marked dependence of its vibrational energy on film thickness for films ranging from 1 to 20 monolayers. In the sub-monolayer limit, on the contrary, the loss feature increases in intensity with MgO coverage, but its frequency always reads ∼71 meV. For its very nature, the FK mode should be present only for multilayer islands. The 82 meV energy recorded for film iii (773 K − FC) fits perfectly with theory, as well as the very weak intensity present at this energy for film vi (450 K − SC). The losses at 75 meV (film i, i.e., 450 K − FC) and at 80−81 meV (films vii and iv, i.e., 773 K − SC, with or without postannealing in oxygen pressure), on the contrary, must have a different origin. The latter is observed for a superstoichiometric film, as discussed in ref 26. We suggest therefore that it is due to the vibration of the MgO monolayer against additional oxygen atoms located at the interface and simulating an incomplete second layer. This hypothesis is justified in view of the
Ag(100) surface. There are at least two possible sites, one corresponding to an O atom has been adsorbed on Ag(100) below the MgO interface species. Here an O sub-monolayer component of a whole range of modes present in the 70 meV formation of MgO films. The absence of the “border” mode at 53 meV for the higher temperature protocols is consistent with the larger size of the islands (for FC) and with their merging into large terraces (for SC). The different ratio of FK and Walls mode intensities is consistent with the formation of double- and/or multilayer islands (for SC).− for FC visualization.

The optimal structures corresponding to the three cases are reported in Figure 8.

It turns out that the most stable configuration corresponds to interface O in the hollow site (Figure 8, left). When the O atom is in a bridge position (Figure 8 - center), the total energy is 0.6 eV higher. This is a metastable configuration. The peroxo group (Figure 8 -right) is considerably different from what found on the surface of bulk oxides. In fact, the O–O unit moves vertically resulting in one O above and the other below the MgO plane; the O–O distance is 2.21 Å, i.e., considerably larger than that of a typical peroxo group. However, this structure is 1.4 eV higher in energy than the interface O (hollow) and probably it is not even a minimum, as a tiny displacement of the O atom results in the spontaneous movement toward the Ag(100) surface. The peroxo group is therefore a species that can form under oxygen pressure and that evolves into the more stable interfacial oxygen.

These results have been obtained with a single O atom in the 4 × 4 supercell. Having established that the interface hollow site is the most stable one, we can start the discussion about the stability of phases with different oxygen content at the interface. First, we compare the stability of monolayer and bilayers of MgO grown on Ag(100) with the bare silver slab and hypothetically isolated 1 and 2 monolayers MgO slab models. As shown in Figure 9, the reference to evaluate the stability of oxygen at the interface is a variable concentration of gas-phase oxygen molecules. Therefore, we define the following quantities:

\[ \Delta E_1 = E(\text{MgO}/O_N/Ag) - E(\text{MgO}/Ag) - N/2E(O_2) \]

\[ \Delta E_2 = E(\text{MgO}/O_N/Ag) - E(\text{Ag}) - E(\text{MgO}) - N/2E(O_2) \]

In the Supporting Information a more detailed analysis of the stability of O atoms at the interface for increasing oxygen coverage is reported.

As reported in Figure 10 (ΔE1), the oxygen incorporation at the oxide metal interface is favorable at all concentrations and for both 1 and 2 monolayers. However, the stability gain by increasing the amount of interface oxygen varies considerably. Indeed, it is almost linear between 0 and 25%, at which concentration the slope decreases. Beyond 75%, the incorporation of additional oxygen is not favorable anymore. From the ΔE2 curves one can see that the adhesion of 1 and 2 monolayers of MgO on top of the Ag slab is always exothermic, independently of the oxygen concentration at the interface. At any given concentration of O, the adhesion energy is larger for the monolayer than for the bilayer.

All of the data reported in Figure 10, however, refer to the theoretical limit of 0 K and disregard the effect of the oxygen pressure. To calculate the thermodynamic stability of variously oxygenated surfaces in more realistic conditions, we define ΔG as

\[ \Delta G = \frac{1}{A} \{ \Delta E - N \Delta \mu_{ox}(T,P) \} \]

where \( A \) is the area of the supercell, \( N \) is the number of O ions hosted at the interface, and \( \Delta \mu_{ox}(T,P) \) is the oxygen chemical potential change at a given temperature and pressure. \( \Delta E \) is the stability at 0 K of the oxidized surface with respect to the clean one and a corresponding number of gas-phase oxygen molecules.

The change in the oxygen chemical potential is defined as follows:
By definition, $P_0$ is set to 1 atm. The values of $\mu_{ox}(T,P_0)$ are taken from the work of Reuter and Scheffler. For each $(T,P)$ value, $\Delta G$ is calculated for models with different loading of oxygen at the interface. The resulting phase diagram (Figure 11) shows the stability domains of these structures. As expected, high temperatures and low pressures stabilize the nonoxygenated phase, while by increasing the pressure and decreasing the temperature other phases appear. Notice that in the diagram of Figure 11 we did not consider the formation of subsurface O, i.e., O that has diffused into the bulk of Ag during the growth and which may eventually segregate. This limitation prevents from a full comparison between experimental results and computational model. Furthermore, for a comparison of the phase diagram of Figure 11 and the experimental results, it is important to mention that the interaction energies used to construct the diagram are obtained with the PBE+D2 functional, and that deviations can be expected due to the accuracy problems inherent to the DFT approach.

The presence of oxygen at the interface has a direct effect on the work function of the system (see Figure 12). The deposition of 1 or 2 monolayers of MgO on Ag(100) has the well-known effect to reduce the work function of the metal from 4.2 eV down to 3.3 eV (1 monolayer) or 2.9 eV (2 monolayers), respectively. The physical origin of this effect is discussed in the literature and is mainly due to a compressive electrostatic effect of the rigid wall represented by the MgO film on the metal electron density. The presence of O atoms at the interface introduces a different effect. Being electronegative, the O atoms induce a charge transfer from the metal substrate, becoming negatively charged and forming a surface dipole, which raises the work function. This effect
increases linearly with the O concentration. With 50% of O atoms at the interface, the work function \( \Phi \) assumes the same value calculated for the bare metal slab. As shown in Figure 12, the MgO monolayer is more sensitive than the bilayer in this respect.

Finally, Table 2 reports the O 1s core level binding energy (with respect to the Fermi level) computed according to the initial state approximation. While the absolute values of the computed \( E_b(O\ 1s) \) cannot be directly compared with the experimental ones due to the missing contribution of the final state screening, core level shifts can be considered for comparison.\(^48\) The presence of different types of oxygen for the MgO monolayer with excess of oxygen at the interface is expected to give rise to different signals. In particular, the \( O^2- \) ions of the ionic MgO film, fully reduced being associated with two extra electrons, are expected to have O 1s levels at smaller \( E_b \) than the O atoms at the interface, which are only partly charged.\(^49\) The following discussion is necessarily qualitative, since the use of initial state core level \( E_b \) neglects final state effects that can be different for O atoms in different environments (e.g., in the MgO film or at the surface of Ag). When no oxygen is present at the interface (0%), only the O 1s core level of the MgO layer is reported (505.8 eV). This peak corresponds to the experimental peak 1 in Table 1. With one O atom at the interface in a hollow site (6.25% oxygen loading), the \( E_b \) of the MgO oxygen atoms shifts slightly to 505.6 eV, while the signal due to the oxygen in hollow sites lies at a slightly higher binding energy (505.9 eV). If the interface O atom is placed at a bridge site, the \( E_b(O\ 1s) \) of the MgO layer, 505.5 eV, and of the O bridge, 505.4 eV, are virtually the same.

Things change with a higher O content (25% coverage). Here we have considered different distributions of O atoms: in one case, all four excess O atoms are in hollow sites; in the other case, two O atoms are in hollow and two in bridge sites homogeneously distributed. When all four O atoms sit on hollow sites, the MgO atoms \( E_b(O\ 1s) \) is remarkably downshifted at 505.1 eV. This is because the O atoms at the interface generate a negative potential, which shifts the core level \( E_b \) of the O ions of the MgO film to smaller values. This is also reflected in the local relaxation of the O atoms of the film in correspondence of an O atom at the interface (see Figure 8). The calculations show that by increasing the O coverage at the interface from 6.25% to 25%, the hollow O atoms show a slightly higher \( E_b \) (506.1 eV versus 505.9 eV). Overall, we observe a shift of about 1 eV between the \( E_b(O\ 1s) \) of MgO and that of hollow O atoms. This is at the limits of the experimental resolution in XPS experiments. If the excess O atoms are equally distributed between bridge and hollow sites (25% coverage), we find three signals at 504.9 eV (MgO layer), 505.3 eV (O bridge), and 505.7 eV (O hollow). The shifts are of the order of 0.4 eV and are expected to result in a broadening of the main signal rather than to give rise to an additional peak.

The last case considered is that of very large, unrealistic, O excess (50%, only hollow sites have been considered). Here we observe that the difference in \( E_b(O\ 1s) \) between oxygen atoms of the MgO layer and interface oxygens in hollow sites is of about 2 eV. This increased difference is mostly due to the decrease of \( E_b(O\ 1s) \) of the MgO oxygen atoms, which feel the presence of the O interface layer.

### DISCUSSION

As it was demonstrated in ref 26, all of the sub-monolayer preparations have a coverage of 0.7 monolayer MgO as estimated by XPS. Films grown at \( T_g = 450 \) K have, however, a nearly unitary stoichiometry within experimental error (O/Mg ratios of 1.22 ± 0.12 and 1.19 ± 0.12 for SC and FC, respectively), while those deposited at \( T_g = 773 \) K show an extra oxygen content (O/Mg ratios of 1.34 ± 0.13 and 1.39 ± 0.14 FC and SC, respectively). This result ensures that all the 0.7 monolayer films presented in this work really correspond to very similar absolute MgO amounts differently organized on the surface. Taking this for granted, we can investigate in deeper detail the differences among growth protocols with the help of an accurate analysis of photoemission spectra and with a careful comparison of microscopic, spectroscopic, and theoretical results.

XPS spectra of Figure 6 were fitted to resolve the different contributions. The outcome of this analysis is summarized in Table 1. Three components in the energy ranges 1301.1 eV ≤ \( E_b \) ≤ 1301.7 eV [Mg(1301) in the following], 1303.4 eV ≤ \( E_b \) ≤ 1303.9 eV [Mg(1303)], and 1304.9 eV ≤ \( E_b \) ≤ 1305.4 eV [Mg(1305)], respectively, are needed to account for the Mg 1s intensity. We note, however, that in all cases more that 80% of the signal is concentrated in the Mg(1303) peak, which corresponds therefore to Mg atoms at regular MgO sites. The minor components can be tentatively assigned to Mg atoms at defect sites and/or in the presence of an adsorbed species. The O 1s region can be reproduced with a main peak at 529.4 eV ≤ \( E_b \) ≤ 530.4 eV [O(530)] in the following and a second component at higher \( E_b \). This latter contribution is in the range of 531.3 eV ≤ \( E_b \) ≤ 532.0 eV [O(531)] in the low-\( T_g \) preparations, while it is at 532.5 eV ≤ \( E_b \) ≤ 533.2 eV [O(533)] for the superstoichiometric films. Only in one case (film i, i.e., 450 K – FC) it was necessary to use all three components to reproduce the experimental curve. From this analysis, we can draw the considerations in the following.

The binding energy of the different components confirms what had already been suggested by the inspection of the raw XPS spectra: the values found for bilayer islands (film iii, i.e., 773 K – FC) are upshifted with respect to the values of all other films (characterized by one single layer of MgO). This behavior is coherent with the trend previously reported by Altieri et al. for the same films,\(^38\) and it is explained by the different chemical environments of Mg and O atoms within a monolayer or a bilayer. Therefore, although photoemission spectroscopy cannot provide structural information, the combination of STM data with the XPS analysis described previously clearly allows one to distinguish between MgO extended monolayers and cubic bilayer islands upon film growth at \( T_g = 773 \) K.

\( \text{Table 2. Calculated Oxygen 1s Binding Energy (} E_b \text{) for MgO(1 monolayer)/Ag(100) with Respect to the Fermi Level (eV) as a Function of the Interface Oxygen Coverage} \)

<table>
<thead>
<tr>
<th>O 1s (%)</th>
<th>MgO layer</th>
<th>O-bridge</th>
<th>O-hollow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>505.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.25</td>
<td>505.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.25</td>
<td>505.5</td>
<td>505.4</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>505.1</td>
<td></td>
<td>506.1</td>
</tr>
<tr>
<td>25</td>
<td>504.9</td>
<td>505.3</td>
<td>505.7</td>
</tr>
<tr>
<td>50</td>
<td>504.2</td>
<td></td>
<td>506.2</td>
</tr>
</tbody>
</table>

\( \text{dx.doi.org/10.1021/jp507718v1 J. Phys. Chem. C} 2014, 118, 26091–26102 \)
Experimental data show that the relative intensity of the O3s component is largest for the preparations at $T_e = 773$ K, i.e., for the films showing an excess of oxygen. The satellite peaks, on the contrary, are much smaller and of comparable intensity for all preparation conditions. On the other hand, for an interface oxygen coverage of 25% (i.e., in the situation closer to the experimental conditions), theory predicts a core level energy shift $\leq 1.0$ eV for both hollow and bridge sites. Such a shift is at the limit of our experimental resolution ($\text{fwhm} \geq 1.06$ eV). Therefore, we can rationalize our finding by ascribing the O3s peak to the superposition of the contributions of O atoms of the film and of O atoms at the MgO/Ag interface, while the O3s and O3s features must have a different nature.

The O3s and O3s satellites are possibly related to some OH/H$_2$O contamination. Their different binding energy may be explained by considering the different morphologies of the films and thus the different adsorption sites available and the different chemical environments of the adsorbate. It is significant in this respect that both the O3s and O3s satellites are present for film i, which has the most irregular morphology, as witnessed by STM images and by the phonon spectrum.

Preparation vii deserves a particular discussion. It corresponds to a 0.7 monolayer MgO film grown at 773 K and SC without performing postannealing in O$_2$. The binding energies of the O 1s and Mg 1s components, in this case, are very close to the ones measured upon 773 K – FC (protocol iii). The corresponding STM images (not shown) indicate that the MgO layer consists indeed of large terraces of irregular shape merged together. The borders between islands are evident at low bias voltages, i.e., under non-topographic conditions. Moreover, a small fraction of bilayer islands is present. The apparently odd behavior can be rationalized by considering that the role of postannealing is to allow for the reorganization of the oxygen layer at the MgO/Ag interface. Such a layer is responsible for the release of the stress due to the small lattice mismatch between metal and oxide, and hence it is the essential element for the formation of extended MgO layers. If SC starts immediately after film growth, the oxygen at the interface may still be unevenly distributed. This interpretation is supported by theoretical results: (a) simulations show indeed that, for monolayer films and in the presence of extra oxygen at the MgO/Ag interface, those Mg atoms lying above the additional O atoms are attracted toward them. This results in some buckling of the film, which helps in reducing the lattice mismatch and hence the compressive stress responsible for film cracking in small islands; (b) ab initio thermodynamics shows that both monolayer and bilayer of supported MgO are thermodynamically stable, but the former has a larger adhesion energy. Furthermore, the 100% limit of oxygen loading at the interface is unreachable, under any realistic thermodynamic condition. Concentrations in the range of 25–50% oxygen at the interface are, on the contrary, very stable.

A second important point to be discussed is the role of the different pre-growth and after-growth treatments on the film morphology. Preannealing is known to affect the surface order of the substrate. Indeed after 60 min at 850 K, the Ag(100) crystal shows very large terraces, independently of the kind of film which will be deposited eventually. Therefore, we concentrate on the effect of after-growth processes. Important information can be obtained by comparing films produced under identical conditions and differing only by the cooling rate or by the presence or absence of postannealing in oxygen pressure. Therefore, we compare films iv (773 K – SC*) and vii (773 K – SC; XPS and HREELS data) on one side and films iv (773 K – SC*) and v (773 K – FC*, STM images) on the other side. Postannealing in O$_2$ atmosphere has no significant influence on the film stoichiometry, which depends only on $T_e$. On the contrary, as previously discussed, the evaluation of films iv and vii suggests an important role of temperature in the reorganization of the interface oxygen atoms, responsible for the release of stress leading to the formation of extended uniform MgO layers. In this respect the theoretical outcome that the optimal interface oxygen coverage is between 25% and 50% (to be compared with the experimentally estimated value of $\sim$30%$^{26}$), strongly supports our interpretation. Comparative inspection of films iv and v (see Figure 4) shows, on the contrary, that the transition from squared bilayer islands (stable at high $T$) to extended monolayers depends exclusively on the cooling rate. The overall picture we can get from these results is thus the following: in the sub-monolayer regime, squared bilayer MgO islands form on Ag(100) at $T_e = 773$ K. If the system is rapidly cooled below a critical temperature, this configuration remains frozen. If, on the contrary, the temperature is reduced very slowly, the transition to the configuration stable at low $T$ occurs and large monolayers of MgO are detected. The extension of these MgO monolayers depends on the structure of the metal/oxide interface. If the extra oxygen accumulating at 773 K has time to organize in an ordered way, the stress of the monolayer film can be efficiently released and MgO terraces limited only by the terrace width of the underlying metal substrate can form. If, otherwise, the organization of extra oxygen is only partial or absent (no postannealing), during the SC process the transition to the monolayer occurs all the same, but the film consists then of irregular islands coalesced together. We can thus safely conclude that the key parameter for the determination of the film morphology is the cooling rate after growth, although a role of postannealing must also be considered. In our previous work$^{26}$ the transition from bilayer to monolayer islands was qualitatively explained considering the very similar surface energy of MgO(100) and of Ag(100) (1.15$^{51}$ and 1.20 J/m$^2$, respectively) and the role of the entropic term. The latter is relevant to determine the growth mode, provided that the deposition rate is low and the diffusion rate high enough to get rid of kinetic effects.

Within this frame, the irregular internal structure present in some islands grown at $T_e = 500$ K (film ii; see Figure 3) and much less frequently at $T_e = 450$ K (film i) is most probably related to a small amount of oxygen accumulation at the MgO interface which, due to the lower temperature, remains unevenly distributed.

**CONCLUSION**

The possibility to grow ultrathin MgO/Ag(100) films of predetermined morphology has recently been demonstrated by some of us.$^{26}$ Due to the relevant implications of this finding for the many applications of MgO nanostructures in several fields of nanoscience and nanotechnology,$^{1–3}$ we have further characterized the system by experimental (XPS, STM, HREELS) and theoretical (DFT) methods. In this work we correlate the final structure of the ultrathin MgO films supported on Ag(100) to the postdeposition treatments, in particular to the cooling rate after growth, and to the accumulation of atomic oxygen at the MgO/Ag interface occurring at high $T_e$. The cooling regime determines whether
the system is quenched into the thermodynamically most stable configuration at the deposition temperature or if it evolves toward the low-temperature equilibrium state. On the other hand, the interface oxygen layer contributes to reduce the stress due to the small lattice mismatch between metal and oxide, and hence it is the essential element for the formation of extended MgO layers. Both elements are therefore necessary for achieving the perfect monolayer.

**ASSOCIATED CONTENT**

 Supporting Information
Figure showing additional computational results about the stability of the MgO/O/Ag(100) structure as a function of increasing interface oxygen content. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) Our data indicate that the critical temperature must be 450 K < Tc < 773 K, since (A) bilayer islands are produced upon Tg = 773 K and Fc, while monolayer ones are detected when growing at Tg = 450 K and with the same cooling regime (see ref 26 and Figure 3 of this paper), and (B) XPS spectra recorded upon Fc and Sc are qualitatively similar for films produced at Tg = 450 K but different for those grown at Tg = 773 K. As a consequence, the time employed to cool the film from T = 773 K to T < 450 K is the essential parameter of the film deposition protocol.