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Physicochemical Interaction and Atomic Structure at Cu-MgO Interfaces

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Abstract. — Physicochemical interactions at Cu-MgO buried interfaces are studied by electron X-ray emission spectroscopy and compared to results obtained for native interfaces. The atomic arrangement is also determined. The role of the characteristics of the substrate is evidenced. Results suggest that weak or strong interactions can be present at the interfaces.

1. Introduction

The determination of the electronic distributions in one, or some, atomic layers at solid-solid interfaces is of fundamental importance. Indeed it gives information at the atomic scale about the physicochemical interactions between the two materials in contact. These interactions determine the mechanical and interfacial properties of the system. In the case of very thin films deposited on a surface, it is known that size effects can perturb the electronic distributions. Then, it is of interest to compare two types of film-substrate interfaces. One is obtained by depositing adatoms or one or two monolayers on the substrate; it is denoted native interface. In the other, the film thickness is sufficient so that its electronic configuration is that of the bulk material. This condition is verified when the thickness exceeds ten nm. This type of interface is denoted buried interface.

Metal-oxide systems are relevant in many applications, microelectronic, composites, heterogeneous catalysis, ... Among those, we have chosen to study the Cu-MgO system because of its interest in the fabrication of superconductor thin films. The band structure of MgO has been widely studied and modelisations of the MgO(100) surface exist [1]. In the present paper, we present a study of the electron energy distributions in buried and native Cu/MgO and MgO/Cu interfaces. Experiments on buried interfaces are performed by EXES (electron X-ray emission spectroscopy) and those on native interfaces by XAES (X-ray Auger electron spectroscopy) and XPS (X-ray photoelectron spectroscopy). Information on the atomic structure is obtained by AFM (atomic force microscopy) and by TEM (transmission electron microscopy) and TED (transmission electron diffraction) by using the milling method. The results are discussed in relation with the chemical properties.

The spectroscopic methods are briefly described in Section 2 and the characteristics of the samples in Section 3. Results are presented in Section 4 and in Section 5, discussion is made in relation with mechanical informations obtained by the pull off method.

2. Experimental Techniques

2.1. EXES

This method makes possible the high resolution energy analysis of the electron distributions around the elements present at an interface buried under some tens of nm [2]. Let us recall briefly that the analyzed emissions correspond to the transitions of valence electrons to a nlj inner hole. Due to the radiative transition probabilities, the valence states involved in the transition are the states which interact with the nlj hole and have the $l \pm 1$ symmetry. Then the transitions have a local and partial character. They describe the spectral densities of valence states characteristic of each type of atoms and each symmetry. From those, mixing of valence states and chemical interactions between atoms are deduced.

Bulk or superficial zone of any sample can be analyzed by this method. Application to buried interfaces is possible by choosing the energy of the incident electrons so that it is slightly above the energy threshold necessary to create the nlj hole when the electrons reach the interface. Only the atoms present in the substrate are concerned by the analysis. Thus, two types of samples were necessary, Cu deposited on MgO and MgO deposited on Cu. Experiments were carried out under UHV with the IRIS apparatus [3].

2.2. XAES and XPS

The measured characteristic was the modified Auger parameter which is defined as the sum of the binding energy of the most intense core level peak and the kinetic energy of the most prominent Auger transition [4]. The MgO substrate was characterized by monitoring Mg 1s, O 1s, Mg $KL_{23}L_{23}$ and O $KL_{23}L_{23}$ lines as a function of Cu coverage. For the copper deposit, Cu $2p_{3/2}$ and Cu $L_3M_{45}M_{45}$ were used. Experiments were carried out in a UHV chamber equipped with a dual Al/Mg X-ray source associated with an hemispherical analyser (HA 100 VSW Sc. Inst.).

3. Preparation and Crystallographic Structure of the Interfaces

The samples were prepared *in situ* by vapor deposition in the UHV preparation chambers of the EXES or XPS devices. Two kinds of buried interfaces were studied: they were grown by condensation of a copper film on a MgO cleavage or by deposition of a MgO layer on copper and are labelled in the following Cu/MgO and MgO/Cu respectively.

3.1. Cu/MgO Interfaces

The morphology and the composition of MgO(001) surfaces obtained by cleavage were studied by AFM in contact mode and also secondary ion mass spectrometry (SIMS). The surfaces appear atomically smooth on large areas, with a mosaïc structure typical of MgO (Fig. 1).

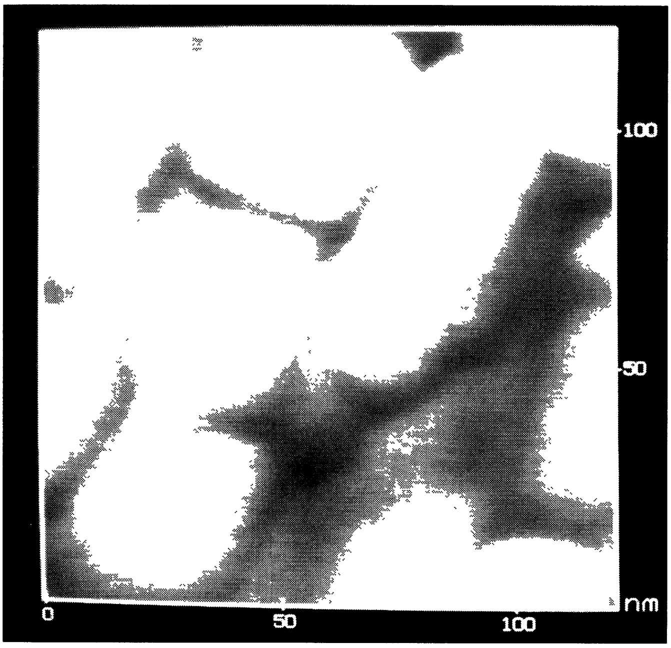


Fig. 1. — AFM image of a MgO (100) cleavage showing the mosaïc stucture of the crystal.

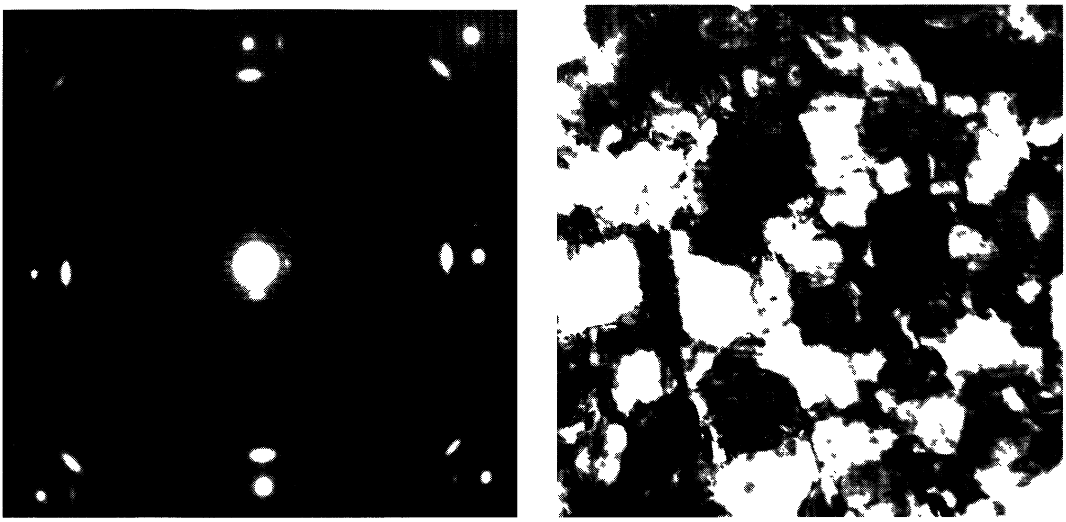
SIMS analyzes evidence CH_4 and OH ligands which can be removed by annealing under UHV (typically 850 K, 1 h) if the sample is quickly introduced under vacuum after cleavage [5].

A Knudsen cell is employed as Cu source. The metal atom flux is calibrated by a quartz balance at a value of 0.2 nm/min (mass equivalent mean thickness). Metal depositions were performed at substrate temperatures in the 300-600 K range. For XPS analyzes of native interfaces, the metal flux was lowered in order to perform sequential deposits.

For TEM observations, samples were reduced to powder. The metal films grown at temperatures lower than 450 K are formed of polycrystalline islands. The surface coverage is achieved for a Cu deposit mean thickness in the 20 to 30 nm range depending on the substrate annealing. When the temperature deposition exceeds 500 K, a perfect parallel epitaxy takes place with only one azimutal orientation (001)Cu // (001)MgO and $\langle 100\rangle$Cu // $\langle 100\rangle$MgO, as shown in Figures 2a, b.

The EXES results were obtained from three Cu/MgO (001) interfaces. For the first one, noted Cu/MgO(1), a 10 nm thick Cu film was deposited at 300 K on the air cleaved surface. X-ray diffraction analysis has shown that coherent diffraction domains are larger than 10 nm and microdistorsions are weak [6]. For the second, noted Cu/MgO(2), 20 nm of copper were deposited at 300 K on a substrate annealed one hour at 750 K. For the last sample, noted Cu/MgO(3), a 20 nm thick Cu film was deposited at 520 K on a same substrate.

Adhesion tests were done by the pull off method on samples prepared at different temperatures. In the 300-600 K range, the adhesion force increases from 2.6×10^6 N/m^2 to 8.2×10^6 N/m^2 [7].



a) b)

Fig. 2. — a) Electron diffraction pattern obtained by transmission at 100 kV on a Cu/MgO interface. The parallel epitaxy between the metal layer and the oxide is perfect. Double diffraction spots are present, they correspond to moiré fringes in the micrography. b) Electron micrography (× 170 000): the layer is continuous and the moirés fringes attest the good quality of the film.

3.2. MgO/Cu Interfaces

MgO/Cu/MgO samples were prepared by deposition of 40 nm of Cu between two MgO layers supported on a NaCl (100) cleavage. Continuous films of MgO were obtained by vapor deposition from an electron bombardment source. The whole film has a thickness of 80 nm; it can be observed in TEM after dissolution of NaCl in water. The superficial MgO layer protects the metal against oxidation during the air transfer of the samples towards the analysis chambers.

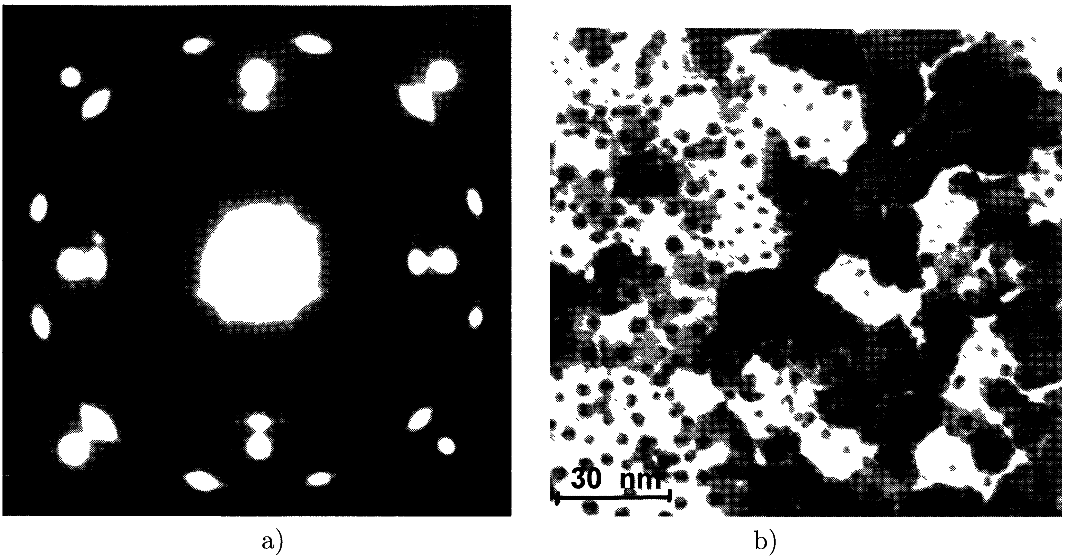
If the deposition temperatures for MgO and Cu are 400 K and 500 K respectively, the three layers are oriented on NaCl with the relationships:

$$\begin{aligned}&(001)\mathrm{Cu} \;//\; (001)\mathrm{NaCl} \text{ and } \langle 100\rangle\mathrm{Cu} \;//\; \langle 100\rangle\mathrm{NaCl}\\ &(001)\mathrm{MgO} \;//\; (001)\mathrm{Cu} \text{ and } \langle 100\rangle\mathrm{MgO} \;//\; \langle 100\rangle\mathrm{Cu}\\ &(111)\mathrm{MgO} \;//\; (001)\mathrm{Cu} \text{ and } \langle 110\rangle\mathrm{MgO} \;//\; \langle 110\rangle\mathrm{Cu}\end{aligned}$$

with two orthogonal azimuthal orientations.

Figures 3a, 3b show TEM micrographies and electron diffraction patterns obtained on these samples. Depending on their orientation the MgO films are formed of platelets with square or hexagonal outlines and sizes ranging from 3 to 30 nm. If the deposition temperature of MgO is below 400 K, the sample is polycrystalline with a (001) texture.

Two MgO/Cu interfaces were analyzed by EXES: one with a (001) texture, noted MgO/Cu(1), the other epitaxially oriented, noted MgO/Cu(2).



a) b)

Fig. 3. — a) Electron diffraction pattern from a MgO/Cu/MgO sample. In the selected area the MgO layer shows three orientations, (001) and two (111) with orthogonal azimuths. The copper is (100) oriented on these surfaces. b) Electron micrography (× 330 000) of a Cu/MgO (100) layer grown at 420 K. Between the Cu crystallites the square mosaïc of the MgO is visible.

4. Results

4.1. Buried Cu/MgO interfaces

4.1.1. Cu/MgO(1)

The O 2p spectral density of a 1.5 nm thick interfacial zone is analyzed [8] and compared in Figure 4a to those of MgO and Cu_2O. At the interface, a strong narrowing is observed towards the high binding energies with respect to MgO and no structure is seen at the position of the main peak of Cu_2O. In contrast, a significant structure is observed towards the low binding energies. The spectral densities of O 2p at the interface and of bulk Cu 3d are plotted in Figure 4b. The two curves are adjusted on the same energy scale by taking into account the O 1s binding energy of MgO, measured at the Cu/MgO native interface, and the Cu $2p_{3/2}$ binding energy of bulk metal. This figure shows a broadening of the O 2p spectral density in the energy range where Cu valence states are present.

We have verified that the O 2p spectral density at the interface cannot be fitted by a weighted sum of the O 2p spectral densities of MgO and Cu_2O. Consequently, at the interface, no valence state of the compound is present but only a mixing of oxygen and copper valence states. When the analyzed thickness is increased up to a ten of nm, the spectral density is that of the bulk MgO. This shows that the interaction between oxygen and copper is present only in a narrow zone at the interface.

4.1.2. Cu/MgO(2)

The analyzed thickness is the same as in the previous case. The O 2p spectral density is plotted in Figure 5. The same broadening is observed towards the low binding energies, indicating the presence of the oxygen-copper interaction. Towards the high binding energies, no narrowing is

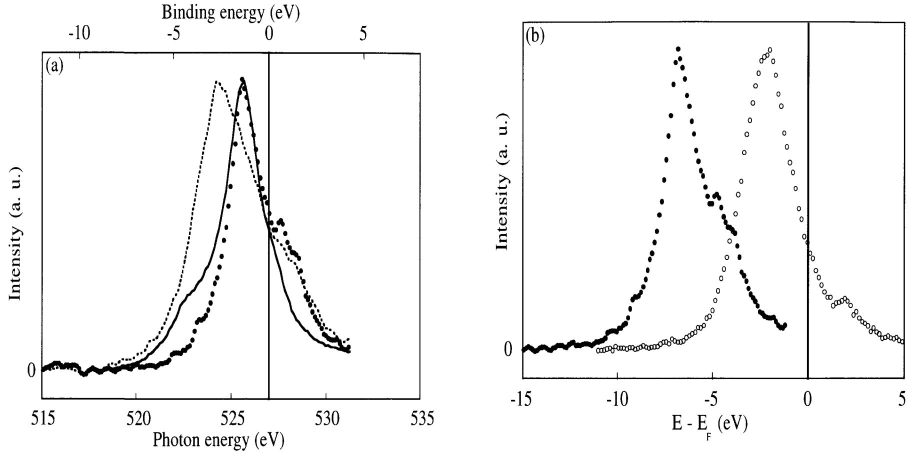


Fig. 4. — a) O 2p spectral densities of a 1.5 nm thick interfacial zone obtained for the Cu/MgO(1) sample (dots), of Cu_2O (dashed line) and of MgO (solid line). b) comparison on a binding energy scale referred to the Fermi level of the O 2p spectral density obtained at the interface (full dots) and of the Cu 3d spectral density of copper (open dots).

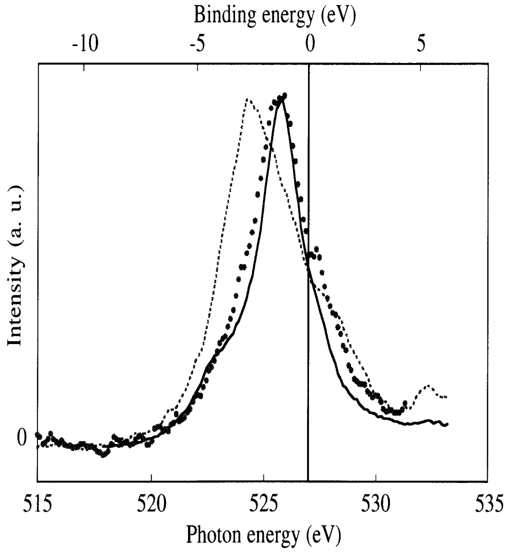


Fig. 5. — O 2p spectral densities of a 1.5 nm thick interfacial zone obtained for the Cu/MgO(2) sample (dots), of Cu_2O (dashed line) and of MgO (solid line).

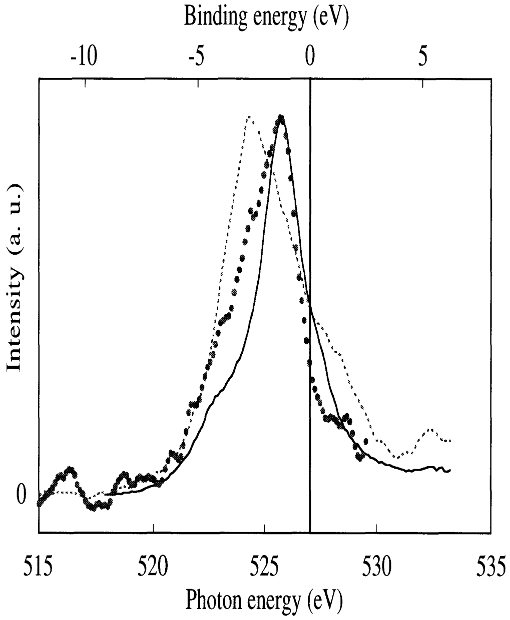


Fig. 6. — O 2p spectral densities of a 1.5 nm thick interfacial zone obtained for the Cu/MgO(3) sample (dots), of Cu_2O (dashed line) and of MgO (solid line).

seen but a slight broadening in the energy range of the Cu_2O peak. This reveals the existence of a Cu_2O-like atomic arrangement.

4.1.3. Cu/MgO(3)

The O 2p spectral density of an interfacial zone with the same thickness as the previous ones, is plotted in Figure 6. The structure of low binding energies is not observed. In contrast, a clear broadening is seen towards the high binding energies, at the position of the Cu_2O peak. Simulation has been made by adding the spectral densities of Cu_2O and MgO. The best fit is obtained for about 30% of Cu_2O and 70% of MgO. By taking into account the analyzed total thickness, we deduce that a Cu_2O-like atomic arrangement is present on about 0.4 nm.

4.2. Buried MgO/Cu Interfaces

4.2.1. MgO/Cu(1)

The Cu 3d spectral densities are plotted in Figure 7a for a 1 nm thick zone at the interface of a MgO/Cu/MgO polycrystalline sample and for bulk Cu and Cu_2O. The structures present towards the high photon energies are due to satellites emissions, *i.e.* transitions in the presence of supplementary excitation or ionisation. Only the main peak is characteristic of the Cu valence states. The Cu 3d spectral density of the polycrystalline film at the interface is slightly different to that of the metal and independent of the deposition temperature between 300 and 520 K. Modelling made by adding 70% of metallic Cu and 30% of Cu in Cu_2O is plotted in Figure 7b. The agreement is good between this curve and the experimental result. By taking

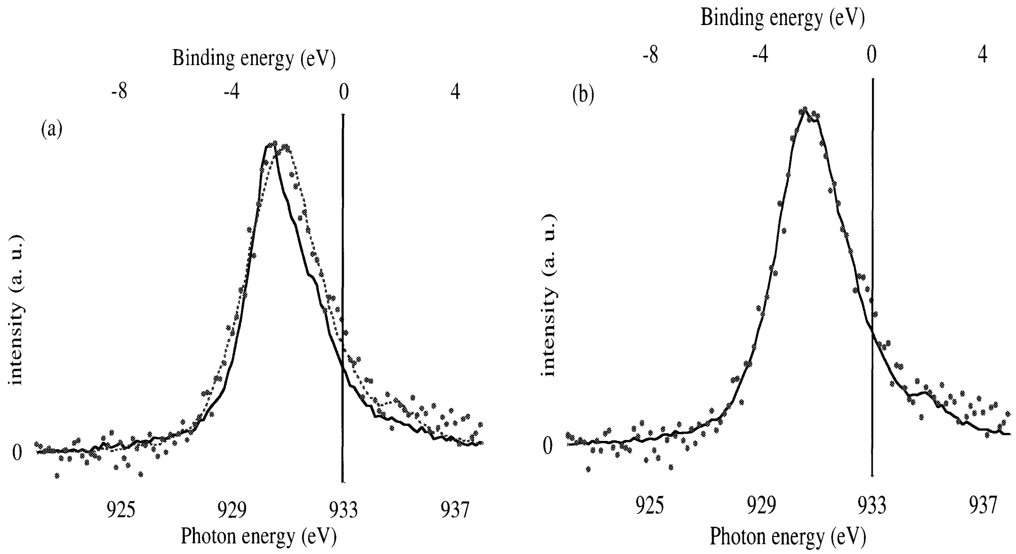


Fig. 7. — a) Cu 3d spectral densities of a 1.0 nm thick interfacial zone obtained for the MgO/Cu(1) sample (dots), of Cu_2O (solid line) and of Cu (dashed line). b) comparison of the Cu 3d spectral density obtained at the interface (dots) and a spectral density simulated by added 70% of Cu and 30% of Cu_2O (line).

into account the analyzed thickness, change of the Cu 3d spectral density is present in an interfacial zone which extends over about 0.3 nm.

4.2.2. MgO/Cu(2)

A different result is obtained for an epitaxial multilayer prepared at 400 K. Comparison between the two types of interfaces is plotted in Figure 8. For the epitaxial multilayer, the Cu 3d spectral density in a 1 nm thick interfacial zone is characteristic of metallic copper.

4.3. Native Cu/MgO Interfaces

For a Cu film between 0-1 monolayer thick, deposited on a MgO substrate, the Cu Auger parameter has the value of the Cu_2O parameter. The O Auger parameter changes strongly with respect to that of MgO while the Mg Auger parameter remains the same. By studying the Cu/NaCl interface in the same experimental conditions [8], it has been verified that the presence of Cu_2O is not due to a contamination.

5. Discussion

From the O 2p spectral density at the Cu/MgO buried interface, two types of changes are observed. First, a mixing occurs between the valence states of O and Cu at the interface. This mixing of states reveals the existence of a "physical" interaction between oxygen and copper. It is observed for cleaved and non treated MgO substrate. Second, oxygen bonded to copper is observed on about one monolayer, making an interaction of "chemical" type exists between oxygen and copper. This is the only interaction when the MgO substrate is treated under UHV at 750 K and the Cu film is deposited at 500 K. Then the heating under vacuum of MgO

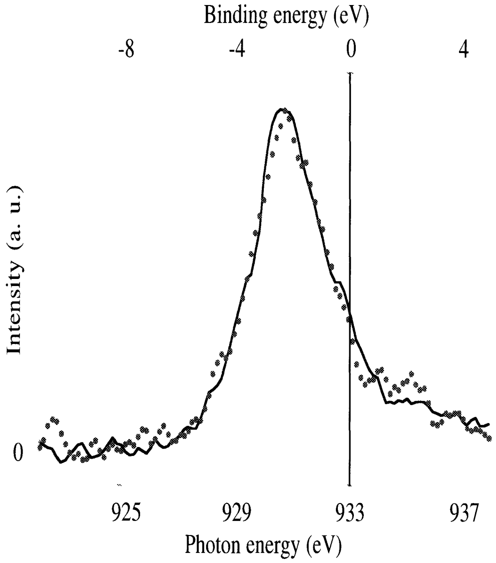


Fig. 8. — Cu 3d spectral densities of a 1.0 nm thick interfacial zone obtained for the MgO/Cu(1) (solid line) and MgO/Cu(2) (dots) samples.

produces a change of the reactivity at the substrate surface and this change induces a chemical interaction between O and Cu. The two interactions, physical and chemical, are also observed simultaneously (Fig. 5). We suggest that in this case the characteristics of the substrate are not uniform on all the surface of the sample.

Mechanical measurements indicate that the pull off is more difficult in the case of Cu/MgO samples prepared at high temperature, *i.e.* when the chemical interaction is present. This points out that this interaction is the strongest.

For Cu/MgO native interfaces, the Auger parameter value of Cu and O suggested a chemical interaction with formation of Cu(I) [8]. Only UHV heated substrates have been used. The results are in agreement with those of buried interfaces.

At MgO/Cu interfaces, the copper is in an environment either metallic or analogous to that of Cu_2O on about one monolayer. Then the two types of interaction, physical and chemical, can be present. In the first case, a simple mixing exists between the valence states of Cu and O. As the Cu 3d spectral density remains unchanged, the mixing occurs between the Cu 4sp and O 2p states as expected from theoretical studies [9]. Physical interaction is the only one in the case of the epitaxied layer, *i.e.* when the quality of the interface is the best. On the other hand, when the copper film is polycrystalline, Cu states form a band analogous to that of Cu_2O and the chemical interaction is present.

Grazing incidence X-ray diffraction of Ag/MgO interfaces [10] has shown that the metal atoms are arranged above the O ions. This is in agreement with theoretical predictions [9]. In the case of the MgO/Cu/MgO epitaxied layer, *i.e.* in the presence of a long range order, one expects the same arrangement. From our results, the epitaxied copper is in metallic arrangement and no chemical interaction is present. Due to the vicinity of Cu and O atoms, weak interaction exists and is revealed by a mixing of the O 2p and Cu 4sp valence states.

Then the presence of a weak interaction is characteristic of the interface between a noble metal and a perfect MgO surface, in agreement with theoretical predictions [11]. On the other hand, when the deposit is polycrystalline, roughness and disorder are present at the interface and chemical interaction is observed, alone or accompanied by the physical interaction.

To conclude, when chemical interaction exists, it is analogous for MgO/Cu and buried and native Cu/MgO interfaces. A Cu_2O-like arrangement is thus observed over about one monolayer. The physical interaction is only seen in the case of the buried interfaces, *i.e.* when the film thicknesses are sufficient so that a tridimensional arrangement could occur. In the case of the buried MgO/Cu interface, metallic Cu is observed when a well-ordered arrangement exists. In contrast, for the Cu/MgO interface, the temperature simultaneously changes the atomic arrangement and the reactivity, making different the behaviour of the two inverse interfaces. Then the nature and the characteristics of the substrate play an important role on the existence of weak or strong interaction at the interface.

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