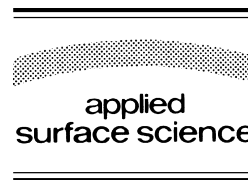




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Stoichiometry and morphology of MgO films grown reactively on Ag(100)¹

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Abstract

The stoichiometry and the morphology of MgO adlayers epitaxially grown on Ag(100) are studied by means of X-ray photoelectron spectroscopy (XPS) and high-resolution spot profile analysis low-energy electron diffraction (SPA-LEED). For comparison, Mg deposited at 200 K is oxidized after and during growth, respectively. The post-oxidized film is dominated by stoichiometric MgO but shows also non-stoichiometric species. Annealing the film to 700 K reduces the latter components. Strong differences have been found for the epitaxy of both kinds of MgO films, depending on the preparation condition. The post-oxidized film shows a clear diffraction pattern with 12-fold symmetry due to MgO(100) grains in three rotational orientations only after annealing to 700 K. Depositing and oxidizing simultaneously the Mg the oxide film shows a better film quality (no metallic Mg, a small MgO₂ fraction) and epitaxy with 1×1 already at 200 K. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Oxide films are important in daily life since they often serve as protective films on material because oxides with wide band gaps, in particular, are inert against many chemical reactions [1]. This property also makes them suited as support for metallic cata-

lysts. For the same reason, oxide substrates are also often used as support for different metallic films or multi-layers and for high T_c superconductors.

A direct interest in ultrathin insulating films of high perfection, which can be represented by oxide films, comes from the demand for a new generation of electronic devices, in which only a few electrons are needed for switching mostly tunnelling currents. The demands on the quality of these films are enormous since they have to be single crystalline and perfectly smooth at a thickness of about 1 nm on a lateral scale of some micrometers. These examples may suffice to illustrate the importance of finding

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ways to grow epitaxial insulating thin films of high crystalline quality.

Since coupling between a substrate and an oxide film is normally weak, basic requirements to form epitaxial oxide films of single crystalline quality are structural similarity and small misfit in lattice constants between the oxide and the underlying substrate. Therefore, the simple oxidation of metal single crystals often leads to unsatisfying results. This is particularly evident for the oxidation of Mg, since MgO crystallizes in the rocksalt structure but not in the hcp structure of Mg. Nevertheless, films have been formed by oxidation of Mg single crystals [2–4].

To deposit the oxide film on an adequate substrate with a much smaller lattice mismatch seems to be more promising. Examples are MgO films deposited on Mo(100) substrates [5–7] or Fe(100) templates [8,9] either by molecular beam epitaxy (MBE) of the oxide or by evaporating Mg in an oxygen atmosphere. These substrates have a lattice mismatch of 5.5% and 3.7%, respectively, aligning the MgO $\langle 100 \rangle$ with the metal $\langle 100 \rangle$ directions parallel to the surface. Better lattice matched substrates are alloys, e.g., $\text{Cr}_{0.7}\text{Mo}_{0.3}(100)$ on which MgO has also been grown [10].

The growth of epitaxial layers of MgO on Ag(100) substrates, on which we report here, seems to be attractive for several reasons. From the comparatively small lattice mismatch of only 2.9% between MgO(100) and Ag(100), a reduced number of dislocations and grain boundaries can be expected. In addition, reaction kinetics of oxygen with the Ag(100) surface is very slow [11], in contrast to the reaction between O and Mg. Thus, most of the complications of substrate oxidation (with corresponding structural changes) during deposition of MgO or oxidation of Mg are eliminated, which have to be expected for more reactive substrates. Furthermore, the combination of MgO with a silver substrate combines a very hard oxide with a comparatively soft metal surface. This combination seems to be attractive, since it might give the system a chance to shift misfit dislocations almost entirely into the metal surface, and to grow a perfect single crystalline oxide film. Taking into account the rather weak coupling between oxides and metal surfaces, the potential corrugation on the metal surface might

even be weak enough so that the oxide film can float on the metal surface without forming dislocations.

This is the reason why we combine in this study measurements with X-ray photoelectron (XPS) and Auger electron spectroscopy (AES) with investigations of the film morphology by high resolution LEED (SPA-LEED) in order to investigate both the stoichiometry and the perfection of structures obtained. Two different growth procedures have been used: oxidation of Mg films pre-deposited at 200 K and Mg oxidation during growth at 200 K. In addition, the effect of annealing on these films has been investigated.

2. Experimental

Chemomechanically polished Ag(100) samples [12] have been cleaned by several cycles of Ar^+ sputtering and annealing. Thereafter, no impurities were detectable, as checked by XPS, and the sample showed a brilliant diffraction pattern in the SPA-LEED experiments. The analysis of the specular spot proves that the sample had a minor mosaic spread of 0.03° and an average terrace width of more than 60 nm.

For this study, Mg was evaporated from a Mg rod by radiation with a deposition rate of 0.5 ML/min, as controlled by a quartz microbalance. An O_2 pressure of 3×10^{-5} Pa was used for the simultaneous oxidation during Mg deposition. Layers of varying thickness between 1 and 7 monolayers have been investigated. Here, we concentrate on the results of the 7 ML thick films, which are representative also for the thinner films.

3. Results

The O1s photo peak gives information about the oxidation state and, after proper weighting different layers, also information about relative quantities of different species. Fig. 1 shows the O1s peaks for MgO films prepared by post-oxidation and simultaneous oxidation. For the curve (a), the film was deposited at $T_s = 200$ K and post-oxidized with 18 L of O_2 at the same temperature. Two transitions are observed in both cases at a higher binding energy

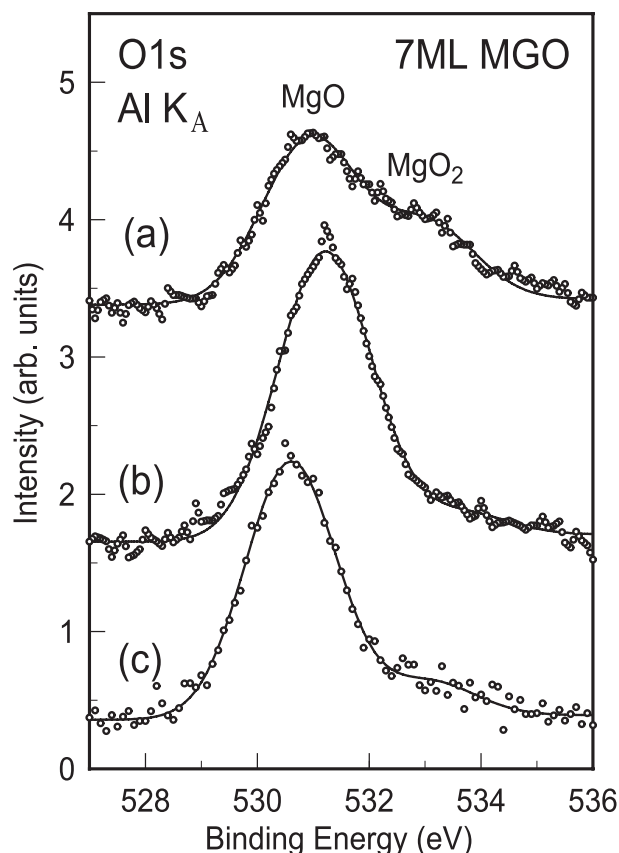


Fig. 1. The O1s spectra for differently prepared 7 ML MgO films. (a) After post-oxidation at $T_s = 200$ K. (b) After annealing to 700 K. (c) After simultaneous oxidation at $T_s = 200$ K. The circles show the experimental data. The solid line is obtained from a least-square fit of the Auger peaks with Gaussians. The spectra show two peaks: a strong peak at high kinetic energy due to stoichiometric oxide and a smaller one at 3 eV higher binding energy due to non-stoichiometric oxide.

(HBE) of 533.5 eV and at a lower binding energy (LBE) of 531.0 eV, respectively. The MgO film post-oxidized at 200 K (curve a) shows the strongest HBE peak. This peak is much smaller for both the post-oxidized film annealed at 700 K (curve b) and the film simultaneously oxidized at 200 K (curve c). Therefore, we conclude that this peak is due to non-stoichiometric oxygen.

The LBE peak is typical for stoichiometric MgO. The HBE peak separated by 2.3 eV from it has been observed also for MgO films grown on Mo(100) [7]. The authors assign it to MgO_2 in agreement with investigations on alkali oxides [15]. Therefore, we

conclude that the HBE peak is due to MgO_x with x close to 2.

The intensity of the HBE peak indicates the fraction of the non-stoichiometric oxide fraction due to different preparations. Thus, MgO films grown by simultaneous oxidation during metal deposition at 100 K on Mo(100) have a large fraction of MgO_2 which decreases due to annealing [7]. This result is very similar to the post-oxidized films studied here: after annealing, the fraction of the non-stoichiometric component decreases drastically as the comparison of curves (a) and (b) demonstrates.

Oxide films prepared by Mg deposition in oxygen atmosphere at 300 K not only grow layer by layer on Ag(100) [13], but we also found for these films that the species causing the HBE peak is completely located on or in the first monolayer [14]. The fraction of the non-stoichiometric component for these films is very similar to the fraction observed here for the annealed post-oxidized film. Therefore, this non-stoichiometric species should also be preferentially located at the surface under post-oxidation conditions at lower temperatures. It is surprisingly stable since its relative amount is reduced upon annealing to 700 K, but it cannot be completely removed at this temperature. On the other hand, the large fraction for curve (a) points to additional non-stoichiometric oxide which is located in the oxide film. These 'bulk' components can be removed by annealing while the surface component remains.

In Fig. 2, we show the spectra of the Mg KLL Auger series recorded for the films of Fig. 1. We concentrate here on the most prominent peaks of the KL_2L_3 series. Three characteristic peaks are observed: at 1185 eV, typical for metallic Mg, at 1180.7 eV and at 1176 eV that are both due to oxidized Mg [16]. In addition, a weak peak at 1183.5 eV can be observed. This peak is most pronounced for the non-annealed post-oxidized film, but missing for the simultaneously oxidized film.

Although the metallic peak is already small, it is obvious that the films prepared at 200 K are only partially oxidized, probably in the deeper layers of the film. Much higher oxygen doses reduced the metallic Mg peak, but did not completely remove it due to slow penetration of oxygen and/or slow dissociation kinetics at a surface that is already almost saturated with MgO. The shoulder at 1183.5

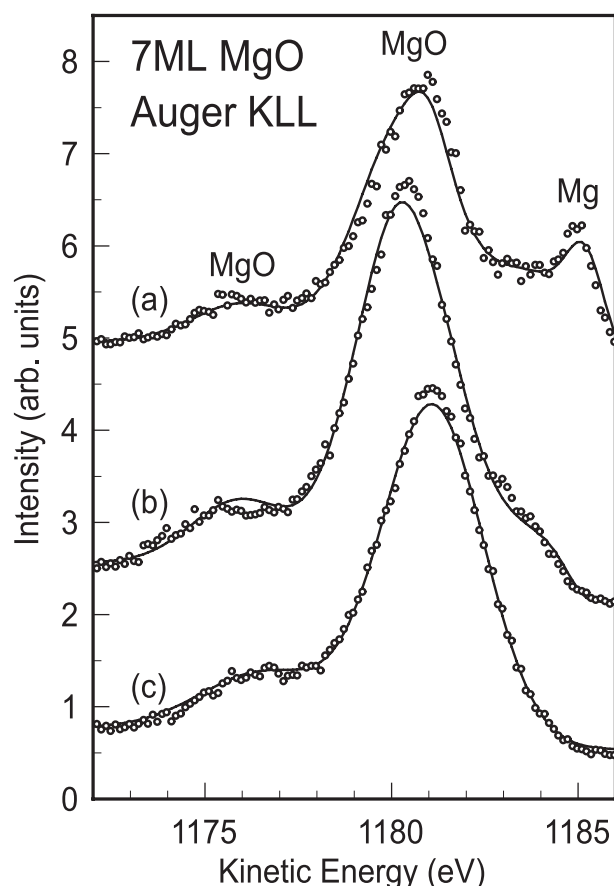


Fig. 2. Auger KLL spectra for differently prepared 7 ML MgO films. (a) After post-oxidation at $T_s = 200$ K. (b) After annealing to 700 K. (c) After simultaneous oxidation at $T_s = 200$ K. The circles show the experimental data. The solid line is obtained from a least-square fit of the Auger peaks with Gaussians. The peak due to metallic Mg (1185 eV) observed for the film post-oxidized film at 200 K vanishes either after annealing to 700 K or oxidizing during growth.

eV is obviously coupled with the incomplete oxidation process for deeper layers under post-oxidation conditions. We therefore assign this peak to understoichiometric MgO_x ($x < 1$).

During annealing, the metallic peak disappears, and the understoichiometric species is reduced because several processes set in. First, non-stoichiometric excess oxygen oxidizes metallic Mg. Second, there will be stronger intermixing than at 200 K between Mg and O in deeper layers, forming partially an understoichiometric oxide as a minority species in deeper layers. Third, probably non-oxidized Mg diffuses to the surface and desorbs from

it above 400 K if it cannot be oxidized by the surface located excess oxygen. Fourth, Mg may diffuse to the interface to the Ag substrate where it forms an alloy. Similar results have been observed for pure layers of Mg deposited on Ag(100) after annealing to 400 K [17].

Oxidation during deposition of Mg at a sufficiently high ambient oxygen pressure (for the exact conditions, see above), however, resulted in Mg KLL Auger spectra that show neither metallic nor non-stoichiometrically oxidized Mg. The peaks are slightly shifted with respect to the post-oxidized films, which might be indicative of a lower defect concentration. The Auger spectrum for the simultaneously oxidized film does not change during annealing, again indicative for an already complete oxidation.

The XPS and AES results show that the composition of the MgO film varies considerably, depending on the preparation conditions. The best stoichiometry of the film is obtained with simultaneous oxidation in oxygen atmosphere during growth. It is important to note, however, that under all conditions tested, an oxygen-rich surface layer is obtained. This property does not depend on the film thickness, and is therefore neither specific to the substrate nor to thin films. This is in agreement with the annealing studies for MgO/Mo(100) although they used even higher annealing temperatures, which is not possible for the Ag(100) substrate [7]. Therefore, the excess oxygen must be strongly bound to the oxide film.

The fact that metallic Mg does not appear for the film simultaneously oxidized at low temperature is easy to explain because here, the oxide film grows from bottom to top. Therefore, oxygen has a large probability to react with metallic Mg directly after it impinges on the surface. On the contrary, oxygen has to diffuse through the film for the post-oxidized film so that not all Mg of the pre-deposited film are oxidized.

Our XPS studies show that well-annealed post-oxidized, as well as simultaneously oxidized, MgO films have essentially the same stoichiometry at least in the topmost layers of the film. There are, however, very significant differences in the epitaxy of these layers on the Ag(100) substrate as found by high resolution SPA-LEED investigations. Fig. 3 presents the diffraction patterns and models of initial

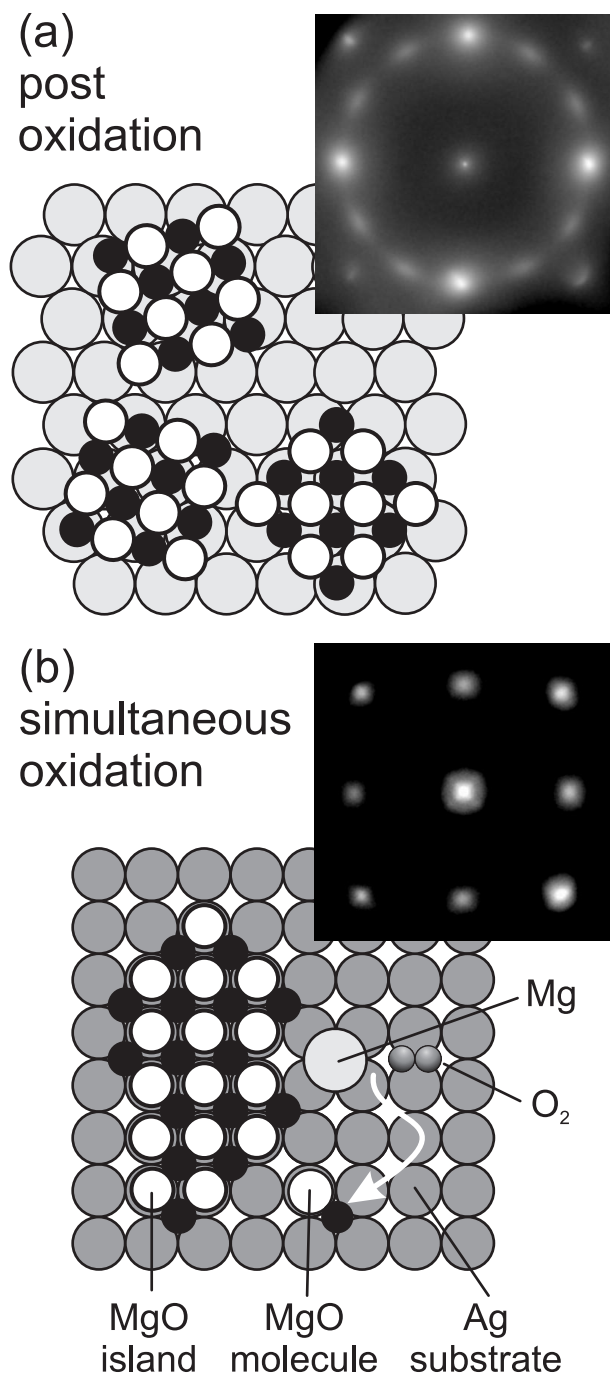


Fig. 3. Comparison of the diffraction patterns obtained from (a) the post-oxidized and well-annealed 7 ML MgO film and (b) for the simultaneously oxidized film. (a) Twelve first-order diffraction spots due to three MgO grains with 4-fold symmetry but rotated by 120° . (b) The 1×1 diffraction pattern due to well-ordered and orientated epitaxial MgO film. The models show the early stages of nucleation (a) on the hexagonal Mg film and (b) on the Ag(100) substrate.

stages of oxidation for both the well-annealed post-oxidized and for the simultaneously oxidized MgO film.

For the post-oxidized film, one observes a ring of 12 first-order spots after annealing to 700 K. This pattern can be attributed to MgO grains with rocksalt structure grown in three rotational grains (rotated by 120°). These grains are formed because MgO starts to grow on the hexagonal structure of the Mg film obtained at 200 K [18]. During the nucleation of MgO islands, the atomic rows of the MgO ($\langle 100 \rangle$ directions) align with the atomic rows of the Mg film ($\langle 1000 \rangle$ directions). The schematic drawing of Fig. 3a presents the lateral alignment of the submonolayer islands grown on top of the Mg film. We like to emphasize that we obtained this diffraction pattern only after annealing the film to 700 K. After oxidizing the Mg film at 200 K, the original bright diffraction pattern from the Mg film vanished totally except for a very weak specular (00) beam.

It is interesting to note that the MgO films prepared under these conditions do not recrystallize to a single domain, although there are no indications for remaining metallic Mg after annealing. The simultaneously oxidized film, on the other hand, shows a bright 1×1 diffraction pattern as Fig. 3b demonstrates. Therefore, the MgO film is orientated epitaxially with respect to the Ag(100) substrate. Defects of the film can be investigated by analysing carefully the profile of the specular (00) beam. We have reported previously that the specular beam has satellites appearing in the $\langle 100 \rangle$ directions which are produced by mosaics slightly tilted with respect to Ag(100) substrate [13]. These mosaics are strongly reduced for films grown in oxygen atmosphere at 500 K.

4. Discussion and conclusion

From ion scattering spectroscopy (ISS) investigations [3], it has been suggested that the MgO film grown by oxidation of Mg(0001) does not show rotational domains as suggested previously from LEED experiments [2]. In our study, we obtain a diffraction patterns for the post-oxidized film equivalent to that obtained after oxidation of the single

crystal. This structure, however, is only obtained after high temperature annealing. The oxide films studied by ISS have been annealed to less than 500 K, where we did not observe any diffraction spot except a weak specular (00) beam. Also, the high background intensity points to poorly ordered oxide film. Therefore, we conclude that the ISS experiments do not contradict our results.

In conclusion, we have demonstrated that MgO films formed either by annealing well post-oxidized Mg films or by oxidation during growth show similar stoichiometry. However, a large amount of non-stoichiometric MgO is found for Mg films post-oxidized at low temperature. Epitaxy, on the other hand, is sensitive to the details of the preparation as demonstrated by electron diffraction even if films show similar stoichiometry. For this reason, post-oxidized films show rotational MgO(100) grains which cannot be recrystallized by annealing whereas oxidation during growth reveals high quality MgO films with 1×1 symmetry.

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