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Experimental and theoretical study of the MgO/Ag(0 0 1) interface

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Abstract

We report on a joint experimental and theoretical investigation of the structure of the MgO/Ag(0 0 1) interface, with emphasis on the determination of the interfacial distance between the Ag surface and the first MgO(0 0 1) plane. Experiments were performed on 1–5 ML thick MgO layers prepared by Mg deposition in a controlled oxygen atmosphere on a sputter-annealed Ag substrate. The intensity angular distribution (IAD) of the Ag LMM Auger emission was measured as a function of the incidence angle of the primary exciting beam, and the interfacial atomic arrangement was determined by modelling the IAD in a single-scattering cluster approximation. The model adopted in theoretical calculations consisted in a two-dimensionally periodic structure composed of a six-layer thick slab of Ag parallel to the (0 0 1) face, covered on both sides by one or two epitaxial MgO MLs. An ab initio density functional theory approach was used with different types of exchange-correlation functionals, and full geometry optimisations were performed. It has been found that MgO accommodates on the substrate with O atoms sitting just on top of the Ag atoms, and that the distance between the Ag surface and the first MgO plane is expanded with respect of both Ag and MgO(0 0 1) interplanar distances. Experimental and theoretical results both indicate for the interfacial distance a value of 2.39 ± 0.06 Å. Significant rumpling occurs in the first ML of MgO, that is removed as the overlayer thickness increases.

Keywords: Magnesium oxides; Silver; Interface states; Electron–solid diffraction; Density functional calculations

1. Introduction

Simple metal oxides thin films on metal substrates attract a growing interest due to several technological applications and for the basic understanding of the metal–oxide interface [1,2]. The MgO/Ag(0 0 1) system is a useful model due to the small lattice misfit between substrate and overlayer

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(3%) and negligible chemical and charge transfer contributions to bonding [3]. In addition experimental investigation by electron spectroscopies is not inhibited by charging effects typical of insulating surfaces. Up to now, only a limited number of structural studies have been performed on this system [4–7]. By reactive deposition, highly ordered, stoichiometric films were obtained, however deviation from the 1:1 composition [6] and a larger concentration of defects [7] was suggested for the very outermost layer. Reactive Mg deposition has been compared with the oxidation of pre-deposited Mg layers [5,6], and with sputter deposition [8]. Adsorption site and interfacial distances have been determined for the inverse case, Ag overlayers on MgO(0 0 1) substrate, by grazing incidence X-ray diffraction [9] and EXAFS [10]; favoured Ag configuration over O, and an equilibrium interface distance within the range 2.4–2.7 Å has been reported, in good agreement with the results of atomistic models [11] and ab initio calculations [12–14].

We report on a joint experimental and theoretical investigation on the structure of this interface, with emphasis on the determination of the interfacial distance d_i between the Ag surface and the first MgO(0 0 1) plane.

The paper is organised as follows. Computational details are first presented, and calculated binding energies as a function of d_i for the three geometries of highest symmetry are shown and discussed. Procedures for both film growth and structural characterisation are then briefly illustrated, and the experimental results are compared with the results of single scattering cluster (SSC) simulations.

2. Theoretical study

The calculations were performed by means of CRYSTAL98 computer code [15], which solves the Schrödinger equation for periodic systems, in the framework of Hartree–Fock (HF) and density functional theory (DFT). CRYSTAL98 adopts ab initio crystalline-orbital LCAO (LCAO: linear combination of atomic orbitals) technique; atomic orbitals are in turn expanded as a sum of localized Gaussian functions. Both HF and DFT approaches were here adopted. In the case of DFT, local (LDA/PZ) and non local (PWGGA [16]) exchange-correlation functionals were tested. The effective core pseudo-potential technique was used for silver atoms in order to reduce the number of electrons involved and the complexity of the calculations: we considered explicitly only 19 electrons per Ag atom, corresponding to the electronic configuration $4s^2 4p^6 4d^{10} 5s^1$. The pseudo-potential and the variational basis set for silver can be found on the web [17]. The basis set for MgO consists of all-electron 8-61G and 8-51G functions for Mg and O respectively. The results of a preliminary study of silver have been recently presented [18] whereas those for MgO were published in past years [19,20].

The band structure of the silver slab is not reproduced accurately at the HF level, nor using hybrid functionals (B3LYP); in fact, it is known that those hamiltonians give a wrong description of the electronic structure of metals in a vicinity of the Fermi level. LDA/PZ and PWGGA functionals have been adopted therefore for the simulation of the MgO/Ag(0 0 1) interface. This system was studied referring to a six layers thick slab of Ag parallel to the (0 0 1) surface "covered" with one or two MgO monolayers on both surfaces. The optimized lattice parameter of Ag was used, ignoring the small lattice mismatch (3%) between Ag and MgO.

The structure of the interface was first investigated with reference to the monolayer coverage; the three geometries of highest symmetry were studied: Mg^{2+} over a surface Ag atom, O^{2-} over a silver atom and both ions over the bridge positions. The distance d_i between the silver surface and the oxide overlayer was optimized, at first considering the MgO films as a rigid entity (Fig. 1, Table 1). For the optimized structure, the counterpoise scheme was used to correct the data for the basis set superposition error (BSSE). Binding energies versus distance between the MgO overlayer and the silver substrate are reported in Fig. 1 for LDA/PZ calculations; the most stable configuration is O^{2-} on silver atom. The equilibrium d_i was found to be 2.45 Å. Very similar results are obtained using PWGGA functionals. In the

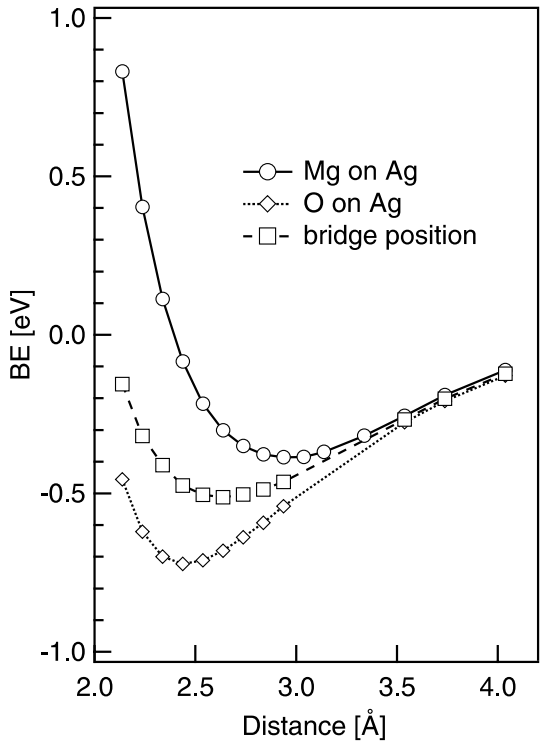

Fig. 1. Binding energy per MgO unit for the monolayer oxide on the Ag substrate vs. interfacial distance. The reported data refer to LDA/PZ calculations without rumpling and BSSE correction.

following only the results relative to this configuration will be presented. Independent optimization of Mg^{2+} and O^{2-} positions, showed that magnesium ion distance from silver surface decreases by 0.1–0.15 Å, with respect to the rigid MgO case d_i, whereas the O^{2-} position remains almost unchanged (rumpling).

A film composed by two MgO layers was next simulated (Table 1): the distance d_i is not relevantly changed by the presence of the second MgO layers, whereas the rumpling of the Mg^{2+} ions at the interface is partly recovered, probably because of electrostatic attraction by the oxygens in the upper plane. The distance between the two MgO layers is very close to the (0 0 1) inter-planar spacing in bulk MgO: with reference to the oxygen sublattice it is 2.08 and 2.10 Å for LDA/PZ and PWGGA respectively. Interfacial effects seem therefore to be quite localized. Table 1 summarizes

Table 1
Structural and energetic properties of the MgO/Ag system in the oxygen on silver configuration

	LDA		PWGGA	
	No rumpling	Rumpling	No rumpling	Rumpling
Monolayer coverage				
Z_{Mg} (Å)	2.45	2.32	2.55	2.39
Z_O (Å)	2.45	2.47	2.55	2.55
BE (eV)	−0.433	−0.550	−0.183	−0.307
Bilayer coverage				
$Z_{Mg}^{(d)}$ (Å)	2.45	2.38	2.55	2.46
$Z_O^{(d)}$ (Å)	2.45	2.47	2.55	2.55
$Z_{Mg}^{(t)} = Z_O^{(t)}$ (Å)	4.58	4.55	4.73	4.65
BE (eV)	−0.426	−0.442	−0.189	−0.199

Z_X is the distance of ion X from silver atoms in the top layer; for the case of two-layer coverage, superscript (d) or (t) distinguishes ions in the "down" and "top" layer, respectively. BE is the binding energy per unit cell of the MgO on the Ag substrate including BSSE correction, and is calculated as the difference between the energy of the isolated systems (separate silver and MgO slabs), and that of the compound system.

geometrical and energy data concerning the structures just described. As concerns energy, the following can be noted: rumpling increases considerably the interaction energy in the case of monolayer coverage (~0.12 eV), much less so for the two-layer case (~0.01 eV). Correspondingly, the interaction energy is decreased, as expected, so confirming that interactions within the ionic system become more important than those with the substrate.

3. Experimental results

Mg atoms were deposited in a molecular oxygen partial pressure of 10^{-8} Torr by a Knudsen cell operating at 295 °C, on the Ag substrate prepared by repeated cycles of sputtering (Ar ions, 600 eV) and annealing (350 °C) held at 190 °C. The MgO deposition rate was 1 ML min^{-1}, as evaluated by the Mg evaporation rate (measured by a calibrated quartz microbalance), and by the relative Mg densities in metallic magnesium and in the oxide. The product of the deposition time and the MgO deposition rate will be referred to as nominal thickness.

The structure of the MgO layer, its relationship with the substrate and the atomic arrangement of the MgO/Ag interface have been investigated by exploiting the modulation of the secondary electron yield induced by the scattering-interference of energetic exciting beam (primary-beam diffraction modulated electron emission). For details on this technique we demand to previous publications [21–24]. Auger measurements were performed by a cylindrical mirror analyser, operating in the first derivative mode (0.6% resolution, 15 eV modulation), with the coaxial electron gun working at 5 keV and 1–2 μA.

The intensity angular distributions (IADs) of the Ag MNN, O KLL and Mg KLL Auger emission as a function of the incidence angle of the primary exciting beam, along the high symmetry [1 1 0] substrate azimuth, were monitored by simply rotating the sample in front of the analyser. IADs of the Mg and O KLL Auger electrons are shown in Fig. 2 (bottom, dashed curves) for the 5 ML MgO film. Maxima in the IADs occur for the primary beam alignment along the principal low-index directions [0 0 1] at 0° and [1 1 1] at 54.7°, as expected for an fcc structure. The strict similarity of the Mg and O distributions to those recorded on clean cleaved (0 0 1) surface of the bulk MgO crystal [8] indicates that the rocksalt structure is established. LEED patterns taken at 168 eV (Fig. 2) show that the MgO films grow with a good long range order. Details on the MgO films growth are reported elsewhere [8].

The interfacial distance between the Ag surface and the first MgO(0 0 1) plane has been determined by investigating the occurrence and extent of changes in the angular position of forward focusing features in the IAD of the substrate Ag MNN signal, induced by the MgO growing overlayer (Fig. 2, continuous lines). In particular an expansion (contraction) of the interfacial distance will result in the occurrence of an additional peak at a lower (larger) angle with respect to the equilibrium [1 1 1] peak at 54.7° in the Ag MNN IAD along the [1 1 0] azimuth (inset of Fig. 2), while minor changes are expected in the anisotropy of the [0 0 1] forward peak at 0° and in the shape of high-order features in the intermediate angular region. An additional forward focusing feature is

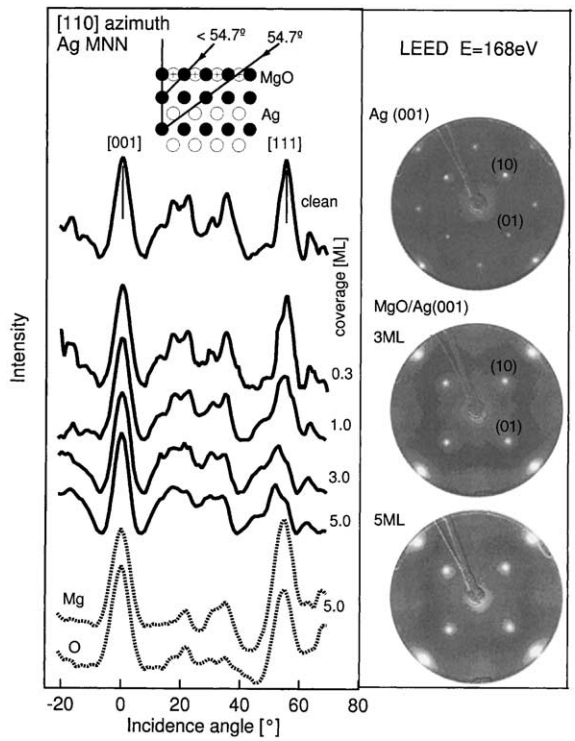

Fig. 2. IAD of the Ag MNN Auger signals along the [1 1 0] azimuth for the clean substrate and for increasing nominal MgO thickness. The corresponding distributions of the Mg and O KLL Auger signals for the 5 ML MgO film are also shown (dashed curves). The inset shows the side view of the MgO/Ag(0 0 1) interfacial atomic structure along the [1 1 0] azimuth. LEED patterns at 168 eV are shown in the right side of the figure.

actually clearly detectable on the low-angle side of the 54.7° peak in Fig. 2. The additional feature is simply a shoulder at 0.3 ML coverage, but it becomes the dominant feature in this angular region for 3 and 5 MgO layers coverage. This support the assignment of this feature to the focusing effect of the MgO overlayer on the underlying Ag atoms. In fact due to the short inelastic mean free path of the 356 eV electrons the Ag MNN emission volume is progressively confined to the Ag outermost layers as the overlayer thickness increases, therefore the contribution of the substrate chains to the anisotropy of the Auger emission intensity reduces with respect to the contribution from the overlayer chains. The occurrence and the angular position of this additional feature in the Ag MNN IAD indi-

cate that the interfacial distance is expanded with respect to the Ag(0 0 1) interplanar distance.

SSC calculations [24] of Ag MNN IAD for the MgO/Ag(0 0 1) system were performed varying independently the MgO film thickness and the distance d_i of the first MgO plane from the Ag substrate. SSC calculations were performed with a cluster larger than the emission volume in order to smear out boundary effects due to the shape of the cluster. The angular position of the [1 1 1] peak in the calculated IAD is shown in Fig. 3 as a function of the film thickness, for three different values of d_i. The angular position of the maximum of the [1 1 1] peak, measured from the experimental IADs of Fig. 2, is also shown. Results of Fig. 3 indicate that the interfacial distance is 2.3 Å or slightly larger, and also suggest that the evaluation of the d_i value by a comparison between experiments and simulations is more accurate for film thickness of 2–4 ML. Therefore a more quantitative evaluation has been performed comparing the Ag MNN IAD measured for a 3 ML MgO deposition with SSC calculations, by means of two r-factors (r_1, r_2), using d_i as fitting parameter. The d_i value was varied between 2 and 3 Å with incremental steps of 0.05 Å. Both the experimental curve and selected, calculated curves are shown in Fig. 4. The r-factor dependence on the d_i parameter is shown in the inset: r_1 [25] compares the derivatives of the IADs,

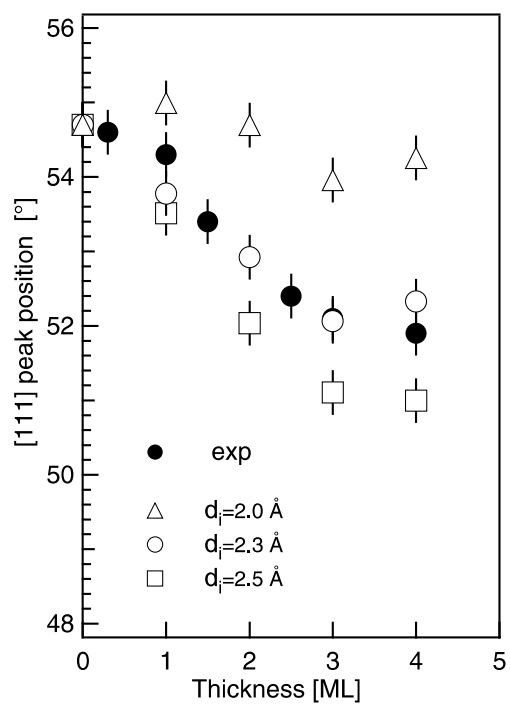

Fig. 3. The angular position of the [1 1 1] peak in the calculated Ag MNN IAD, as a function of the MgO film thickness, for three different values of the interfacial distance d_i. The angular position measured from the experimental distributions is also shown.

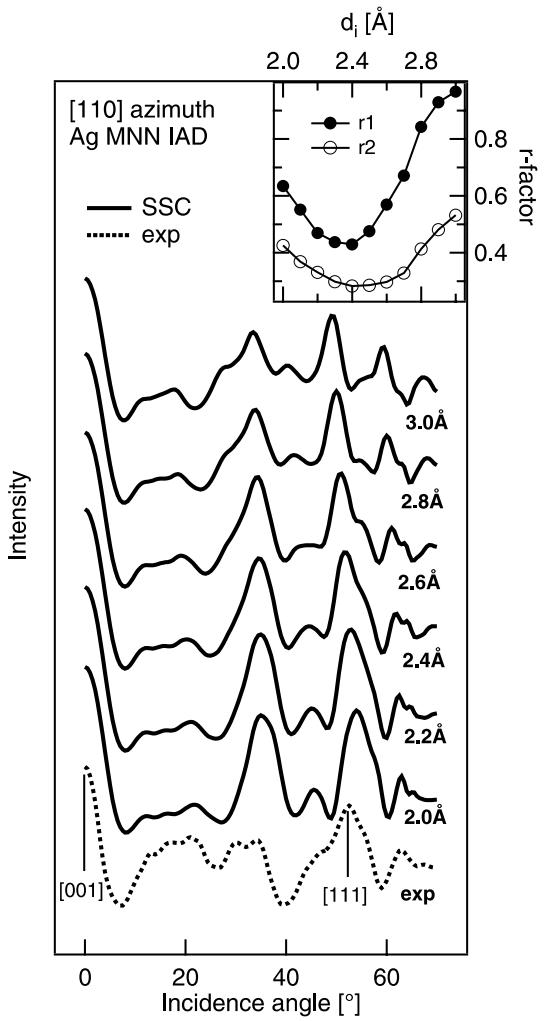

Fig. 4. Measured (dashed line) and calculated (continuous line) Ag MNN IAD for 3 ML MgO overlayer on Ag(0 0 1). The calculated distributions are shown for incremental steps of 0.2 Å of the interfacial distance d_i in the range between 2 and 3 Å. The r-factor dependence on the d_i parameter is shown in the inset, for two distinct r-factors (see text).

being more sensitive to their slope at each angle; r_2 [26], mainly used for PED analysis, measures the difference between the intensities of the experimental and calculated distributions. Values of d_i of 2.34 and 2.45 Å respectively were obtained from the two r-factors, with an accuracy of ± 0.06 Å. Therefore the distance of the first MgO plane from the Ag substrate was measured to be 2.39 ± 0.06 Å.

4. Conclusions

The structure of the MgO/Ag(0 0 1) interface has been investigated both theoretically and experimentally. It has been found that MgO accommodates on the substrate with O atoms sitting just on top of the Ag atoms, and that the distance between the Ag surface and the first MgO plane is expanded with respect of both Ag and MgO(0 0 1) interplanar distances. Within the experimental accuracy, the measured interplanar distance (2.39 ± 0.06 Å) quantitatively agree with that obtained by LDA (2.45 Å) calculations. Similar values are reported for the Ag/MgO(0 0 1) interface (2.43 ± 0.02 and 2.53 ± 0.05 Å by EXAFS [10] and GIXRD [9], respectively) suggesting that the expanded equilibrium interfacial distance originates in a very local interaction between the overlayer and the outermost substrate's layers. Theoretical results indicate that for 1 ML MgO film a significant corrugation of the interface occurs, with Mg and O atoms located at a distance of about 2.35 and 2.50 Å, respectively from the Ag surface. This corrugation is removed as a second layer is added to the MgO film.

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