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Epitaxial silver layer at the MgO(100) surface

A. M. Flank, R. Delaunay, P. Lagarde, and M. Pompa
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, 91405 Orsay, France

J. Jupille
Laboratoire Centre National de la Recherche Scientifique/Saint-Gobain "Surface du Verre et Interfaces," Boîte Postale 135, 93303 Aubervilliers, France

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The Ag/MgO(100) interface has been studied by EXAFS. At room temperature, in agreement with previous investigations, silver at low coverage is shown to form a two-dimensional layer at the MgO(100) surface. EXAFS data demonstrate that the lattice parameter of the silver overlayer is expanded so as to fit the MgO parameter to give rise to an interface having $(100)_{\mathrm{Ag}}\|(100)_{\mathrm{MgO}}$ and $[100]_{\mathrm{Ag}}\|[100]_{\mathrm{MgO}}$ orientation. Interface Ag atoms are atop the oxygen atoms of the MgO(100) surface at a distance of 2.53 ± 0.05 Å.

I. INTRODUCTION

Among the metal/oxide systems, special attention has been paid over the past decade to the Ag/MgO(100) interface, which appears as a testing ground for experimental and theoretical approaches of the metal-oxide interface structure. The major reason for such activity is that the rather small mismatch of 3% between the MgO(100) surface and the Ag(100) surface favors the epitaxial growth of silver on the (100) faces of MgO and several groups have indeed produced experimental evidence for this interface to have $(100)_{\mathrm{Ag}}\|(100)_{\mathrm{MgO}}$ and $[100]_{\mathrm{Ag}}\|[100]_{\mathrm{MgO}}$ orientation.[1–4] Moreover, this and the fact that MgO has a rocksalt structure which is rather convenient for model calculations render the Ag/MgO(100) interface quite attractive[5–8] for theorists.

From a simple examination of the primitive MgO cell, it is clear that the MgO(100) surface offers only three sites of high symmetry for adatom adsorption. These are atop the surface magnesium atom, atop the surface oxygen atom, and above the hollow site surrounded by two surface oxygen and two surface magnesium ions. From a high resolution transmission electron microscope (HRTEM) study, Trampert *et al.*[3] have inferred that the Ag layer sits on top of either the surface Mg atoms or the surface O atoms, the lattice mismatch being accommodated by a dislocation network. At variance, following a calculation of the Ag/MgO(100) interfacial energy involving the Coulomb interaction between the ions and their images and short-range repulsions, Duffy, Harding, and Stoneham[5] predict that the likely adsorption site of silver is atop the surface magnesium atom, though they also suggest[6] that it might be more complex. Finally, *ab initio* calculations[7–9] all conclude that the most favorable Ag adsorption site is atop the surface oxygen atom, the theoretical determination of the Ag-O distance varying between 2.34,[9] 2.38,[9] 2.50,[8] and 2.70 Å.[7]

To date, the only microscopic characterization of the Ag/MgO(100) comes from a HRTEM study[3] of 100-nm-thick silver films. In fact, the three-dimensional growth mode of silver on MgO(100), which is consistent with the poor work of adhesion at this interface, renders difficult the detailed analysis of that system by any surface technique. However, for very low silver coverages, Didier and Jupille[10,11] have observed the formation of two-dimensional silver layers on MgO(100) [three-dimensional silver clusters appear at higher coverage; a similar behavior has been reported[12] for Cu/ZnO(0001)]. The two-dimensional morphology offering a nice opportunity for applying surface techniques, we have analyzed it by extended x-ray-absorption fine structure (EXAFS), which is a local probe well suited to determine if there exists a unique Ag adsorption site at the Ag/MgO(100) interface, as well as the nature and the geometry of this site.

II. EXPERIMENT

The EXAFS spectra have been recorded above the L_{III} edge. The data have been collected at the Laboratoire pour l' Utilisation de Rayonnement Electromagnétique (LURE) at Orsay, on the SA32 beam line of the Super-ACO storage ring, which is equipped with an upstream focusing mirror and a two-crystal Ge(111) monochromator. The incoming photon flux is monitored by the drain current from a 0.8-μm aluminum foil. The adsorption is measured through the sample total electron yield. The EXAFS data collection can benefit from the linear polarization of the synchrotron photon beam by aligning the sample normal either perpendicular or nearly parallel (15° off) to the photon electric field.

The air-cleaved MgO(100) crystal is mounted in an ultrahigh vacuum chamber (base pressure 1×10^{-8} Pa) which has been installed on the beam line. The sample is clamped on a platinum plate so that it can be heated in vacuum via an electron bombardment of the plate. Gases are introduced in the chamber by means of a leak valve. Silver is evaporated from a Knudsen cell. Silver fluxes are calibrated by means of a quartz microbalance (a rate of 3 Å per min was used in the present work).

The sample is cleaned by heating at 1200 K for 10–20 min under an oxygen partial pressure of 5×10^{-4} Pa. The oxygen pressure is maintained all the way through the cooling,[10,13] until the sample is back to room temperature. The surface being clean, as checked by Auger electron spectroscopy, a rather good low-energy electron diffraction pattern can be obtained.

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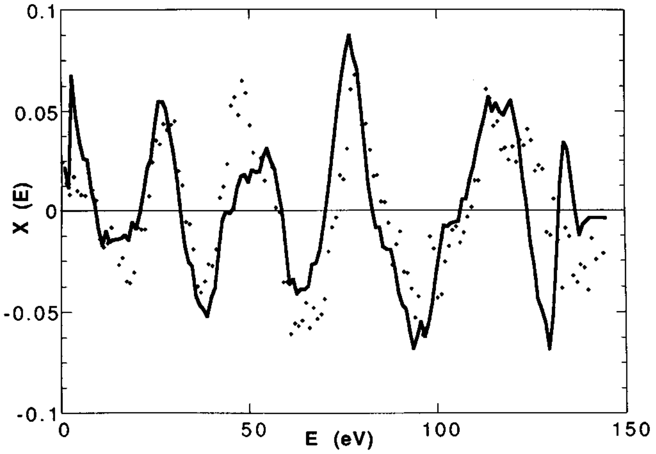

FIG. 1. Ag L_{III} edge SEXAFS data from a silver monolayer deposited on a MgO(100) surface at 300 K with the electric vector of the light: (a) in the surface plane (dots) and (b) close to the surface normal (15° off normal, solid line).

III. RESULTS

In the previous x-ray photoemission spectroscopy work,[10,11] a two-dimensional growth mode of the Ag/MgO{100} system has been observed for low Ag coverages, at room temperature, a three-dimensional growth mode appearing slightly above one monolayer (ML). One Ag ML corresponds to one Ag atom per surface MgO pair. The present work being aimed at characterizing the two-dimensional growth mode, EXAFS data are recorded on 1-ML Ag deposits. The substrate is at 300 K for both silver deposition and data collection.

The EXAFS data $\chi(k)$ are analyzed in a conventional way. The atomic background is modeled by a five-order polynomial and the normalization uses the Heitler formula.[14] Prior to being Fourier transformed, the $k\chi(k)$ data are multiplied by a Kaiser window spanning 1.5 to 6 $\mathrm{\AA}^{-1}$. This very narrow energy domain, due to the presence of the L_{II} absorption edge, will be the main limitation of the accuracy of the data analysis. To fit the data, phase shifts and amplitudes are taken from Rehr's FEFF6 code[15] by applying this multiple scattering calculation to elemental silver and to Ag_2O. The same energy edge shift of about 9 eV found between these calculations and the experimental data has been applied for the analysis of the Ag/MgO(100) system. This EXAFS analysis for an L_{II} or an L_{III} edge has to take into account both the $p \rightarrow s$ and $p \rightarrow d$ transitions. Usually, for centrosym-

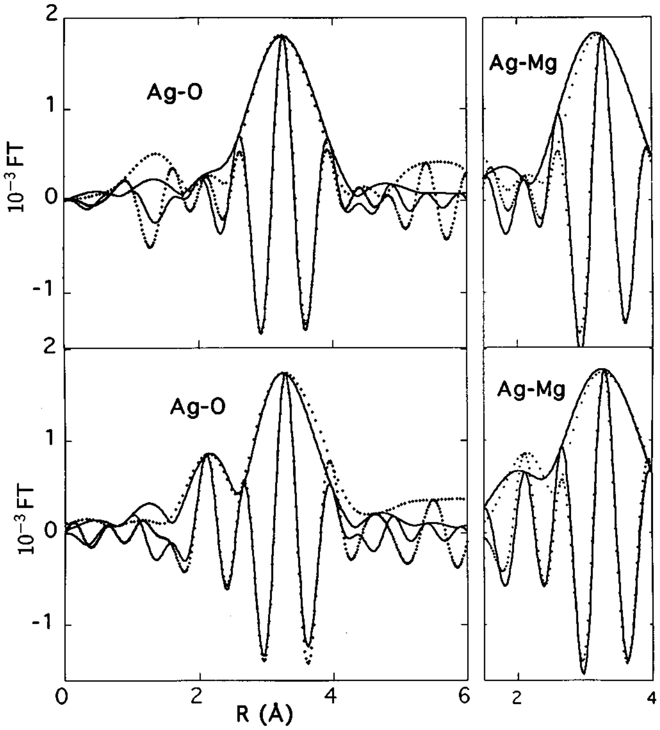

FIG. 3. Modulus and imaginary part of the Fourier transform of Ag L_{III} edge SEXAFS data from 1 ML Ag/MgO(100) at 300 K (dots) compared with those of the best theoretical fits (solid lines). Top: electric vector of the light in the surface plane; bottom: close to the surface normal (15° off normal); left: silver atop oxygen surface atoms; right: silver atop magnesium surface atoms.

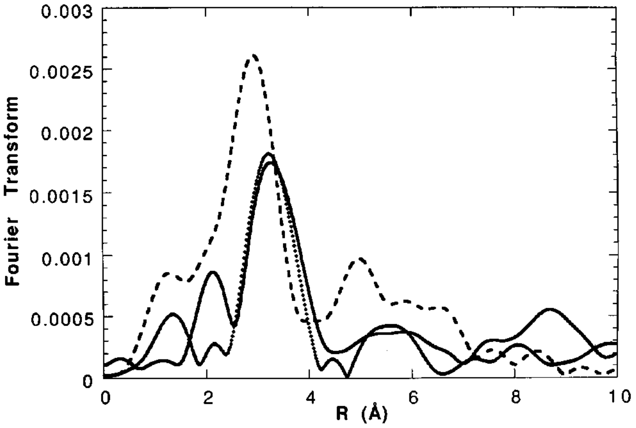

FIG. 2. Fourier transform of the Ag L_{III} edge EXAFS from bulk polycrystalline silver (dashed line), 1 ML Ag/MgO(100) with the electric vector of the light in the surface plane (dotted line), and close to the surface normal (15° off normal, solid line).

TABLE I. Results of the best fits (see Fig. 3) for the two incidences (roman characters) compared with the expected coordination numbers from the structural model (italic) as described in the text.

	N^* *N^* theor*	R (Å)	σ (Å)
	Normal incidence		
Ag-Ag	8.3 (±1) *8.5*	3.02 (±0.05)	0.07 (±0.01)
Ag-O	1 (±1) *0.25*	2.55 (±0.05)	0.03 (±0.01)
	Grazing incidence		
Ag-Ag	7.3 (±1) *7*	3.03 (±0.05)	0.07 (±0.01)
Ag-O	2 (±1) *1*	2.53 (±0.05)	0.03 (±0.01)

metric systems, the EXAFS is assumed to be dominated by the latter. However, such an approximation is less grounded when polarization effects are important. In the present case, as will be discussed in a forthcoming paper, we have checked that neglecting the cross term does not affect the conclusions given below.

Within the above assumptions, the EXAFS can be analyzed in the same way as a K edge, provided that, within a given atomic shell, the apparent coordination number N^* that enters the EXAFS formula takes the following form:

$$N^* = \sum_j \tfrac{1}{2}(1+3\cos^2\theta_j), \qquad (1)$$

where θ_j is the angle between the electric field and the jth interatomic direction. The sum runs over all the surrounding atoms.

Raw EXAFS spectra collected above the Ag L_{III} edge from a 1-ML Ag deposit are presented in Fig. 1. The spectrum is restricted to the L_{III}-L_{II} energy range. Fourier transforms of EXAFS data are shown in Fig. 2. The main peaks are assumed to originate from similar first-neighbor Ag-Ag contributions. In the data corresponding to 1-ML Ag deposits (dotted and solid line), the shift of this main peak as compared to that related to pure bulk silver (dashed line) indicates a change in the interatomic distance with respect to the bulk. In addition, a quite strong peak appears at about 2 Å (uncorrected from phase shift) when the electric vector of the light is close to the surface normal (solid line). It is likely that is comes from adsorbate-substrate bonding.

In Fig. 3 the imaginary part and the modulus of the Fourier transforms of the raw experimental data collected on Ag overlayers are compared for the two polarizations to the fits obtained by assuming that silver adatoms sit either above surface oxygen atoms (left) or above surface magnesium atoms (right). The best agreement corresponds to the Ag-O solution with the structural parameters displayed in Table I.

IV. DISCUSSION

The surface-extended x-ray-absorption fine structure (SEXAFS) data collected on the Ag monolayer deposits clearly demonstrate that the Ag-Ag distance is increased with respect to bulk silver (2.89 Å). Within the experimental errors, the value of the Ag-Ag distance in the overlayer is that of closest equivalent atoms within the MgO(100) face, i.e., 2.98 Å. The Ag substrate contribution is prominent when the Ag/MgO system is probed with light at grazing incidence, showing that this contribution has a strong component perpendicular to the surface. In addition, interface Ag atoms are concluded to sit on surface oxygen atoms since changing from oxygen to magnesium alters drastically the quality of the fit for data collected with light at grazing incidence.

Clearly, the only way to reconcile these three results is to assume that the silver film is in registry with the MgO(100) surface. This is strong evidence that the lattice parameter of the silver overlayer is expanded by about 3% so as to fit the MgO parameter and give rise to an interface having $(100)_{\mathrm{Ag}}\|(100)_{\mathrm{MgO}}$ and $[100]_{\mathrm{Ag}}\|[100]_{\mathrm{MgO}}$ orientation. Interface Ag atoms are atop surface oxygen atoms, in full agreement with first-principles calculations[7–9] and x-ray-diffraction experiments.[16] This discards the hollow site[6] for which the Ag substrate bond should contribute both experimental spectra, with light at either normal incidence or grazing incidence.

Our value of the Ag-O distance, 2.53 ± 0.04 Å, is in good agreement with the theoretical value of Schönberger, Anderson, and Methfessel,[8] 2.50 Å, but higher by more than 0.1 Å than the experimental value obtained by Guénard, Renaud, and Valette[16] by means of x-ray diffraction. In a way which compares quite well to Cu/Zn(0001),[12] previous experiments[11] have shown that for deposits around 1 equivalent ML, the silver covers effectively about 60% of the MgO(100) surface, and therefore that the film consists of 2-ML-thick islands. The numbers in italic characters in Table I have then been calculated using Eq. (1), within a structural model where the atoms of the second layer sit above the hollow sites of the first layer with the same interatomic distance. The agreement between the experimental results and those from the model justifies the structural model and confirms the previous data.

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