Rocksalt metal-oxides: structure, morphology and metal growth

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In the last three decades a considerable insight into physical and chemical properties of metallic and semiconducting surfaces was gained. Surface structures and chemical phenomena were investigated with increasing scientific depth and thin film and interfaces were prepared, studied and understood.

In contrast to this extensive research, less work has been done on oxides. Nevertheless oxide surfaces are more relevant than metal surfaces, since they cover the vast majority of metals in real world devices with a thin native oxide film. This oxide skin influences the surface properties of the metals and therefore their possible applications. The delay in the studies about oxides is motivated by the difficulties in the preparation of bulk crystalline samples in a controlled manner and furthermore in their analysis. Actually a lot of investigation techniques in surface science have been developed for metals, leading sometimes to problems for their use on insulating samples. This is the case, for example, of Scanning Tunneling Microscopy (STM). The following invention and improvement of other Scanning Probe Microscopies, like Atomic Force Microscopy (AFM), that do not involve the use of electron currents, has allowed the investigation of these new surfaces into deeper and deeper details. Moreover the use of Molecular Beam Epitaxy (MBE) for thin oxide film growth has overcome the problem of the insulating character of the oxides and extended their studies.

Oxides can be employed in a wide range of applications, such as in catalysis, magneto-electronic devices, gas sensors, etc. In all these fields, where miniaturization is the key word for future improvements in the performances, the quality and the properties of the devices are governed by surfaces and interfaces.

Additionally they can provide a large contribution as support for the growth of metals in various forms. Some oxides, like MgO, can act as inert support, without any strong interaction with the metals on top. Therefore they allow the study of magnetic and electronic properties of the deposited metals without any influences from the substrate underneath. On the other side, also the possible interfacial interactions can be interesting due to the novel magnetic, electronic or catalytic properties that they can lead to. It is therefore crucial to know first the characteristics of the thin oxide films and surfaces and the processes involving both oxide-metal and metal-oxide interfaces.
In recent years surface science and technology are moving from the interest for films and multilayers to a further reduction in the size of the devices and therefore to the lateral confinement of their components. For this reason a wide range of methods to prepare nanostructures has been developed, proceeding in two opposite ways: top-down and bottom-up. The first way starts from a macroscopic material and reduces its size by means of several techniques like lithography, ion and electron bombardment and so on. The second way, to which this work and its further perspectives are dedicated, is the self-assembling of nanostructures induced by the properties of the materials employed or by a template on the substrate surface. In particular the use of a template is appealing since it can induce the formation of a well-ordered array of nanostructures.

Templates on metallic and semiconducting substrates have been extensively prepared and studied. Now the same is going to be done on oxides. Several attempts have been tried to produce patterned surfaces in ways similar to those employed for other materials, using both bulk and thin film oxides. These procedures applied to oxides can lead to nanostructures whose properties can depend almost only on their reduced dimensionality, when the substrate is inert. Otherwise, when interactions at the interface are present, changes in the properties typical of films due to the lateral confinement can be studied.

In spite of the difficulties, the promise of metal-oxide systems is the appearance of novel properties induced by the reduced dimensionality and the interfacial interactions, that for metal substrates could still be hidden, opening therefore to new fields and applications.

The aim of this work is the growth of metals on rocksalt oxides. For this purpose two prototype oxides have been chosen: MgO, that acts as an inert support, and NiO, that on the contrary is reactive and antiferromagnetic. Since these systems are interesting both for multilayer applications and for nanostructure studies, first of all the properties of the interfaces have been investigated, to ascertain if there is and what kind of interaction is present. In particular this has been done for Fe and Au films, that can represent two opposite situations: Fe is very reactive, while Au should be almost inert.

The knowledge of the processes involving the interfaces becomes extremely important when nanostructures are considered. If there is any kind of interaction in fact this can lead to different properties of the overlayer and of the system in general. This is the case for example of Fe on MgO and on NiO. In the first case the interface is proved to be sharp, therefore a small influence of the substrate on the Fe properties is expected. On the contrary Fe/NiO system has a strong intermixing in the first layers and this can influence the expected magnetic coupling of the Fe clusters with the antiferromagnet underneath.

In order to grow and study metal nanostructures, templates have been prepared on oxide surfaces, in particular of MgO. For this purpose both bulk and thin films of MgO have been employed. Bulk MgO has been used for the preparation of vicinal surfaces, exhibiting a regular
array of steps, that can act as preferential nucleation centres for metal atoms. Thin films have been prepared on Mo(001) and Ag(001) and, especially in the first case, a deep investigation of the oxide structure, morphology and properties has been carried out, due to the lack of information present in literature. In particular the formation of a surface pattern due to a network of interfacial dislocations has been investigated.

Finally a brief discussion is given about the morphology of Fe clusters on one of these templates, namely MgO mosaics on Ag(001).

Thus this work is a first step on the long way to the comprehension of morphology, electronic and magnetic properties of a wider range of metal nanostructures (one- and zero-dimensional) on oxide templates.

This thesis is organized as follows. Chapter 1 is an overview of the state of the art on the oxide preparation, vicinal surfaces and dislocation formation. Chapter 2 describes the experimental apparatus used and the less common techniques employed for this work. In chapter 3 the preparation procedure for stepped MgO surface is described. Chapter 4 and 5 deal respectively with the preparation of MgO/Mo(001) and MgO/Ag(001) and with the successive investigation of the morphology of Fe depositions on top. Finally a comparison with the metal/NiO system is carried out in chapter 6. Conclusions and future trends are finally discussed.
Chapter 1

State of the art

1.1 Why MgO?

MgO is one of the most investigated oxides both in the form of a bulk and as thin film. Furthermore it is interesting from many points of view.

MgO has a high oxide heat of formation, that makes it thermodynamically favoured and stable upon deposition of some reactive metals on top. It is predicted to have a negligible electronic interaction with most metal overlayers. Therefore it can be prepared for the successive growth of metal nanostructures of reduced dimensionality (2D, 1D and 0D).

![Figure 1.1: The rocksalt structure of bulk MgO.](image)

Its large bandgap of 8 eV introduces severe charging problems when applying electron spectroscopies. This problem can be overcome by using MgO ultrathin films on suitable metal substrates.

MgO has the rocksalt structure shown in Fig. 1.1, with a lattice parameter $a = 4.211$ Å. The simple crystalline configuration is attractive both from an experimental and from a theoretical point of view. This crystal structure is compatible with the epitaxial growth of MgO on a variety
of substrates with a small lattice mismatch with respect to the oxide. The lattice mismatch \( m \) is defined as

\[
m = \frac{a_f - a_s}{a_s}
\]

(1.1)

where \( a_f \) and \( a_s \) are respectively the equilibrium lattice parameters of the film and the substrate. Additionally some metals like Fe can be grown epitaxially on top of MgO.

The most used substrates for epitaxial MgO growth are Ag(001), Fe(001) and Mo(001). Ag has a fcc structure with lattice parameter \( a = 4.085 \) Å, Fe and Mo are bcc with \( a = 2.867 \) Å and \( a = 3.147 \) Å respectively. The lattice mismatches \( m \) with respect to MgO are equal to 3.0, 3.7 and 5.4% respectively. Ag seems to be the most promising substrate because it does not get oxidized at the O pressures and temperatures used for reactive MgO growth. Additionally it has the smallest mismatch, therefore it is expected that the lowest density of dislocations is induced in the film. It is a soft metal, suggesting the possibility that the misfit dislocations shift into the metal surface, leaving an almost perfect single crystalline oxide film. However interesting features can arise from the deposition of MgO on a metal with a large lattice mismatch as a consequence of the formation of a network of dislocations, as in the case of Fe and of Mo. In these cases, however, the reactivity of the substrate to oxygen is higher, complicating the situation at the interface and making the deposition conditions more critical.

In this chapter I will present a brief state-of-the-art introduction to the systems studied in this work. In Sec. 1.2 a first way to pattern the oxide is described, i.e. the production of vicinal surfaces. In the following sections the state of the art about MgO is discussed, in form of a film deposited on Mo(001) (Sec. 1.3) and on Ag(001) (Sec. 1.4), giving a description of the growth procedures and the film quality from a chemical, structural and morphological point of view. In Sec. 1.5 the formation of dislocation networks in oxide films is discussed. This is a second way to pattern an oxide for the growth of self-organized metal nanostructures. Finally in Sec. 1.6 a discussion about the interests for the metal growth on oxides is reported.

Table 1.1: Structure and lattice parameters (in Å) of some materials interesting for this work. \( a \) is the cubic lattice parameter (see Fig. 1.1), while \( d = a\sqrt{2} \) is the diagonal of the face.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>( a ) (Å)</th>
<th>( d ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>fcc</td>
<td>4.085</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>bcc</td>
<td>3.147</td>
<td>4.451</td>
</tr>
<tr>
<td>MgO</td>
<td>rocksalt</td>
<td>4.211</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>rocksalt</td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>bcc</td>
<td>2.867</td>
<td>4.055</td>
</tr>
</tbody>
</table>
A vicinal surface is obtained by cutting a crystal along a plane making a small angle $\theta$ with respect to a low index plane normal to the direction $\vec{n}_0$. Such a surface can be viewed as a periodic succession of terraces normal to $\vec{n}_0$ with equal width and separated by steps of monatomic height $h$. The width of the terraces is determined by the number of atomic rows $p$ parallel to the step edges. A vicinal surface corresponds to an atomic plane with high Miller indexes normal to $\vec{n}$. It can also be denoted with the Lang notation $p(h, k, l) \times (h', k', l')$, $(h, k, l)$ and $(h', k', l')$ being respectively the Miller indexes of planes parallel to the terraces and the ledges (Fig. 1.2).

The representation with large low-index terraces and monatomic steps is metastable at low temperature, since the high density of defects on the step edges increases the free energy. Thus to reduce the surface energy the vicinal surface should form facets with Miller indexes lower than those of the vicinal surface or at least relax the atomic position of atoms along the step edges. This does not occur for every vicinal surface because its preparation includes an annealing at high temperature, where the ordered step distribution is favored. When the temperature is decreased to working conditions, the kinetic for the reordering is too slow to allow a transition back to facets. Therefore, provided that the preparation conditions are optimized, vicinal surfaces with large periodically arranged areas can be stabilized on different materials.
However other effects can contribute to determine the surface morphology.

First of all entropy can provide a mechanism for step-step repulsion, thus favoring the formation of regular steps, even if with a broad distance distribution. Further interaction originating at the step edges from the periodic lattice distortion or the dipole-dipole interaction can help or interfere with the organisation of the surface in a regular array of steps. If this interaction is repulsive, as shown for some metal surfaces, it provides a regular arrangement of the steps. On the contrary an attractive interaction can prevent the formation of equally spaced steps and can be responsible for a strong step bunching. Furthermore entropy can lead to a destruction of step ordering in some cases. This determines a roughening of the steps and a slow cooling is required to prevent the freezing of the roughened morphology.

When step bunching dominates the mechanism for the formation of the vicinal surface, steps become higher and terraces are larger and consequently the stable surface is no more the ideal one shown in Fig. 1.2. One of the motivation can be found in the Ehrlich-Schwoebel barrier. This is an energy barrier experienced by atoms moving on a stepped surface when they reach the step edge. The atom on a terrace has a certain number of nearest neighbours. When it reaches the edge of the terrace, the number of neighbours decreases suddenly and the resulting decrease in binding energy is manifested as a barrier for diffusion over the edge. Therefore if a velocity gradient for the steps is present, they can collide and form larger terraces and higher steps.

![Figure 1.3: Surface processes relevant for growth on vicinal surfaces.](image)

The regular array of steps determines the functional centres of the vicinal surface and therefore its properties. They play in fact a prominent role in the formation of adsorbate structures near step edges via step decoration.
The processes involved are a subset of those playing a role in thin film growth (Fig. 1.3). Step decoration is the dominant process during growth in the range between island nucleation and the monolayer completion. Therefore the growth processes in the low coverage regime are fundamental. These are the compromise between the energetically favored adsorption sites and the diffusion processes. When an adatom diffuses on a terrace, it can encounter other atoms and form a cluster (island nucleation) or diffuse till it reaches a step edge (step decoration). The first process is dominant at low temperature, when the diffusion length on a terrace is reduced, for large terraces and high deposition rates. The second process dominates in the other cases. Therefore a perfect step decoration is obtained when the potential energy of an adatom at a step is lower than that of an adatom on a terrace and the temperature is high enough to have active diffusion processes. Furthermore, at this temperature, the alloying with the substrate should be unfavorable, otherwise this can prevent diffusion and step decoration.

Extended reviews on both vicinal surfaces and step decoration can be found in literature, giving deeper details on the subject here only briefly discussed [1, 2].

The preparation of MgO vicinal surface is more complicated than that of metal surfaces, since MgO has a stronger chemical bonding between atoms. This leads to a reduced mobility of surface atoms and requires the use of higher annealing temperature to help the step arrangement during the preparation. Unfortunately this can favour the step bunching.

The studies regarding vicinal oxides are in an extremely smaller quantity with respect to vicinal metal surface reports. The insulating character of the oxides in fact has further complicated the investigation of surface morphology because of the impossibility to image them by means of STM. The main part of the works is very recent and employs Atomic Force Microscopy (AFM). They report studies of the morphology of both flat and stepped MgO surfaces, discussing the necessity to anneal the samples to temperatures above 1200 K to obtain a good crystalline quality and the reorganization of the surface topography [3–5]. However these surfaces have often been employed as substrates for superconducting film deposition and successive studies. This indicates that they are good substrates but have never been extensively investigated for the growth of 1D nanostructures and step decoration. In Ch. 3 a deeper investigation of stepped MgO surface morphology is carried out, in order to have more information which provides a basis for the study of metal deposition on top.

1.3 MgO/Mo(001)

The first studies on the MgO/Mo interface date back to 1991. Those studies were mainly focused on the chemical aspects, with investigations of the growth procedures, the stoichiometry and the thermal stability of the obtained films [6–8]. In Ref. [7] two different oxide preparations are compared: post-oxidation of Mg deposited on Mo and MgO growth via Mg evaporation in O₂
atmosphere. In the first case a gradient of decreasing oxygen content going deeper into the film, due to the reduced oxygen diffusion, is observed. A further annealing promotes the oxidation of the remaining Mg atoms. In the second case the film grows stoichiometric by the evaporation of Mg at a rate of 1 ML/min in $P(\text{O}_2)=1\times10^{-6}$ Torr, with the substrate kept at 300 K. Additionally the work by Wu et al. [6] shows a stoichiometric growth for $P > 1 \times 10^{-7}$ Torr. LEED patterns show broad spots and high peak-to-background ratio, indicating an epitaxial growth of the film with MgO(001)/Mo(001). The crystalline quality does not improve after post-growth annealing or using higher O$_2$ pressure. Temperature Programmed Desorption (TPD) spectra indicate that the desorption of a film grown in these conditions is obtained at around 1270 K.

**Figure 1.4:** a) 700×700 Å$^2$ STM image of a 8 ML MgO film deposited at 300 K (+3 V, 0.8 nA). b) 900×900 Å$^2$ STM image of 2 ML MgO deposited at 300 K and annealed at 1100 K. The lines running diagonally across the two images correspond to a monatomic step in the Mo substrate. c) 800×800 Å$^2$ image of MgO deposited at 1100 K (+3 V, 3 nA). The directions indicated refer to the MgO film [9].

Recently the interest for MgO/Mo(001) system has grown again and the use of scanning probes has provided some information about the surface morphology. The advantages in the use of Mo as a substrate are mainly ascribable to the possibility to heat the film at very high temperature, due to the high melting point of the metal as compared to Ag or Fe.

To my knowledge only one work reports STM images of the MgO/Mo surface [9], that describes the study of the surface morphology as a function of the preparation conditions. In Fig. 1.4a and b STM images of a room temperature (RT) grown 8 ML MgO film before and after annealing at 1100 K indicate the presence of almost round islands covering uniformly the surface. The average diameter increases from between 20 and 60 Å to about 100 Å after annealing, but the morphology does not significantly change. Therefore the authors conclude that a post-growth annealing does not improve either the morphology or the structure (studied by LEED). This situation holds till a deposition temperature of 900 K is used. Deposition of the film at temperatures above 1100 K produces the surface shown in Fig. 1.4c, with large
three-dimensional islands and parts of the substrate uncovered. The borders align preferentially along the ⟨100⟩ directions of MgO.

Figure 1.5: a) 750×750 Å$^2$ image of 2 ML of MgO at 1000 K (+3.3 V, 180 pA), b) 250×250 Å$^2$ image indicates the size and symmetry of the checkerboard pattern on a single terrace. The directions indicated refer to the MgO film. [9].

In the intermediate temperature range for 900 K < T < 1100 K, the surface is covered by large MgO terraces with well-defined steps oriented along the MgO ⟨100⟩ directions. Fig. 1.5 shows one of these terraces, characterized by a “checkerboard pattern” with the sides aligned along the MgO ⟨100⟩ directions and a periodicity of 80 Å. The authors interpret this feature as a coincidence pattern, generated by the superposition of the two lattices of MgO and Mo. The difference in the cation-cation separation (4.21 Å for MgO, 4.45 Å for Mo) yields coincidence between the positions of cations in the film and in the substrate with a periodicity of 80 Å. The origin of the contrast can arise both from periodic strain relief at the surface and from a spatial variation in the electronic density of states. Instabilities in the tunneling conditions prevented the author to distinguish between the two cases.

In Ref. [9] there is however a lack of information about the dependence of the observed morphology on the film thickness. Results about the subject and further investigation on MgO/Mo(001) system properties will be discussed in Ch. 4.

1.4 MgO/Ag(001)

Growth of MgO/Ag(001) has been investigated in the last years from a chemical, structural and morphological point of view. Thin films have been deposited by post-oxidation of pre-deposited Mg, by Molecular Beam Epitaxy (MBE) and by sputtering of an MgO target. In the first case Mg is deposited on clean Ag and exposed to oxygen keeping the substrate at 200 K [10]. XPS analysis reveals the presence of metallic Mg besides part of stoichiometric MgO and non-stoichiometric MgO$_x$, independent on the oxygen dosage. The film prepared in such way
does not show a LEED pattern, apart from a weak (0,0) beam. Annealing the film to 700 K, the Mg\(^0\) peak disappears from the Mg KLL spectrum, but the MgO\(_x\) component is still present. The LEED evolves to a pattern characterized by 12 spots corresponding to rocksalt domains in three rotational configurations on an hexagonal layer (pure Mg). The film never reaches the formation of one single crystalline domain, indicating that the post-oxidation is not the best way to obtain a MgO film mimic of the bulk.

On the other side, MBE preparation produces a stoichiometric film, that grows layer-by-layer and is epitaxial to the Ag substrate \[10, 11\]. The LEED shows a sharp p(1×1) pattern, indicating good long range order. The growth of MgO by means of sputter deposition is compared to the MBE deposition by Valeri et al. \[11\], who prove that the stoichiometry and the crystalline quality is very similar in the two cases, with the only differences that the sputtered film relaxes the strain at a slightly lower thickness and the fractional coverage of the substrate reaches the saturation of the 100% at about 10 ML, a value higher than in the case of MBE film, where the Auger signal are compatible with a fractional coverage of about 95-100% starting from 1 ML.

![Figure 1.6](image)

**Figure 1.6:** a) Evolution of the in-plane lattice parameter as a function of MgO thickness \[12\]. b) Out-of-plane vs in-plane nearest neighbours distance obtained by the analysis of Mg K-edge and O K-edge EXAFS data for different film thickness and for reference samples in Ref. \[13\].

From a structural point of view, the MBE grown oxide film shows the epitaxial relationships with Ag expected from bulk lattice parameters (see Tab. 1.1): MgO(001)/Ag(001) and MgO[100]/Ag[100] \[12\]. Films in the 1-3 ML range grow pseudomorphic to the substrate, with the out-of-plane lattice parameter expanded, as expected from the classical theory of elasticity. Increasing the oxide thickness up to 6 ML, the film starts relaxing the misfit strain. Valeri et al. \[12\] have determined the in-plane lattice parameter by LEED and the out-of-plane parameter by
Primary-beam Diffraction Modulated Electron Emission (PDMEE). Their results are in agreement with a following work by Luches et al. [13], that determines the lattice parameters with a higher precision by means of Extended X-ray Absorption Fine Structure (EXAFS). They prove that the film is almost relaxed for a 10 ML film and completely relaxed at 20 ML. Additionally they observe that no intermixing occurs at the oxide/metal interface. The interface is expanded with respect to the bulk values of both the film and the substrate and O atoms sit on Ag atoms, with Mg in hollow sites [13–15].

For this reasons MBE deposition of MgO films has been chosen as the best way to produce epitaxial films that can be considered mimic of the bulk, from a chemical and a structural point of view.

![STM images of (a) 2 ML MgO/Ag(001) (3 V, 1 nA) [16], (b) 1 ML MgO nominal deposition (1 V, 0.3 nA). The inset shows a multilayer MgO island. c) Current image of the same region of panel b) [17].](image)

**Figure 1.7:** STM images of (a) 2 ML MgO/Ag(001) (3 V, 1 nA) [16], (b) 1 ML MgO nominal deposition (1 V, 0.3 nA). The inset shows a multilayer MgO island. c) Current image of the same region of panel b) [17].

On the other side, the morphology and the defectivity of the film is never comparable to the surface of a cleaved bulk MgO. STM images on thin oxide films reveal that even if the growth is almost layer-by-layer, the surface is covered by square islands up to 3 ML high even at 1 ML (Fig. 1.7). Furthermore the surface is far from perfect: it disrupts and Ag atoms move and form islands on top of flat MgO islands. To compensate this, MgO fills the holes left from the metal on the surface, determining a complex model to describe the surface [17]. The orientation of the islands has been observed along both the [100] [16] and [110] [17] directions (Fig. 1.7). Calculations have proved that polar borders are stabilized by the presence of the metal support,
becoming quasi-iso-energetic with respect to the non-polar ones [18].

A combined analysis of STS, EELS and UPS has determined the electronic structure of thin oxide films [16]. 3 ML MgO shows already the electronic levels of the bulk surface, with a band gap of 6 eV. For thinner films a state is present in the gap associated to MgO-Ag interfacial states.

1.5 Dislocations formation and mosaics

In this section I will discuss the dislocation formation in thin films growth only in the case when the deposit and the substrate possess the same symmetry of the crystal faces [19]. When two

![Figure 1.8](image)

**Figure 1.8:** Three possible modes of misfit accommodation: (a) coincidence lattice, (b) homogeneous strain (pseudomorphic growth), c) misfit dislocations [19].

geometrically dissimilar crystals (being A the substrate and B the overlayer) come into contact, the atoms in the vicinity of the interface are displaced by their ideal positions. Two lateral forces act on each atom. The first is the force exerted by the neighbouring atoms of the same crystal which tends to preserve its natural crystal lattice. The second is the force exerted by the atoms of the adjoining crystal which tends to force the atoms to occupy the lattice sites of the foreign crystal. When the interfacial bonding $\psi_{AB}$ is very weak compared with the bond strengths ($\psi_{AA}$ and $\psi_{BB}$) both crystals tend to preserve their natural lattices. In such a case the difference of the periodicities of the two adjoining crystal lattices degenerates in a range of misfit. A special case is when the ratio of the lattice parameters $a$ and $b$ is a rational number, i.e. $ma = nb$, with $m$ and $n$ small integers and $m = n + 1$. Then every $m$th atom of A
1.5 Dislocations formation and mosaics

coincides with every \( n \)th atom of \( B \) and we obtain the coincidence lattice model (Fig. 1.8a).

In this case the azimuthal orientation with maximum coincidence points is considered as the minimum energy orientation. The other limiting case is when \( \psi_{AB} \gg \psi_{BB} \) and \( \psi_{AB} \simeq \psi_{AA} \).

Here the overlayer \( B \) is forced to adopt the lattice of \( A \) and is homogeneously strained to fit the substrate (pseudomorphic growth, Fig. 1.8b). However, the elastic strains and the energy of \( B \) increase with the thickness. Therefore beyond a critical thickness the pseudomorphic growth becomes energetically unfavorable and the homogeneous strain is replaced by a periodical strain that attenuates with increasing film thickness. Thus misfit dislocations are introduced at the interface to accommodate the lattice misfit. The smaller the misfit, the greater will be the critical thickness for dislocation formation. In the intermediate case \( \psi_{AB} \simeq \psi_{AA} \simeq \psi_{BB} \) the interfacial forces are not strong enough to produce pseudomorphic growth for a considerable thickness and the misfit dislocations accommodate the misfit from the beginning of the growth process.

Misfit dislocations (MDs) represent atomic planes in excess in the material with the smaller atomic spacing and are useful concepts to describe the lattice distortion at the interface (Fig. 1.8c). If the atomic spacing of the overlayer is smaller than that of the substrate, the chemical bonds in-between the MDs will be stretched out but the bonds in the cores of the dislocations will be compressed. Thus an interface with a sequence of MDs is characterized by a periodic elastic strain with a period equal to the dislocation spacing \( p \) with

\[
p = \frac{a \cdot b}{a - b}
\]  

The energy associated to this periodic elastic strain decreases rapidly with the distance \( h \) from the interface and practically vanishes at a distance equal to \( p/2 \) (Fig. 1.9). Therefore atoms of a film thicker than half of the dislocation spacing do not feel anymore the presence of the substrate.

Dislocations are denoted by a dislocation-displacement vector, the Burgers vector \( \vec{b} \), as shown in Fig. 1.10 [20]. Fig. 1.10a is the section normal to a cube plane intersected by an edge dislocation, while Fig. 1.10b depicts a perfect reference lattice. First a closed Burgers circuit is drawn on the distorted lattice (a), which encloses the dislocation. Then the same circuit is drawn on the perfect lattice (b). The vector required to close the latter circuit is defined as the Burgers vector \( \vec{b} \). In the same picture the dislocation line vector \( \vec{\xi} \) is in the direction perpendicular to the plane. The sense depends on the Burgers circuit and is therefore arbitrary. The motion of this dislocation along \( \vec{\xi} \) by the displacement parallel to \( \vec{b} \) generates a plane over which glide displacement has taken place. This plane is called glide plane and is defined by the plane normal given by \( \vec{b} \times \vec{\xi} \) (Fig. 1.12b). In Fig. 1.10a \( \vec{b} = [100], \vec{\xi} = [00\bar{1}] \) and the glide-plane normal is given by \( [100] \times [00\bar{1}] = [010] \). Therefore the glide system is represented by \( \{h,k,l\}{\{h',k',l'\}} \) indicating first the Burgers vector and then the glide plane. For a detailed description and overview of dislocations, see Ref. [19, 20].
Figure 1.9: Plots of the strain energy $\Delta E_b(h)$ stored in the overlayer B beyond a distance $h$ from the interface as a function of $h/p$. Curves 1 and 2 correspond to misfits equal to 2% and 20% respectively [19].

Figure 1.10: Description of a Burger circuit and the corresponding Burgers vector on (a) section normal to a cube plane intersected by an edge dislocation and (b) a perfect reference lattice.

The formation of misfit dislocations plays an important role on the quality of the oxide-metal interface and has important consequences on the surface morphology. It has been shown by means of LEED that a periodic interfacial dislocation network can produce an elastic deformation of the surface, resulting in a spot splitting in LEED that is independent on the film thickness and on primary energy when Ge is deposited on top of Si(111) [21]. On the other side different rocksalt films have been shown to determine a spot splitting in LEED due to an elastic deformation of the surface of a thin film that depends on the atomic displacements associated with individual misfit dislocations rather than with their organization into a periodic array. This kind of deformation produces a spot splitting that depends both on the thickness and the
primary energy [22–26].

This surface deformation was first observed on the system NaCl/Ge(100) [22]. Here LEED spots are characterized by a four-fold symmetry, where every spot is surrounded by four satellite spots at $\pm \Delta K_{//}$. The position in the Brillouin zone of these satellites changes linearly with the primary energy, consistent with a surface containing mosaic crystals slightly tilted with respect to the surface plane [23]. In this system these tilted regions originate from the presence of monatomic steps on the Ge substrate, that the NaCl film cannot replicate, due to the two different bulk structures (respectively diamond like and rocksalt). Therefore the only possible accommodation is reached by introducing elastically distorted regions closed to the steps, while the film grows in registry with the substrate far away from the steps.

The same phenomenon has been observed on rocksalt oxides like MgO and NiO grown on Fe [24], Ag [25] and Pd [26]. In the case of MgO/Fe [24] the LEED (Fig. 1.11) shows the presence of four satellite reflections along the $\langle 100 \rangle$ directions, surrounding each fundamental Bragg spot. Also in this case the satellites move in the Brillouin zone linearly with primary energy, showing that they are due to a disorientation of surface planes. Increasing the MgO thickness, the separation between the satellites and the fundamental spot decreases. Calculation of the diffracted intensity from a surface whose profile is determined by a displacement field created by $\frac{1}{2}\langle 011 \rangle\{011 \}$ misfit dislocations at the interface are in good agreement with both sets of results. The displacement field is calculated using the isotropic elasticity theory (Fig. 1.12a). In the model shown in Fig. 1.12a the occurrence of a glide plane generates a monatomic step on the surface. No evidence of the presence of such monatomic steps has been found in STM measurements [16]. However STM images have always been acquired on thin MgO films, while

![Figure 1.11: LEED pattern of 23 Å MgO/Fe(001) for an incident beam energy of 200 eV. The reflection labeled O is the specular reflection. A and B are two fundamental Bragg peaks. $\delta x$ is the distance between the Bragg peak and a satellite. [24].](image-url)
the critical thickness for dislocation formation can be higher, not excluding the presence of such steps on thicker films.

Figure 1.12: (a) Displacement field of a dislocation created by glide having a Burgers vector $\mathbf{b} = \frac{1}{2}[011]$ 10 ML beneath a (001) free surface in MgO, as calculated using isotropic elasticity theory [24]. (b) Scheme of a glide system.

Figure 1.13: Specular (00) beam after depositing 10 ML (a) NiO and (b) MgO, respectively. Additional satellites are visible along the ⟨001⟩ directions. (c) Model for the mosaic formation in MgO/Ag(001) due to interface dislocation with (110) glide plane as reported in Ref. [25].

The same model is used to describe an analogous behaviour in the case of MgO and NiO grown on Ag(001) [25]. Also in this case a SPA-LEED (Spot Profile Analysis - LEED) investi-
1.5 Dislocations formation and mosaics

gation observes the same characteristics of the surface: the presence of satellites along the \langle 100 \rangle directions around each spot (Fig. 1.13a,b), with the same dependence as a function of thickness and energy described above for MgO/Fe. The assumption here is that the misfit dislocations formed at the interface above a critical thickness determine the tilt of some regions of the surface, to accommodate the in-plane lattice parameter of MgO. The surface is then covered both by flat and out-of-plane-tilted areas (Fig. 1.13c). The difference in the sharpness of the satellites between the two oxides is attributed to the less ordered mosaics on MgO and to the presence of a distribution of angles.

The same situation is observed for the LEED patterns on MgO/Mo(001) [9] and NiO/Pd(001) [26]. In particular in the latter case anisotropy in LEED spots and island borders in STM change from \langle 100 \rangle for low thickness and temperature to \langle 110 \rangle direction for thicker films and higher annealing or deposition temperature (Fig. 1.14a-d). Mosaics are again observed by SPA-LEED, with the same characteristics shown above, and change their orientation accordingly to the change in island shape. Moreover, a superstructure is observed in STM, that can be assigned to a Moiré pattern or to a periodic height modulation related to the presence of ordered defects, such as interface dislocations (Fig. 1.14e).

Figure 1.14: SPA-LEED patterns for (a) 4 ML, (b) 6 ML, (c) 12 ML and (d) 20 ML thick NiO films grown on a Pd(100) surface at room temperature, recorded with an electron energy of 124 eV. The scan range is given in % of the surface Brillouin zone of the Pd(100) substrate. (e) 750×750 Å² STM image illustrating the superstructure formed after annealing a 6 ML thick NiO film at 400°C (U = +3 V, I = 0.1 nA); the superstructure unit cell is indicated on the image, with the sides alligned along the NiO \langle 110 \rangle directions [26].

Dislocation networks have acquired a large interest recently due to their possible use for the fabrication of highly ordered, two-dimensional nanostructure arrays through the nucleation of deposited metal atoms on substrates with periodic elastic deformation. In particular this has been observed on semiconductors, where the reduced mobility of the dislocations induces the
islands to line up in one dimension, without a periodicity in two dimensions [27]. On the contrary in thin films the misfit dislocations are more mobile and repulsive and often form a highly ordered periodic pattern. The repulsive nature of the dislocations reduces the adatoms diffusion, inducing them to nucleate on specific sites, transferring the periodicity of the dislocation network to the two-dimensional island superlattice. In the case of Fe and Ag deposited on Cu and Ag thin films on Pt(111) [28], the presence of a trigonal dislocation network (Fig. 1.15a) determines the nucleation of the adatoms inside the quasi-hexagonal cell and the high energy barrier for diffusion across the cells limits the diffusion and induces the confinement of the islands (Fig. 1.15b).

![Figure 1.15: STM images showing the confined nucleation of adatom islands on a dislocation network. (a) STM image of the ordered (25×25) dislocation network formed by the second Ag monolayer on Pt(111) on deposition at 400 K and subsequent annealing to 800 K. The inset shows a model of this trigonal strain relief pattern. (b) A superlattice of islands is formed on deposition of 0.1 ML Ag onto this network at 110 K. Inset: the Fourier transform of the STM image shows the high degree of order and the hexagonal symmetry of the nanostructure array [28].](image)

Similar observation have been reported for the deposition of Co on Ag grown on MgO(001) by Leroy et al. [29], but in this case the dislocation network is buried at the interface between Ag and MgO. It is formed again by the relief of misfit strain, but, due to the small mismatch, the thickness necessary to relax the film is higher and the dislocations remain buried under 5 nm of Ag. The dislocation spacing $p$ is 11 nm, therefore $h$ is still less than $p/2$. By means of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and ab initio calculations they determine the distribution of Co particles on top of dislocations crossing lines.

The large amount of observations reported in literature and the many advantages described above, together with the results discussed in the present work about the presence of mosaics and misfit dislocations in rocksalt oxides, strongly suggest that these oxides, in particular MgO,
can be used as substrates and templates for the growth of ordered arrays of metal nanoparticles. This subject will be briefly discussed in Ch. 5 in the case of Fe/MgO system.

1.6 Why metal nanostructures on oxides?

When a transition metal is arranged in a structure of reduced dimensionality, such as an adatom, a cluster or an ordered one- or two-dimensional system, strong changes in its electronic and magnetic properties are expected. The latter show a tendency to evolve towards those observed in the atomic limit because of the reduced coordination number and larger interatomic distance as compared to a bulk. This is accompanied by a sharp reduction in 3d electronic states hybridization and charge fluctuations i.e. strongly enhanced electron correlations.

Modifications in the electronic properties in 3d transition metals reflect in the appearance or enhancement of correlation satellites in core level and valence band photoemission and in Auger spectra [30–33]. Since the valence band width of 3d metals progressively decreases moving from left to right of the 3d series, also the strength of the electronic correlations increases in the same direction. In Ni, Cu and Zn, at the end of the 3d series, the satellites are easily observed in the bulk form [30, 31], while in Fe and Cr the two holes satellites have been observed only by Hüfner et al. using resonant photoemission [33], after their absence was asserted for years [34–36].

A reduction of the dimensionality of the systems is expected to enhance electronic correlations. In Mn strong correlation satellites have been shown to appear when 3d hybridization is reduced by growing single layers on Ag(001) [37]. In a previous experiment it has been shown that on the Fe/Cu(001) system the valence band holes lifetimes are affected by changes in the Fe atomic environment [38]. In the mentioned studies, however, metals have been used as substrates, with non negligible hybridization between overlayer and substrate states. Therefore the use of an inert oxide like MgO as a substrate can determine an increase in the modifications of the electronic structure in the reduced dimensionality.

A consequence of the reduced dimensionality is the formation or enhancement of local magnetic moments. The reduction of the coordination number reduces the electronic delocalization and the crystal field contribution, causing an increase in the magnetic moments, particularly of the orbital moment $m_L$. The orbital magnetization via the spin-orbit interaction connects the spin magnetization to the atomic structure of a magnetic material, giving rise to magnetic anisotropy. The knowledge of the dependence of these effects on system dimensionality, lateral size and substrate interaction can be useful to find applications for example in data storage technology. Some examples are shown in the works of P. Gambardella and coworkers [39, 40]. The first work points to the study of the magnetic properties of Co monatomic chains grown on Pt(997) [39]. By means of X-ray Magnetic Circular Dichroism (XMCD) the authors evidence the presence of an increased orbital magnetic moment. This determines an increase in the magnetic anisotropy energy to 2 meV/atom as compared to the value of 40 $\mu$eV for a bulk hcp Co.
The same effect becomes stronger reducing further the dimensionality to 0D, where Co atoms
on Pt(111) show a magnetic anisotropy energy increased to 9.3 meV [40]. The origin of this
effect consists not only in the reduction of the coordination number of an atom adsorbed on a
surface, but also in the strong spin-orbit splitting of the Pt 5d states, that adds an additional
anisotropy component. Increasing the cluster size the orbital magnetic moment decreases rapidly
approaching the quenching and consequently the magnetic anisotropy energy breaks down while
the system moves toward the bulk situation.

When the cluster size increases to such extent that the electronic configuration is almost
bulklike and the coordination does no more play a role, another important effect appears. The
reduction in the size, and therefore in the volume, of a nanostructure from a bulk to a cluster pro-
duces a decrease in the magnetic order due to thermal fluctuations that become more important.
When the nanostructure ferromagnetism is destroyed by temperature, the system becomes superparamagnetic. The limiting temperature under which the magnetic order is restored is called
blocking temperature. It has been shown in fact that 1D Co chains have short-range order at 45
K, where the system is superparamagnetic and it is made of blocks of exchange-coupled atoms,
with unstable magnetic orientation due to thermal fluctuations [39]. Decreasing the temper-
ature to 10 K, also the long-range order is visible, due to the alignment of the blocks. The
influence of the substrate can play an important role also in the case of superparamagnetism.
The coupling between a ferromagnet (FM) and an antiferromagnet (AF), called exchange bias,
can in fact add an additional component to the anisotropy of FM nanoparticles, increasing the
blocking temperature and improving therefore the thermal stability of the moments. It has been
shown that FM Co particles embedded in a paramagnetic matrix of C or Al₂O₃ show a blocking
temperature of 10 K [41]. The same particles embedded in an AF matrix, namely CoO, show
an increase of the blocking temperature up to 290 K, the Néel temperature of CoO. When the
AF becomes paramagnetic over its Néel temperature, the FM loses its anisotropy source and
thus the magnetic order. The same approach should hold also for FM nanoparticles deposited
on an AF film, such as in the case of Fe deposition on NiO.

However another interesting perspective is the study of the metal properties avoiding the
influence of the substrate. In this case the properties observed will depend only on the reduced
dimensionality. This can be achieved by the use of an inert substrate, such as a stable oxide like
MgO, both in form of a bulk or a film, that has the advantages provided by the presence of a
metal substrate underneath (use of electron-based techniques), without a strong coupling with
the metal nanostructures.
Chapter 2

Experimental apparatus and procedures

The main part of the results presented in this work have been obtained at the SESAMO laboratory at the University of Modena and Reggio Emilia. Therefore a description of the experimental apparatus used in the laboratory is given in Sec. 2.1, together with a brief description of two electron diffraction techniques, Primary-beam Diffraction Modulated Electron Emission (PDMEE) and X-ray Photoelectron Diffraction (XPD), performed in Modena. In Sec. 2.2 the apparatus used for the measurements of MgO/Mo shown in Sec. 4.2, is described. This experiment was in fact performed in Berlin, at the Chemical Physics Department of the Fritz-Haber-Institut of the Max Planck, in collaboration with the group of Prof. H.-J. Freund and Dr. N. Nilius. In that section the Photon Emission Spectroscopy technique, performed in Berlin, is also briefly introduced.

2.1 Experiments at SESAMO

In Modena at the SESAMO laboratory a UHV system is available for the cleaning procedures, growth and analysis of the samples. The system, shown in Fig. 2.1 and 2.2, is composed of four chambers, connected in UHV conditions with transfer drivers that permit to carry the samples from one chamber to the other.

The main chamber is equipped for chemical and structural analysis and for the preparation of the clean substrates. A load-lock allows the introduction of substrates without breaking vacuum. The chamber is pumped by an ion pump cooled with liquid nitrogen and by a system of turbo-molecular pumps (SEIKO SEIKI 300, Varian V70D) and a diaphragm pump. A typical background pressure for this chamber is $1 \times 10^{-10}$ Torr, which can be further lowered to $3 \times 10^{-11}$ Torr by an accurate use of nitrogen cooling of the ion pump.

A high precision manipulator with five degrees of freedom, three for translation (x, y, z)
and two for rotation ($\theta$, around the manipulator axis, and $\phi$, around the normal to the sample) provides the movements through the chamber. All the manipulator movements are driven by stepping motors controlled by a computer. The manipulator can be cooled down to liquid nitrogen and heated up to $\sim 1200$ K. Facilities to prepare the surface are also available, like an ion gun for sample cleaning. One side of the chamber is equipped for evaporation with an e-beam evaporator and a quartz microbalance.

The chamber is equipped for analysis with:

- A cylindrical mirror analyser (PHI 590A) operating in the first derivative mode, with a coaxial electron gun (LaB$_6$ filament). This analyser is used both for Auger Electron Spectroscopy and PDMEE. The beam incidence direction is varied by moving the sample in front of the analyser with an accuracy of $\pm0.1^\circ$. The centre of the sample is automatically kept in the focus of the electron beam, during sample rotation, via software.

- A conventional non-monochromatic Mg-Al twin anode X-ray source and a conventional He UV lamp.

- A Concentric Hemispherical Analyser Omicron EA125 for XPS and UPS, which has a set of seven channel electron multipliers. This analyser can achieve a maximum energy
resolution of 0.6 eV (pass energy 20 eV) for XPS and 0.03 eV (pass energy 5 eV) for UPS. Photoelectron diffraction measurements are also allowed thanks to the high precision manipulator.

- A three-grid Omicron LEED apparatus with a LaB$_6$ filament. Diffraction pattern are recorded on a computer controlled 16 bit CCD camera (Apogee ALTA U2000). The sample surface can be positioned at the LEED working distance with an accuracy of ±0.01 mm.

The main part of the materials grown for this work, both metals and oxides (apart from Fe), have been prepared in the growth chamber. This is kept in UHV at a typical pressure of $5\times10^{-11}$ Torr by means of an ion pump that can be cooled with liquid nitrogen. A manipulator with five degrees of freedom moves the sample from the transfer position to the evaporation position in front of the cells and is equipped with a filament to heat the sample up to 1200 K.

The chamber contains five Knudsen cells for the evaporation of metals. They are equipped with a shutter, that can be mechanically opened to start and stop abruptly the metal deposition. A quartz microbalance is used to calibrate the metal flux. The oxide deposition rate was estimated by the measured metal flux and taking into account the density of metal atoms in the oxide. A further check of the deposition rate was made by quantitative XPS or Auger analysis. A gas inlet terminated by a nozzle provides the O$_2$ for oxide deposition. The gas line is pumped by a scroll pump.

![Figure 2.2: Drawing of the main, the connection and the STM-AFM chambers in the SESAMO laboratory.](image_url)

A separate chamber has been built for the Omicron RT STM-AFM apparatus. The chamber
has a typical pressure of $5 \times 10^{-10}$ Torr, and is pumped by an ion pump with a Ti sublimation pump. The STM-AFM is equipped with a stage for the storage of samples and tips. The STM is insulated by external vibrations by suspension with springs and Eddie currents. For the STM images acquired with this apparatus etched W tips have been used.

The AFM has been used in contact mode, using Si or silicon nitride cantilever tips. The feedback signal is the component of the interaction force perpendicular to the surface. The deflection of the cantilever is measured by detecting the deflection of a laser beam reflected by the back of the cantilever onto a position sensitive detector.

The fourth chamber is the connection chamber between the main and the STM chambers (see Fig. 2.2). It is also equipped with a heating stage, that can reach 1800 K by electron bombardment, and a gas line, to perform annealing in gas partial pressure.

**Electron diffraction**

Electron diffraction is one of the most used techniques in the work of this thesis. Therefore I will give here a general description of two of these techniques, Primary-beam Diffraction Modulated Electron Emission (PDMEE) and X-ray Photoelectron Diffraction (XPD). An exhaustive review on the more commonly used LEED technique can be found in Ref. [42].

![Figure 2.3: Basic processes involved in incident (left) and excident (right) electron scattering. Only single scattering is indicated for simplicity [43].](image)

XPD and PDMEE are based on the modulated electron emission, where the spatial modulation of a primary electron wave (incident electrons or outgoing photoelectrons) in a solid is due to the interference with the scattered waves centred on its neighbours. The strongest modulations are given by the forward focusing effect, that allow the identification of the high symmetry
axes of the crystal structure. The forward focusing is the strong enhancement of the wave in the forward direction for kinetic energies (KE) in excess of several hundreds of eV. When the forward direction corresponds to a dense atomic chain, an increase in the intensity is observed, leading to a pronounced feature in the intensity modulation at the corresponding incidence or emission angle, depending on the geometry [43].

The difference between the two techniques is in the role of detectors and emitters. In PDMEE the incident wave flux produced by a collimated electron beam is modulated in the region below the surface by the focusing interference process described above. The atoms of the solid can be considered as localized detectors of such a modulated flux resulting in a marked dependence of the electron emission yield on the electron incidence angle. In this case integration over a large take-off angle is required to prevent the outgoing electron diffraction to contribute to the measured intensity modulation. Therefore a cylindrical mirror analyser is used for PDMEE.

On the contrary, in XPD a photon illuminates an emitting atom at or near the surface and an electron from a core-level is ejected to a detector far away from the surface. The photoelectron wave can reach the detector both by direct propagation and via a number of scatterings from atoms in the neighborhood of the emitter. The quantum interference (diffraction) between the different pathways depends sensitively on the relative atomic positions and the intensity measured as a function of the emission angle includes information about the atomic structure around the emitter. In this case only the outgoing electron diffraction contributes to the IAD, therefore an angle resolved analyser, like a hemispherical analyser, is necessary.

For a preliminary analysis, the parameters that can be extracted from these electron diffraction plots are the anisotropy and the peak positions.

The anisotropy of forward focusing peaks is a property of the crystal, depending both on the chemical composition of the sample (the scattering factors of the atoms) and the geometrical arrangement of atoms (number of scattering centres in a row, their alignment and relative distance). Therefore anisotropy is a good parameter to test the crystalline quality of the films grown epitaxially. The anisotropy is defined as

$$A = \frac{2(I_{\text{max}} - I_{\text{min}})}{I_{\text{max}} + I_{\text{min}}}$$

where $I_{\text{max}}$ ($I_{\text{min}}$) is the maximum (minimum) signal intensity of the considered feature. Due to multiple scattering effects the first few scattering atoms along the row are focusing, the following are defocussing. The number of atoms involved depends on the KE and on the emitter-scatterer distance. Therefore in a thin film a reduced anisotropy can be related not only to the reduced crystalline order, but also to the small number of scatterers.

The peak position indicates the orientation of the considered atomic row within the crystal lattice. The growth of thin crystalline films on a crystalline substrate is epitaxial when there is a unique geometrical relationship between the two structures. The overlayer can be of the same material of the substrate (homoepitaxy) or different for composition or structure (heteroepitaxy). Heteroepitaxy of thin crystalline films usually forces the unit cell of the film to match the substrate one. This is called pseudomorphic growth. In general the film unit cell and the
substrate cell can differ in the angle $\varphi$, in the length of the interatomic distances $a_1$ and $a_2$ and in the ratio of the sides $a_1/a_2$ (Fig. 2.4a). In particular in this work only cubic structures are considered, where the substrate and overlayer cells have the same angle and sides ratio and differ only by a scale factor. The parameter that evaluates this difference is the lattice mismatch $m$, defined by Eq. 1.1. Pseudomorphic growth creates a deformation of the film lattice, since the in-plane and the out-of-plane parameters are not deformed in the same way. The in-plane parameter $a$ can be determined by means of LEED, while the out-of-plane parameter $c$ is related to the peak position of the main forward focusing feature in XPD and PDMEES plots along the [100] azimuth (Fig. 2.4b):

$$\tan \theta = \frac{a}{c}.$$  

(2.1)

If the lattice cell is cubic, then $a = c$ and $\theta$ is 45°. If the film is tetragonally distorted, $a \neq c$ and $\theta$ deviates from 45°. This deviation can be measured on XPD and PDMEES plots with an accuracy of 0.2°, therefore leading to the determination of the out-of-plane parameter, when $a$ is known.

These techniques offer many advantages.

First of all they are surface sensitive and give information only about the topmost layers. The advantages with respect to other surface diffraction techniques, like LEED, are that they give information on the structure in direct space and not in reciprocal space. Additionally they do not need a long-range order, because they sample the local environment of atoms.

Both techniques exploit the chemical sensitivity of Auger and photoelectron spectroscopy. Therefore they can probe the local structure around different atoms that form the lattice.

The differences between the two techniques are mainly related to the kinetic energy of the primary waves. PDMEES has a primary beam of some KeV (2-5 KeV), leading to a stronger focusing and therefore to narrower peaks. Thus the accuracy in the determination of the peak

Figure 2.4: (a) In-plane and (b) out-of-plane view of the lattice cell of a cubic crystal.
positions from PDMEE plots is higher than from XPD. The latter can provide comparable peaks if high-energy photons are employed. In this case the photoelectrons have a high KE, but the probing depth is higher than in PDMEE and therefore less surface sensitive. However XPD can resolve intensity modulation from atoms of the same element in different chemical states. It is therefore useful to study for example interfaces that show chemical reactions and intermixing (see Sec. 6.1 and 6.2).

In order to obtain a complete and precise description of the crystal structure investigated, simulation codes can be developed for XPD and PDMEE plots. The simulation codes for PDMEE plots available [43] include only single scattering processes and therefore overestimate the anisotropy and do not give information on the higher order diffraction features. This is the reason why no PDMEE simulations have been made in this work. On the contrary the MSCD (Multiple Scattering Calculation of Diffraction) code [44] has been used to interpret the XPD spectra.

The energy- and angle-resolved photoemission intensity $I(\vec{k}, \theta, \phi)$ at the detector can be written in general as

$$I(\vec{k}, \theta, \phi) \propto |\psi_0 + \sum_j \psi_{sj}|^2 \quad (2.2)$$

where $\vec{k}$ is the final electron wave vector, $\theta$ and $\phi$ are the polar and azimuthal angles of photoelectron emission respectively, $\psi_0$ is the wave-component travelling directly to the detector and $\psi_{sj}$ are the wave-components travelling via paths involving single or multiple scattering by one or more atoms. The multiple-scattering order is defined as the number of scattering atoms in a path: $j = 1$ represents single scattering, $j = 2$ is double, etc. Higher-order scattering processes are less important because of the roughly $1/r$ falloff of the outgoing distorted spherical wave represented by $\psi_0$, damping due to inelastic processes and loss of diffraction modulation due to thermal vibrations (Debye-Waller effects). The explicit sum in Eq. 2.2 includes all possible scattering paths inside the solid. The multiple-scattering expansion for spherical scatterers is conveniently formulated in terms of diagonal plane wave scattering t-matrices with elements $t_l = \sin(\delta_l) e^{i\delta_l}$ and matrix elements of the free propagator $G_{L,L'}(\vec{\rho}) = \langle L, \vec{R} | G | L, \vec{R}' \rangle$ with an angular momentum $L = (l, m)$ and in the site basis $|L, \vec{R}\rangle$. $\vec{\rho} = k(\vec{R} - \vec{R}')$ denotes the dimensionless vector between two sites and $k = |\vec{k}|$ is the wave number. The exact multiple scattering expansion of the propagator successfully calculates the photoelectron diffraction intensity, but requires large computing times for large clusters. The MSCD code reduces the computational time introducing an exact separable representation of the free propagator matrix elements based on the Rehr-Albers (RA) theory [45]. This representation introduces an approximation that reduces the matrix sizes, therefore reducing the computational time. A more detailed description of the theory used in the code can be found on the website$^1$.

Experimental apparatus and procedures

The approximation parameters that can be optimized are the RA approximation order, multiple scattering order and the pathcut. Ref. [44] reports a study of these parameters. Here we briefly summarize the information necessary for this work.

The RA approximation order decides of the size of the matrices representing the propagator and the scattering amplitude. As a general rule, it can be stated that the optimal order is the \((l + 1)\)-th, where \(l\) is the angular momentum of the photoelectrons.

The multiple scattering order \(n_{\text{max}}\) indicates the maximum scattering order considered in the simulation. For \(n_{\text{max}} \geq 6\) the approximated simulations are almost identical to the exact ones. In this work a \(n_{\text{max}} = 8\) has been chosen.

The pathcut \(P\) permits to exclude paths of the multiple scattering that are almost irrelevant. The code considers all the possible scattering centres. Then all the elements of the scattering amplitude matrix less than \(P\) times a reference element are excluded from the calculation, neglecting all the corresponding scattering paths. Studies of the accordance between approximated and exact calculations determined an acceptable value of \(P = 0.001\). In the present work a value of \(P = 0.01\) has been chosen, good enough when \(\text{KE} > 100\ \text{eV}\) and reducing further the simulation times.

Additional input parameters are the cluster size, the inelastic mean free path (IMFP), the temperature that accounts for vibrational effects and the inner potential.

The limited cluster size is justified by the fact that inelastic attenuation of the signal permits to neglect atoms far enough from the emitter. Small clusters speed up the calculation, but give less contribution to the higher order diffraction features. Simulations reported here involve large clusters with about 300 atoms. The cluster is defined as an ellipsoid with radius \(r\) and depth \(h\). The radius is chosen around 10 Å, while the depth is around 25 Å, depending on the number of layers considered and in order not to exclude important scattering atoms.

Inelastic scattering contributions are accounted for by the electron Inelastic Mean Free Path (IMFP), calculated by means of the TPP-2M formula [46].

Thermal vibrational effects are described by the Debye-Waller attenuation factor

\[
W_j = e^{-k^2(1-\cos \theta_j)\frac{\hbar^2 T_m}{2m k_B}}
\]

with \(\Theta_D\) the Debye temperature and \(\theta_j\) the scattering angle.

The inner potential represents the physical kinetic energy lost when the electron travels from the scattering potential edge to the detector. Thus it is approximately the sum of the work function and the valence bandwidth.

The accordance between measured and calculated XPD plots has been evaluated by means of the R-factor

\[
R = \frac{\sum_i (\chi_{ci} - \chi_{ei})^2}{\sum_i (\chi_{ci}^2 - \chi_{ei}^2)}
\]
where $\chi(\theta) = [I(\theta) - I_0(\theta)]/I_0(\theta)$, with $I(\theta)$ the photoemission intensity as a function of the angle $\theta$, $I_0(\theta)$ a background appropriately chosen, $\chi_{ci}$ and $\chi_{ei}$ the $\chi$ curves calculated and measured respectively.

2.2 Experiments at FHI

Experiments at the Chemical Physics Department of Fritz-Haber-Institut in Berlin have been performed in two UHV chambers connected by a transfer drive.

The first chamber is equipped for the cleaning procedure and the film growth. It is pumped by a system of turbo-molecular pumps that lead to a base pressure of $P < 2 \cdot 10^{-10}$ mbar. This chamber is equipped with a manipulator with four degrees of freedom, three for translation and one for rotation ($\theta$, around the manipulator axis). For the substrate preparation an ion gun for sample cleaning and a heating stage that can reach about 2300 K are present. The sample temperature is measured by means of an optical pyrometer put outside of the UHV chamber in front of the annealing stage. For the film growth two evaporators are used, filled with different metals for the growth of the metal itself or for the deposition of the oxide by reactive growth. A gas inlet for O$_2$ terminated by a nozzle completes the growth apparatus. The chamber is also equipped with a three-grid LEED system.

The main chamber is the STM chamber. It is equipped with a home-made beetle type STM. To maximize the acceptance angle for the detection of photons emitted by the electron injection from the tip, STM has the open construction shown in Fig. 2.5b. The microscope head is completely surrounded by a parabolic mirror, with the tip-sample region placed in the focal point, which collects the photons emitted from the tunneling junction. Outside the vacuum chamber, the light is focused by a second mirror on the entrance slit of a grating spectrograph and detected with a liquid nitrogen cooled CCD camera. Due to the large acceptance angle of the optical system and the high quantum efficiency of the CCD chip, detection and spectral analysis of extremely small photon intensities is achieved down to some hundred photons per second. The accessible energy range for photon detection is between 1 and 6 eV and is restricted by the performance of the CCD-chip [47].

**Photon emission spectroscopy combined with STM**

Conventional electron and optical spectroscopies are limited in the lateral resolution and average the results over macroscopic areas. The use of STM based spectroscopies overcomes this obstacle, leading to the possibility to have information about the single nanostructure or surface region. The concept of the Photon-STM (PSTM) [48] technique is to use the tip of a STM as a source of low-energy electrons to locally excite photon emission and thus to study luminescence phenomena on nanometer-sized features of surfaces and nanostructures (schematic drawing in Fig. 2.5a).
This method offers several advantages. First, photons can provide a wide range of information, due to the high intensity and spectral distribution accessible by sensitive optical methods. Second, the emission of visible or infrared light is a chemical specific characteristic of many excitations of solids and molecules. Finally, the tunneling current in the STM as an excitation source has a lateral extension in the nanometer range and the distance between tip and sample can be controlled with high precision.

Significant photon emission was observed in two distinct ranges of tip bias voltages. For $V > 100$ V the field emission regime is present, where electron emission is essentially determined by the enhanced electric field at the tip resulting in a propagating electron impinging on the surface. For $V < 50$ V the emission occurs in the proximity-field regime, while for $V < 4$ V it is stimulated by the tunneling current.

On metal surfaces the injected electrons produce electromagnetic radiation via transition radiation, surface plasmon excitation and bremsstrahlung. In particular in the proximity-field and in the tunneling regime the reduced distance between tip and sample induces an interaction between the two bodies, called tip-induced plasmon. The wavelength of the emitted light is longer than the tip-sample distance in the tunneling regime. Therefore the resulting electro-
magnetic coupling of tip and sample is expected to cause new emission, not observed in the far field emission regime. The excitation mechanism is the inelastic tunneling in the tunneling gap. On semiconductors the excitation mechanism for photon emission is the hot-electrons decay creating a hole by impact ionization, therefore leading to emission from electron-hole pair recombination and in general from transitions between impurities, excitonic states and electronic bands. No influence of the STM tip was identified on these materials.

The emitted photons and thus the optical properties can be measured in different ways. The first one is the collection of wavelength resolved luminescence spectra, that contain direct information on the emitting transition. In this case the detection implies the use of a grating spectrometer, that reduces the sensitivity. Therefore the STM construction and the tip shape are of fundamental importance. They should avoid to act as an obstacles and reduce as much as possible the loss of photons along their path from the sample surface to the spectrometer. The other way is the simultaneous acquisition of topographic data and of photon intensity for each pixel of the image in a constant-current mode, by the use of a photomultiplier. This are called photon maps and permit to identify the regions where the photon emission takes place, correlating them with topographic data. In this case the photons are not wavelength resolved.

In the experiment presented in Sec. 4.2, field-emitted electrons from the tunnel tip are injected into the sample surface. The electron energies are typically adjusted between 300 and 50 V and the electron current is around 1 nA. The spectra collected are wavelength-resolved and the light emission mechanisms are discussed in relation to the properties of the material considered.
Chapter 3

MgO stepped surfaces

The first way to pattern an oxide surface presented in this work is the preparation of stepped surfaces.

As already discussed in Sec. 1.2, the interest for vicinal surfaces has been very strong in the last years, due to the wide possibilities offered by this kind of substrates. However this has always been focused mainly on metals and semiconductors. Few studies of insulating vicinal surfaces are reported on TiO$_2$, Al$_2$O$_3$, NaCl and MgO. Nevertheless in the latter case no deep investigation of the morphology has been reported to my knowledge. Insulators are more difficult to prepare, due to the reduced mobility of atoms. However, if suitably chosen, they can serve as inert supports for the growth and the study of metal 1D nanostructures. If the interfacial interaction between the metal and the insulator is small, then the electronic and magnetic properties can be considered as characteristic of the reduced dimensionality of the metal, with a negligible influence from the substrate.

Here we present the procedure to prepare a stepped surface from a bulk MgO(001) in form of a paper submitted to Surface Science. The procedure does not give an actual vicinal surface, if for vicinal we mean the presence of monatomic steps. In any case, samples are characterized by the presence of a quite regular array of steps. In spite of their non-monatomic steps, they provide a one-dimensional pattern, where the self-organized growth of some 1D 3d metals (such as Fe) can be investigated.
3.1 Preparation and characterization of MgO stepped surfaces

S. Benedetti, P. Torelli, P. Luches, E. Gualtieri, A. Rota and S. Valeri
Surf. Sci., in press

Abstract
We present a study of the preparation procedure for stepped MgO surfaces which can be used as templates for the deposition of metallic nanostructures. A cleaved sample of MgO(001) was mechanically polished to reach the desired miscut angle along the [110] direction. Then a thermal annealing was performed. The effect of an intermediate chemical etching has been also studied. The surface was analyzed by means of contact AFM in air, LEED and XPS in UHV. The role of the chemical etching and the dependence of the final morphology on the annealing time and temperature were investigated. The influence of the miscut angle on the final surface topography is also briefly discussed.

Introduction
Stepped surfaces provide interesting substrates for the growth of self-assembled nanostructures because of the presence of a high density of periodic defects arranged in a regular step structure over distances significantly larger than the substrate lattice constant. The main interests and applications are driven by the enhanced chemical reactivity and nucleation ability of the steps [49–51], that make these surfaces appealing as templates for the growth of nanostructures by selective step decoration [52, 53]. The presence of arrays of steps deeply influences the electronic, magnetic and transport properties of the stepped surface itself [54] and also the properties of the films grown on top of them, because of the lateral confinement of the overlayer induced by the substrate [39, 55]. The preparation of this kind of templates is therefore important because it allows the creation of controlled structures with a lateral size in the range of some nanometers. The substrate patterning will involve macroscopic areas, allowing the use of non-spatially-resolved analytical techniques.

In particular, stepped MgO surface is a good candidate for the growth of “self-standing” magnetic metallic nanowires, in particular Fe. MgO is a non magnetic insulator with a negligible electronic interaction with Fe, showing no significant oxidation-reduction reaction at the interface [56, 57]. The small lattice mismatch with Fe will favour the growth of epitaxial single crystalline nanostructures. Preparation procedures of oxide substrates, to be employed for film or nanostructure growth, have already been reported for flat MgO(001) surface [58, 59] and other insulating oxides, e.g. Al₂O₃ and NaCl [60–62]. In particular S. S. Perry et al. [63, 64] investigated the morphology of the flat MgO surface at each step of the preparation. Similar procedures have also been used for the preparation of miscut MgO [3–5], but in these
cases the surface morphology has never been investigated in details by means of scanning probe
microscopies.

In this work we discuss the preparation of stepped surfaces with a miscut angle of a few
degrees with respect to the (001) crystal plane. We define the miscut direction as the direction
perpendicular to the steps that will form on the surface due to the miscut. Since we are interested
in the application of such substrates for the growth of Fe nanowires, we have chosen the miscut
direction aligned with the [110] of the (001) oxide surface (see Fig. 3.1). This orientation
corresponds to the [100] orientation of crystalline Fe films deposited on top of the oxide [57].
Starting from a preparation procedure similar to those reported in literature [63, 64], we have
studied the morphology of stepped MgO surface at each preparation stage and in particular
as a function of annealing temperature and time, and miscut angle. The different results are
compared and discussed. The contamination and the crystalline order are also discussed at every
step of the procedure, in order to obtain surfaces chemically and structurally comparable to the
bulk oxide.

**Experimental**

![Figure 3.1: Illustration of the surface obtained with the polishing procedure described in the Experimental
section. The thin solid lines indicate the cleaved MgO crystal, while the thick solid lines are the final surface with
a miscut of α degrees with respect to the (001) plane along the [110] direction.](image)

The MgO samples used in the experiment were cleaved from a cube of bulk MgO(001). The
mechanical polishing was performed by mounting the MgO crystal on a stainless steel block
with a slope corresponding to the desired miscut and by using different alumina pastes till a
final particle size of 0.05 µm. The crystal was polished with a miscut of 2° and 6° with respect
to the (001) surface plane, with the miscut direction along the [110] direction (Fig. 3.1). The
mounting system is affected by an uncertainty in the alignment of the miscut direction of ± 3°
with respect to the [110] direction. After polishing the sample was cleaned in organic solvent.
The subsequent thermal annealing was performed in a quartz tube oven in a flux of 50% oxygen
and 50% nitrogen. The samples were thermally heated at a rate of 10 K/min up to the annealing temperature. Afterwards they were annealed for a time between 30 and 360 minutes. Finally they were slowly cooled down at a rate of 5 K/min to room temperature. Before the annealing, a few samples were chemically etched for 30 s in 85% w/v H$_3$PO$_4$ and rinsed in de-ionized water.

The surface topography was studied using an Omicron UHV AFM-STM apparatus operated in AFM contact mode in air at room temperature. Chemical and structural characterization was performed in an UHV chamber (base pressure of 6·10$^{-11}$ Torr) using XPS and LEED apparatus, respectively. For the XPS a non-monochromatic X-ray source and a hemispherical analyzer at a normal take-off angle were used. The analyzer was operated at its lowest angular resolution ($\Delta \theta = \pm 10^\circ$), in order to partly average out possible intensity modulations due to photoelectron diffraction. Mg-K$\alpha$ photons were used for the contaminants quantification, in order to prevent the excitation of Mg 1s electrons and the appearance of the Mg KLL peak at around 300 eV of BE, that could have prevented the quantitative analysis of the Ca 2p peak. For the O 1s and Mg KLL peaks acquisition for the determination of the stoichiometry, Al-K$\alpha$ photons were employed. LEED analysis was performed using a rear-view, three-grid apparatus and diffraction patterns were recorded using a computer-controlled CCD camera.

**Results and discussion**

In the first approach MgO stepped surfaces were prepared following the three-step-procedure reported in literature [63, 64]. After the cleavage MgO(001) samples were mechanically polished at a miscut angle of 2°, to minimize the interaction between steps, with the miscut direction aligned with the [110] of the oxide surface (Fig. 3.1). Fig. 3.2 shows the surface topographies according to the steps of the preparation procedure as discussed in the following. In Fig. 3.2a and 3.2c, the AFM images taken before and after the polishing are shown respectively. The values of roughness are listed in Tab. 3.1. Roughness is calculated as the standard deviation of the heights on the whole 1000×1000 nm$^2$ image considered. The polished surface is characterized by a roughness of 0.4 nm, larger with respect to the cleaved sample, and is completely covered by small clusters with a mean diameter of 20 nm. No terraces are observed. The LEED after the polishing (not shown here) shows a p(1x1) pattern with broader spots and more intense background with respect to the cleaved surface (Fig. 3.2b), indicating a reduced but still present long range order. The second step was a chemical etching in H$_3$PO$_4$ for 30 s and successive rinsing in water, in order to remove the impurities left on the surface by the mechanical polishing [59]. The AFM image after the etching (Fig. 3.2d) shows the presence of big round clusters of 80 nm in diameter homogeneously distributed all over the surface and determining a surface roughness of 3.7 nm. These preparation steps produce images comparable to those previously reported in literature for the same preparation procedure applied to flat MgO(001) surface [63]. Therefore, no difference can be identified before the annealing between a miscut and a flat (001) surface. Parallel to the AFM study a chemical analysis was also performed, in order to determine
the surface contamination level induced by the preparation procedure described before. XPS indicates the presence of a 5% of C as contaminant, coming from the solvents used to remove part of the polishing material. The chemical etching does not reduce the contamination of C.

**Figure 3.2:** AFM images (1000×1000 nm²) of 2° MgO miscut surfaces after: (a) cleavage, (c) polishing, (d) chemical etching, (e) annealing at 1270 K 30 min, (f) annealing 1470 K 30 min. (b) LEED image of the MgO cleaved surface shown in (a) (Ep=235 eV).

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<td>-</td>
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<tr>
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<td>-</td>
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<td>20</td>
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<td>-</td>
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<td>30</td>
<td>3.20</td>
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**Table 3.1:** Parameters characterizing the MgO surface at each preparation step, including etching. The first column reports the treatment, the second and third the annealing parameters when performed, the fourth the roughness of the surface. The last column indicates the size of the clusters on the surface.
To restore the crystalline order and favour the rearrangement of the surface the samples were annealed at high temperature in a mixed O₂ and inert gas (N₂) atmosphere, as described in previous section. The dependence of the final morphology of the etched surfaces on the annealing was investigated and the resulting values versus temperature and time are reported in Tab. 3.1. Because of the large roughness generated by the etching, no reorganization is evident for annealing temperatures below 1270 K. In Fig. 3.2e the morphology of the sample after 30 min annealing at 1270 K has the characteristics of the as-etched sample. It is necessary to anneal at least for 30 min at 1470 K to obtain some surface steps aligned along the [110] direction of the MgO crystal surface (Fig. 3.2f). However, the presence of a large amount of clusters, reminiscence of the etching, is still increasing the roughness and breaking the regularity of the steps. The chemical composition at the end of the preparation shows the presence of a small quantity of Ca and B, the main contaminants of bulk MgO that segregate after prolonged annealing at temperatures above 1170 K [65, 66].

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<td>41±6</td>
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**Table 3.2:** Parameters characterizing the MgO surface at each preparation step, obtained without chemical etching. The first column reports the treatment, the second and third the annealing parameters when performed, the fourth the roughness of the surface. The last two columns indicate the size of terraces and steps, when observed.

To a second approach a different procedure was exploited, that bypassed the etching step. The large roughness created by the chemical etching in fact requires very high temperatures and long time to reorganize the surface, therefore increasing the quantity of Ca on the surface without a significant reduction of the amount of C. Bypassing the etching it is then possible to reduce the subsequent annealing temperature and time and, as a consequence, the step bunching [5, 58]. Furthermore, for the samples annealed directly after the polishing, the contamination is the same for identical annealing conditions. The evolution of the simply polished, non-etched surface with annealing temperature and time is shown in Fig. 3.3. The parameters characterizing this evolution are listed in Tab. 3.2. After heating 30 min at 1120 K, the topography remained almost unchanged (Fig. 3.3b). A temperature raise to 1220 K was sufficient to make steps appear on the surface, aligned perpendicular to the miscut direction (Fig 3.3c). Here the terraces are
50 nm large and the step height varies between 0.5 and 1 nm that means 2 to 5 atomic layers. Nevertheless, the surface morphology is still inhomogeneous because of the large terrace width distribution and the breaking of the steps at a length of about 500 nm. A further step to 1270 K produced a more regular surface with narrower terrace width distribution (Fig. 3.3e). If the annealing time was raised to 60 minutes (Fig. 3.3f), we observed a further improvement in the regularity of the steps, although terraces were still comparable in width and length to the previous stage. This suggests that a strong annealing is necessary to increase the mobility of the surface atoms. Areas up to 10×10 μm² are found free of irregularities. Finally, increasing the annealing time to 360 minutes led to an equilibrium condition and longer annealing does not change further the morphology. The surface was characterized by steps longer than 1000 nm. In those conditions, the terraces doubled their width and considerably increased the step height up to 5 nm (Fig. 3.3g and Tab. 3.2). The corresponding LEED pattern is shown in Fig. 3.3h and is as good as that obtained on the cleaved sample, indicating that the crystallinity of the surface is still comparable to the bulk. Terrace width as small as 20-30 nm was reported by H. Zheng et al. [5] for a 2° miscut surface of MgO. The reduced terrace width with respect to the present work is probably ascribable to the shorter annealing (1370 K 10 min), that reduces further the step bunching. Results in Ref. [5] confirm the trend of the step bunching with increasing annealing.
time we observe in the present work, indicating that annealing conditions are fundamental to
determine the final surface topography.

In order to determine if the structures described above depend also on the miscut angle, we
prepared a sample with 6° miscut in analogous annealing conditions (1220 K 30 min, Fig. 3.3d,
last row of Tab. 3.2) to the non-etched sample reported in Fig. 3.3c. The terrace width is now
slightly smaller but their distribution is clearly narrower. Because of the similar terrace width,
the steps are higher than for the 2° miscut surface, to preserve the higher miscut angle.

Figure 3.4: O1s spectra taken after polishing and after annealing are shown normalized to the intensity of the
peak measured on a clean MgO. The shoulder on the high binding energy side of the main peak appears after the
polishing and is assigned to OH⁻ groups. It progressively disappears during the annealing. In the inset the Mg
KLL lineshape for a clean bulk and a polished and annealed sample are shown.

In order to investigate the stoichiometry of the sample, we performed XPS measurements
after the annealing. In Fig. 3.4 the O 1s and Mg KLL peaks for a clean bulk MgO and a
sample annealed up to 1220 K for 30 min are shown. The relative intensities of the two XPS
peaks are comparable in the two cases, indicating that the annealed sample is stoichiometric. In
Fig. 3.4 A change in the O1s lineshape with respect to a clean MgO(001) surface is evident for the different procedure stages. After the polishing a shoulder is present, shifted by about 2 eV to the high-binding-energy side of the main peak, assigned to OH$^-$ groups chemisorbed at the oxide surface [67–69]. The mechanical polishing was in fact performed using an aqueous solution for the alumina pastes. The annealing progressively decreases the intensity of this component that almost disappears after 30 min at 1220 K and restores the complete cleanliness of the oxide surface after 360 minutes at 1270 K.

Conclusions

We obtained a stepped (001) MgO surface by a preparation procedure based on cleavage, mechanical polishing at 2° miscut angle along the [110] direction of the (001) plane and a thermal annealing. The surface shows a quite regular array of steps, whose morphology depends on the annealing time and temperature. Chemical etching after the mechanical polishing increases the roughness and requires the application of a stronger thermal treatment. The performance of a longer annealing produces a more regular array of longer but higher steps due to step bunching and increases the surface contamination. Avoiding the chemical etching, the annealing time and temperature can be lowered and we obtain regular surfaces with 55 nm large terraces and 2 nm high steps (1270 K for 30-60 min in 50% oxygen) and a reduced surface contamination. An increase of the miscut angle to 6° improves the regularity without any dramatic change in the final morphology.

If the step orientation were changed to [100], we would expect an increased stability of the steps and a reduced step bunching, due to energetic considerations. However the situation is more complex and more energy terms are involved. A deeper analysis of these aspects is out of the scopes of this work.

Acknowledgments

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Chapter 4

The MgO/Mo(001) system

As already discussed in Ch. 1, the MgO/Mo(001) films represent an interesting substrate for the growth of metals, due to the possibility to treat the samples at high temperatures and consequently to prepare flat surfaces. These surfaces can have different features that will deeply influence its properties. Surface defects like colour centers (or O vacancies) and low-coordinated sites can play in fact an important role in the catalytic properties of the surface and in the nucleation of metal deposits. Additionally the quite large mismatch between MgO and Mo can induce the formation of a dislocation network, as discussed in Ch. 1, that can compete with the defects as nucleation centers and can induce the growth of an ordered array of clusters.

The aim of this work is to deepen the knowledge of the system characterization and surface properties in order to be able in future to correlate them to those of metals (Fe, Co, Au...) deposited on top.

In this chapter the results about the MgO/Mo(001) system will be presented. First of all a chemical and structural investigation of the system is presented in Sec. 4.1. The morphology and optical properties of the system are discussed in Sec. 4.2 in form of a paper. The results of this last section are due to a collaboration with the group of Prof. Freund and Dr. Nilius and the measurements have been performed in Berlin at the Fritz-Haber-Institut of the MPG. Sec. 4.3 presents a discussion on the dislocation formation.
4.1 Chemical and structural analysis

Experimental

The preparation of the Mo(001) single crystal can be performed in different ways [70]. The most used is the flashing procedure that consists in repeated cycles of annealing at 1300 K in O\textsubscript{2} atmosphere and flashes to 2300 K in UHV. Due to technical problems another procedure has been performed in Modena at the SESAMO laboratory to avoid the flashing step. The Mo surface has therefore been prepared by means of successive annealing at 1270 K in O\textsubscript{2} partial pressure of $1 \times 10^{-7}$ Torr and successive sputtering at 1170 K (Ar\textsuperscript{+} ions, 600 eV) till the sample showed no C or O Auger signals. The clean substrate shows a sharp (1\times1) LEED pattern and a surface morphology with large terraces and monatomic steps in STM images.

Then MgO films of increasing thickness from 2 to 20 ML have been grown on Mo(001) by reactive deposition of Mg in an O\textsubscript{2} partial pressure of $4 \times 10^{-8}$ Torr with the Mo substrate held at room temperature. After deposition, the sample is annealed for 10 min at a temperature between 970 and 1120 K. The nominal thickness of the films has been estimated by measuring the deposition rate of Mg (about 2 Å/min) with a quartz micro-balance. The effective thickness of the films has been determined by the XPS quantitative analysis shown below. The chemical and structural analysis has been performed by means of XPS, LEED and PDMEE.

A sample of bulk MgO has been also prepared as a reference sample. It has been freshly cleaved in air and immediately introduced in UHV. Then it has been annealed for 30 min at 730 K in vacuum to eliminate water and C contamination from the surface.

Chemical analysis

First of all a calibration of the film thicknesses has been performed, in order to assign a precise thickness to all the samples shown in this chapter. For this purpose the XPS intensity ratio $I_{\text{Mo3d}}/I_{\text{Mg1s}}$ has been measured and plotted as a function of nominal MgO thickness in Fig. 4.1. The dashed line indicates the ratio calculated with a simple exponential attenuation model in the assumption of a continuum material and a layer-by-layer growth. The photoemission intensity can be expressed in fact as

$$I \propto \sigma \phi T n Q(s, \lambda),$$

where the proportionality coefficient is connected to the intensity of the X-rays into the viewed area and cannot be measured, but it is constant for constant measurement conditions. $\sigma$ is the ionization cross section, $\phi$ is a function of the asymmetry parameter $\beta$, depending on the asymmetry of the excited atomic levels, and on the angle between photons and photoelectrons. $T$ is the analyser transmission function and $n$ is the atomic density. $Q(s, \lambda)$ is the attenuation of the photoelectron intensity due to inelastic scattering through a sample of thickness $s$ and depends on the inelastic mean free path (IMFP) $\lambda$ of photoelectrons. $\sigma$ and $\phi$ have been calculated and
tabulated by different authors, see for example Ref. [71], and, once the experimental apparatus is fixed, they depend only on the atomic environment, that can be approximated as almost identical for a film or a bulk of a determined material. The analyser response function $T$ of the Omicron EA125 is proportional to the inverse of the kinetic energy of the photoelectrons and therefore does not change from a bulk to a film if the photon is not changed. The same holds for the atomic density $n$. The only term depending on the film thickness is $Q(s, \lambda)$:

$$Q(s, \lambda) = \lambda \left(1 - e^{-s/\lambda}\right).$$  \hspace{1cm} (4.2)

For a bulk ($s \gg \lambda$) the term into parenthesis is 1, obtaining that $Q(s, \lambda) = \lambda$. For these reasons the prefactor $\sigma \phi T n \lambda$ has been determined by measuring the intensities of Mo 3d and Mg 1s from two bulk references. Therefore the model is simply

$$\frac{I_{\text{Mo}3d}}{I_{\text{Mg}1s}} = \frac{I_{\text{Mo}3d}^{\text{bulk}}}{I_{\text{Mg}1s}^{\text{bulk}}} \frac{e^{-s/\lambda_{\text{Mo}}}}{1 - e^{-s/\lambda_{\text{Mg}}}}.$$  \hspace{1cm} (4.3)

The IMFP $\lambda$ has been evaluated by means of the TPP-2M formula [46], considering an energy gap of 8 eV, a density of 3.6 g/cm$^3$, a molecular weight of 40.3 g and 8 valence electrons. The resulting IMFP values are $\lambda_{\text{Mg}} = 6.7$ Å ($E_K = 183$ eV), $\lambda_{\text{O}} = 20$ Å ($E_K = 956$ eV), $\lambda_{\text{Mo}} = 24.7$ Å ($E_K = 1259$ eV). In Fig. 4.1 the dashed line is calculated with the model shown in Eq. 4.3

![Figure 4.1: $I_{\text{Mo}3d}/I_{\text{Mg}1s}$ ratio as a function of MgO thickness for the as grown film (○) and after annealing (■). The solid line is the calculated intensity ratio in the assumption of a layer-by-layer growth with a simple exponential attenuation model. The marker size represents the error bar.](image)

and the IMFP indicated above for the nominal thicknesses. The pre-annealing samples have thicknesses almost coincident with the nominal ones. After annealing the thinner films show an increase in the ratio with respect to the calculated values for a layer-by-layer growth, indicating
the formation of islands: the 2 ML film results in a fractional coverage of 63%, the 5 ML film of 73%. Above 5 ML no modification is observed after heating to 1070 K.

Then the stoichiometry is evaluated by the comparison of the $I_{Mg\,1s}/I_{O\,1s}$ measured ratio $I_m$ with the calculated one $I_c$ expected for a stoichiometric film, in the assumption of a perfect bulk MgO with $n_{Mg}/n_O = 1$. The calculated ratio is evaluated in the same way described before:

$$I_c = \frac{I_{bulk\,Mg\,1s}}{I_{bulk\,O\,1s}} \cdot \frac{1 - e^{-s/\lambda_{Mg}}}{1 - e^{-s/\lambda_O}}$$

and $I_m/I_c$ is the ratio of Mg to O atoms. From this evaluation the 2 ML sample results reach in oxygen of about a 10%, due to the accumulation of oxygen at the interface in the first stages of growth (see below). Increasing the coverage the film is perfectly stoichiometric, indicating that no loss of oxygen takes place during the annealing at 1070 K.

![Figure 4.2: XPS O 1s (left panel) and Mg 1s (right panel) lineshapes for increasing MgO thickness collected at normal emission. The dashed lines indicate the reference spectra from a bulk. The dotted lines have been acquired on the same sample after annealing. The curves are normalized to the bulk intensity and shifted to align the Mo 3d peaks. The inset shows the O 1s FWHM as a function of MgO ML before (○) and after the annealing (●). The bulk value is also reported for comparison (▲).](image)

In Fig. 4.2 O 1s and Mg 1s lineshapes are shown for increasing MgO thickness. It is evident especially in O 1s (and to a minor extent also in Mg 1s) that the peaks move towards higher
4.1 Chemical and structural analysis

Binding energy (BE) as MgO approaches a bulk-like situation. This has already been shown for MgO/Ag(001) and attributed to the reduced Coulomb and charge-transfer energies in MgO thin films, due to the presence of strong interfacial image potential screening [72]. The same effect is observed after annealing on thin films, due to the reduced fractional coverage and the increase in the effective thickness of the MgO layer. Additionally, the peaks become narrower, with the effect becoming more evident upon annealing at 970-1120 K (dotted curves). The effect is quantitatively reported in the inset in Fig. 4.2, where the FWHM of the O 1s peak before and after annealing is plotted. This effect is present also on the Mg 1s peak, even if smaller. The change with annealing can be attributed to the presence of an oxidized Mo phase at the interface and of water on the surface after deposition, that desorbs after annealing, while the narrowing with increasing thickness is related to the approach of a bulk-like electronic configuration [37].

These hypotheses are confirmed by the lineshapes of Mo 3d and O 1s acquired at grazing emission shown in Fig. 4.3 (solid line), therefore more sensitive to the surface. The evaluation of the presence of an oxidized phase is easier in the Mo 3d lineshape than on O 1s. In that case an enlargement is evident after the growth of thin MgO films with respect to bulk Mo, but never disappears even on thicker films (not shown here). The enlargement is attributed to the presence of oxidized Mo atoms with 3d levels at higher BE. The Mo 3d peak becomes narrower at normal emission, therefore the oxidized Mo layer is placed above the metallic Mo. It is reasonable to suppose that it is located at the interface and not on top of MgO. The thickness and the stoichiometry of the oxidised Mo are estimated by the determination of the difference spectrum between the line collected after the growth of MgO film and on the clean Mo at grazing emission. The Mo 3d peaks have been aligned and normalized in order to match the high BE side of the peak, that is not affected by the presence of Mo oxides. The lineshape of the difference spectra is compatible with the lineshape of MoO₂, with the Mo 3d₅/₂ at 228.7 eV BE (vertical line in Fig. 4.3a) and a spin-orbit splitting of 3.1 eV reported in Ref. [73]. The ratio \( I_{Mo^{3d}} / I_{Mo^{3d+3d}} \) has been compared to the calculated one via an exponential attenuation model that supposes the oxide placed at the interface. The \( I_{Mo^{3d}}^{bulk} / I_{Mo^{3d+3d}}^{bulk} \) ratio has been assumed as 1. In fact the \( \sigma \phi T \lambda \) factor is almost identical in the two cases, while the atomic density of the Mo atoms in the two phases can be assumed as almost unchanged, because the oxidised layer is supposed to be more likely a chemisorbed layer than an actual MoO₂ bulk phase. The thickness thus determined is of about 2 Å, almost constant for increasing MgO deposition. This indicates that the oxidised Mo layer is formed in the first stages of MgO growth due to the exposure of Mo to O₂. The lineshape does not sharpen after annealing, giving a difference spectra identical to the as-grown film. Since the fractional coverage is reduced and the substrate signal increased, a decrease (but not the complete disappearance) of the oxidized layer is evident, probably due to migration of oxygen into the bulk Mo or, in case of mixed Mo-Mg oxide formation, to the complete formation of MgO, leaving Mo atoms more metallic.

In Fig. 4.3b the O 1s lineshape of a clean MgO reference sample is compared to those obtained
after exposure of clean Mo to $O_2$ at room temperature (RT) and successive annealing at 1120 K. In both cases the peak has additional components on the HBE side, where the appearance of $MoO_x$ contributions is expected between 0.5 and 0.8 eV BE higher than the O 1s in MgO [73]. In particular after annealing the O 1s intensity decreases with respect to the Mo 3d intensity (not shown here) while the lineshape is unchanged, indicating a reduction in the quantity of oxidised Mo in accordance to what observed for the Mo 3d. For the 2 ML spectra the presence of the oxidised Mo layer is not straightforward, due to the small changes that affect the O 1s peak. A clear additional shoulder appears at grazing emission at about 532 eV, about 2 eV higher than the main peak. This component completely disappears after annealing, leaving a peak almost identical to the bulk one (apart from the small difference in FWHM shown in inset of Fig. 4.2). Therefore it is assigned to $OH^-$ groups adsorbed on the MgO surface [67] after the deposition and desorbed after annealing.

In principle the possible presence of a mixed Mg-Mo oxide could be determined by the eval-
4.1 Chemical and structural analysis

Evaluation of the $I_{Mo^{+3d}}/I_{Mg^{1s}}$ ratio as a function of the emission angle, compared to the expected values for a sharp MgO/MoOx/Mo interface. Unfortunately in this context the thickness of the MoOx is small (2 Å) compared to the IMFP of Mo electrons (24.7 Å), giving an angular dependence of the ratio that is almost constant. Additionally the small Mo oxide contribution, especially at normal emission, and the subtraction procedure introduce an error bar larger than the deviations of the intensity ratio with the angle. Therefore it is hard to distinguish if an interfacial mixing is present, because its distinctive characteristic is the invariance of the intensity ratio with the angle for thin MgO films. Possible shifts in the Mo and Mg peaks are ruled out due to the small quantity of oxidised Mo layer. Furthermore shifts on the Mg peaks are negligible, while on Mo 3d the peak should have a position very near to the Mo$^{6+}$ 3d5/2 and Mo$^{4+}$ 3d3/2 [74].

Structural analysis

![LEED patterns and in-plane parameter](image)

Figure 4.4: LEED pattern of (a) clean Mo, (b) Mo surface exposed to O$_2$ at RT and successively annealed at 1120 K, (c) 2 ML MgO after annealing at 970 K, (d) 10 ML MgO as grown and (e) after annealing at 1070 K (Ep=140 eV). (f) MgO in-plane parameter as determined by means of LEED. The references values for bulk MgO (dashed line) and Mo (solid line) are reported.

Moving to the structural characterization, Fig. 4.4a shows the LEED pattern of a clean Mo(001) surface. Exposure to O$_2$ and successive annealing at 1120 K (conditions similar to
the MgO preparation) produces a p(2×2) superstructure (Fig. 4.4b). 2 ML MgO have a LEED pattern with the same cell size as compared to the Mo one within the error bar, suggesting the epitaxial growth of MgO film (Fig. 4.4c), tough this could be partly due to the signal coming from the substrate, that, even if minimized, it is not zero. Additionally a weak superstructure p(2×2) is visible, in analogy to Fig. 4.4b, ascribed to the underlying oxidised Mo layer, in accordance with XPS analysis. The spots broadening and their evolution into satellites is discussed in Sec. 4.2 and in Sec. 4.3. For further deposition the improvement in the crystal quality due to the annealing is evident (Fig. 4.4d-e) and confirms the importance of this preparation step.

To determine the evolution of the lattice strain, the in-plane lattice parameter can be determined directly by LEED images, where the distance between diffraction beams corresponds to the surface parameter in reciprocal space. This can be done only if images are acquired all exactly in the same conditions (sample position and beam energy) and compared with a known standard sample. This was possible thanks to a high precision manipulator with an accuracy of 0.01 mm. In addition errors due to possible small misalignments of the sample are reduced by averaging over the distances between different equivalent spots. The standard reference sample is the clean Mo surface. Images taken at an energy of 140 eV have been chosen, since this energy corresponds to a maximum in the I(V) of the (1,1) spots in MgO and a minimum for the corresponding Mo spots. The values thus obtained are reported in Fig. 4.4f, together with lines representing the bulk MgO and Mo values. The in-plane lattice parameter shows a gradual relaxation for increasing MgO amount and is completely relaxed at 20 ML.

PDMEE plots have also been measured to obtain the information complementary to LEED (see Sec. 2.1). Fig. 4.5 shows the Intensity Angular Distributions (IAD) of the O and Mg KLL Auger signals along the [100] MgO azimuth for 2 to 20 ML thick MgO films. The plots are normalized to the 0° peak anisotropy \( A \), defined as \( A = 2(I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}}) \), where \( I_{\text{max}}(I_{\text{min}}) \) is the maximum (minimum) signal intensity of the considered feature. For sake of clarity, all crystallographic directions are given with respect to the MgO, otherwise else stated. Panel (a) presents the IAD for the as grown films. Although the high noise, the main features of the rocksalt structure are evident and correspond to those depicted in Fig. 4.6. Forward focusing peaks occur at 0° and 45°, corresponding to the primary beam alignment along the [001] and [101] atomic chains respectively. Other features are mainly generated by higher order interference and cannot be directly related to specific atomic alignments, tough characteristic of MgO structure, as can be seen on the bulk IAD. On the other side, Mo MNN IAD shows different features, mainly at 0° and 54.7°, corresponding to the alignment along respectively the [001] and [111] atomic chains of a bcc (001) structure rotated in plane by 45° with respect to the MgO structure. This confirms the supposed epitaxial growth with the MgO [100] direction aligned to the Mo[110], that cannot be directly deduced by LEED.

The O KLL IADs for 2 ML MgO shows a broadened feature at about 45° (Fig. 4.5b). This
could be due to the simultaneous presence of both [101] and [111] features and is a further indication of the presence of a oxidised Mo layer, that is constituted by O in the Mo bcc structure.

![Figure 4.5: IADs of the O KLL (dotted line) and Mg KLL (solid line) Auger signals along the [100] MgO azimuth for 2-20 ML MgO (a) on the as-grown film and (b) after annealing (Ep=5 KeV). IAD of bulk MgO is also shown for comparison. The dashed line represent the Mo MNN IAD from the clean substrate. Each spectrum has been normalized to its 0° peak anisotropy.](image)

The IADs at low thickness are characterized by the [101] and [111] (not shown here) peaks shifted at higher angle, indicating a tetragonal distortion of the MgO film, that is induced by the larger lattice parameter of the substrate. The relaxation of the strain occurs for increasing thickness and the peaks move towards their bulk positions. In Fig. 4.7a the \(a/c\) ratio is reported
The MgO/Mo(001) system

Figure 4.6: Left: Top view of the crystal structure of rocksalt MgO (top) and bcc Mo (bottom). Center: side view of the same structures in the plane which contains the MgO [100] direction; Right: same as center but in the plane which contains the MgO [110] direction.

For both the as grown and annealed films as deduced from the angle position of the [111] peak. The peak position changes not only with increasing thickness but also due to the annealing, suggesting that it improves the crystal quality and helps the film relaxation, as already revealed by the LEED in Fig. 4.4. Part of this improvement can be ascribed also to the reduction of the fractional coverage after annealing, that increases the effective film thickness and therefore induces a stronger relaxation. Both the hypotheses are confirmed by the increase in the intensity anisotropy of the 0° peak in Fig. 4.5. However 20 ML of MgO are not enough to release completely the strain.

From the $a/c$ ratio obtained from the PDME plots and using the $a$ values in Fig. 4.4f, the out-of-plane parameter has been calculated as a function of increasing MgO thickness and reported in Fig. 4.7b. On the same figure the MgO bulk $c$ parameter is indicated with a dashed line, while the solid line has been determined supposing a bulk value of the Poisson ratio $\nu = 0.173$ [20] and the film completely pseudomorphic to the substrate. The Poisson ratio $\nu$ is defined as

$$\nu = \frac{E - 2\mu}{2\mu} = \frac{1}{1 - 2s_{xx}/s_{zz}},$$  \hspace{1cm} (4.5)$$

where $E$ is the Young’s modulus, $\mu$ the shear modulus and $s_{xx}$ ($s_{zz}$) is the in-plane (out-of-plane)
relative strain

\[ s_{xx} = \frac{(a - a_0)}{a_0} \]
\[ s_{yy} = s_{xx} \]
\[ s_{zz} = \frac{(c - c_0)}{c_0}, \]

with \( a_0 \) and \( c_0 \) the parameters of the equilibrium bulk lattice.

The out-of-plane parameter starts from a value smaller than the expected one, compatible with the possible higher Poisson ratio for a thin film, and it does not reach the bulk parameter. This discrepancy with LEED, that indicates a complete relaxation for thick films, can be ascribed to the different probing depth of the two different techniques. In fact while in LEED we use low energy electrons with a probing depth of a few atomic layers, in PDME the Auger electrons have \( \lambda \) values around 20 Å. Therefore, supposing a gradient in the film relaxation, the LEED can see only the topmost layers, completely relaxed, while the PDME can see also the deepest, where a strain component is still present.
4.2 Morphology and optical properties of MgO thin films on Mo(001)

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Abstract

Thin MgO films with a nominal thickness ranging between 1 to 60 ML have been grown on a Mo(001) surface. The film morphology was studied by LEED and STM, revealing the presence of a coincidence pattern with the Mo support in the low coverage regime, a dislocation network at medium thickness and a rather flat and defect-poor MgO surface for thicker layers. The MgO optical properties were investigated as a function of film thickness by analyzing electroluminescence spectra obtained via electron injection from the STM tip into well-defined surface areas. The spectra are characterized by two distinct emission bands at 3.1 and 4.4 eV. Their origin is discussed in the light of earlier photo-luminescence measurements on MgO nano-cubes and smokes.

Introduction

Insulating metal oxides have attracted wide interest in recent years due to their potential applications as support for metal nano-particles in electronic devices, heterogeneous catalysts and gas sensing systems [75, 76]. In particular, they are often used in the form of thin films, because of novel properties arising from interactions with the metal substrate and the possibility to investigate such systems with surface science methods based on electrons or ions, in spite of their insulating character.

Among these materials, MgO is especially promising thanks to its wide band gap and the good chemical [57] and thermal stability [6]. The compound is easy to prepare due to the high oxygen affinity and low melting temperature of Mg. The simple rock-salt structure allows the growth of epitaxial films on a variety of substrates, as long as the lattice mismatch with the MgO does not exceed 5-7%. Stoichiometry, structure and morphology have been intensively investigated for MgO deposited on Ag(001) [10–12, 16, 77], Fe(001) [78, 79] and Mo(001) [6, 7, 9, 80]. Particularly interesting is the use of Mo supports, because of the possibility to treat the films at high temperatures. High temperature deposition or post-growth annealing, which is not applicable for Ag and Fe substrates, is usually performed to improve the film morphology and reduce its defectiveness. In spite of these advantages, the morphology of the MgO/Mo system has not been extensively investigated in the past. The only work [9] published so far shows that the surface changes dramatically for a MgO deposition temperature above 1100 K, whereas deposition at 300 K followed by post-annealing does not improve the film morphology.
4.2 Morphology and optical properties of MgO thin films on Mo(001)

The physical and chemical properties of oxide surfaces are often dominated by the presence of defects, which might occur in the form of vacancies and low-coordinated sites. While bulk MgO, for example, does not absorb nor emit light in the range between 200-900 nm, pronounced luminescence bands have been observed for MgO smokes [81–83] and powders [84, 85] at energies much lower than the bulk band gap. These emission bands have been assigned to the presence of low-coordinated sites and colour centres at the surface; however, no consensus is reached so far on their relative contribution to the photon signal. In addition, the adsorption of molecules and atoms has been traced back to the abundance of defects in the MgO surface, emphasizing their important role for the nucleation behaviour and the catalytic properties of this oxide material.

This Letter aims to provide new information on the interplay between the morphology of MgO thin films and their optical properties. For this purpose, MgO films of varying thickness have been prepared on Mo(001) and studied by means of LEED, scanning tunnelling microscopy (STM) and luminescence spectroscopy induced by field-emitted electrons from the STM tip [86]. These methods give complementary information on the topographic and optical properties of MgO thin films.

Experimental

Experiments are carried out with a beetle-type STM operated at liquid-nitrogen temperature (100 K) and ultra-high vacuum conditions ($p \approx 5 \times 10^{-10}$ mbar) [86]. A parabolic mirror surrounding the microscope head collects photons emitted from the tunnel junction. A second mirror outside the vacuum chamber focuses the light onto the entrance slit of a grating spectrograph attached to a liquid-nitrogen cooled CCD detector. A LEED system enables easy control of the sample quality after preparation. The Mo(001) single crystal is prepared by repeated cycles of annealing at 1300 K in O$_2$ atmosphere and flashes to 2300 K in UHV. This produces a sharp $p(1\times1)$ LEED pattern and a surface with large terraces (>200 nm) delimited by monatomic steps. The MgO film is grown by reactive deposition of Mg in an O$_2$ partial pressure of $1\times10^{-7}$ mbar with the Mo substrate held at room temperature. Magnesium is evaporated from a crucible heated by electron bombardment. After deposition, the sample is annealed for 10 min at 1100 K to improve the crystallinity of the film. For sub-monolayer films, the MgO coverage is directly deduced from STM images, whereas for thicker films, a nominal thickness is defined as product between MgO deposition rate and exposure time.

Results

Fig. 4.8 shows a series of LEED patterns of MgO films with increasing thickness. In all cases, a square ($1\times1$) structure is observed. From the identical size of the primitive cell on the clean substrate and the film, epitaxial growth of the oxide on Mo(001) is concluded.
The MgO/Mo(001) system

Figure 4.8: LEED pattern of MgO films on Mo(001): a) 0.85 ML, b) 1.75 ML, c) 7 ML and d) 30 ML (Ep=55eV). The circle in (a) marks one of the (2×2) superstructure spots. e) Positions of [100] satellites with respect to the central spot in the Brillouin zone shown as a function of the scattering phase $S=\Delta K_\perp /2\pi$ [25]. The lines are linear fits to the data and yield information on the tilting angles with respect to the ideal (001) surface.
Hereby, the MgO(001) plane is parallel to Mo(001) while the MgO[100] direction aligns with the Mo[110] direction, as expected from the 5% lattice mismatch between the primitive cells of bcc Mo (3.15 Å) and rock-salt MgO (2.98 Å). For sake of clarity, all crystallographic directions in this letter are given with respect to the MgO. The appearance of a p(2×2) super-structure in the low-coverage regime (Fig. 4.8a) is attributed to the formation of a Mg-Mo interface layer. Evidence for such alloying effect is gained from STM and optical measurements and will be presented in a forthcoming paper. The fundamental spots in low-thickness preparations show an anisotropic broadening, which evolves to clear and distinct satellites oriented along the MgO [100] at 2-5 ML nominal thickness (Fig. 4.8a). Depending on the primary electron energy, the central spot of each fundamental reflex appears and disappears in this growth stage and additional satellites become visible along the [110] direction (not shown here). We attribute this behaviour to interference effects between neighbouring MgO domains in antiphase scattering configuration. With increasing film thickness, the [100] satellite spots move towards the central spot and finally disappear at around 5 ML thickness (Fig. 4.8b). The splitting of fundamental reflexes with respect to the first Brillouin zone depends linearly on the primary electron energy, as shown in Fig. 4.8e. This observation is compatible with a Moiré structure comprising tilted MgO facets, in agreement with the STM results discussed below. For a nominal thickness between 5-12 ML, distinct crosses appear in the LEED pattern around each fundamental spot oriented along the [110] direction (Fig. 4.8c).

Similar observations were reported earlier for MgO/Ag(100) [25] and MgO/Fe(100) [24] and assigned to the formation of mosaics spanned between a dislocation network that relaxes the strain in the oxide layer. The size of the [110] crosses in LEED is directly connected to the inclination angle of the tilted regions and decreases with increasing thickness. Finally, for films consisting of more than 15 layers a simple (1×1) pattern appears in LEED, indicating a flat and defect-poor surface structure (Fig. 4.8d).

The evolution of the MgO morphology with increasing film thickness was also analysed by STM as summarized in Fig. 4.9. After deposition of approximately one layer, the film still exhibits large holes, confined by non-polar [100] and polar [110] oriented edges (Fig. 4.9a). The presence of a significant fraction of polar borders has already been observed for thin MgO films on Ag(100) and ascribed to a stabilization effect of the metal support [18]. On the oxide surface, a regular square pattern with a mean size of 55 Å becomes visible, which is aligned with the MgO [110] direction. The pattern persists until 5 ML nominal film thickness, which corresponds to the range where [100] satellite spots are present in LEED. The square structure is interpreted as coincidence lattice resulting from the 5% lattice mismatch between MgO and Mo and would be compatible with 18 MgO unit cells overlaying 17 substrate cells along the MgO[110]. The calculated size of such Moiré structure amounts to 53.5 Å, in good correspondence to the periodicity of the measured square pattern. The visibility of the Moiré structure is apparently enhanced by an electronic effect, as large topographic contrast is only obtained for sample voltages above 3.5
The occurrence of four satellite spots around each fundamental LEED reflex suggests furthermore that each Moiré unit cell consists of four regions tilted along the MgO ⟨100⟩ directions. From the change of the relative position of the LEED satellites in the first Brillouin zone as a function of energy, a maximum tilting angle of 5° with respect to MgO(001) is concluded for ultra-thin films, which rapidly reduces to zero with increasing film thickness (Fig. 4.8e).

The surface Moiré pattern fades away for a nominal MgO thickness of 3-5 ML. The dominant structural elements on the surface are now step edges, dislocation lines and small rectangular holes of 20-50 Å diameter (Fig. 4.9b). Whereas for thinner films, dislocation lines have no preferential orientation, they begin to align with the MgO[100] direction for thicker ones. In particular cases, the presence of screw dislocations can be recognized, as shown in the inset of Fig. 4.9c. The formation of a dislocation network is a well-known mechanism to reduce stress and strain in thin epitaxial films caused by a lattice mismatch with the support [28]. The presence of a

Figure 4.9: STM images of MgO thin films on Mo(001): a) 150×150 nm² of 0.85 ML MgO (I=0.23 nA, $U_{\text{sample}} = +3.4$ V). The inset shows a 25×25 nm² region of the same sample. b) 1.75 ML MgO (I=0.05 nA, $U_{\text{sample}} = +3$ V); c) 7 ML MgO (I=0.14 nA, $U_{\text{sample}} = +3.7$ V); d) 18 ML (I=0.15 nA, $U_{\text{sample}} = +12.5$ V). Images (b-d) are 100×100 nm² in size. The inset in image c shows a screw dislocation, which is frequently observed in 5-10 ML thick MgO films.
dislocation network at this growth stage is also reflected by the characteristic crosses around each fundamental spot in the LEED measurements (Fig. 4.8c). Above 7 ML film thickness, the oxide gradually flattens and the global roughness decreases, indicating good layer-by-layer growth. This trend finds its correspondence in the LEED pattern, where the complex spot structure transforms into single (1×1) LEED spots. For a nominal thickness exceeding 15 ML, STM experiments become increasingly difficult due to the vanishing conductivity of the film and only step edges remain visible at the surface (Fig. 4.9d).

Figure 4.10: Photon emission spectra collected from MgO films with increasing thickness. Excitation conditions were kept constant in all spectra (electron energy: −200 eV, current: 1 nA, acquisition time: 60 sec).

To correlate the structural properties described above with optical parameters, luminescence measurements were performed on thin MgO films grown on Mo(001). The photon emission is excited via electron injection from the STM tip into well-characterized surface areas imaged prior to spectroscopic measurements. Emission spectra are acquired for electron energies ranging between 50-200 eV; whereby current and acquisition time are limited to 1 nA and 60 s,
respectively, to reduce electron-induced damage of the film. With increasing electron energy, an exponential increase of the photon yield is observed; however, the spectral characteristic of the emission remains unchanged. Fig. 4.10 presents a series of photon emission spectra taken at −200 V tip bias for MgO films containing up to 60 layers. Spectra excited with lower electron energies (50 eV) are qualitatively similar, but show reasonable signal to noise ratios only for extended accumulation times. In all spectra, two emission bands are identified, located around 280 nm (4.4 eV) and 400 nm (3.1 eV), respectively\footnote{Bremsstrahlung created by the injection of high-energy electrons into the sample has to be taken into account as additional source of UV photon emission. Due to the wavelength cut-off of the CCD detector, this produces an artificial emission maximum around 250-270 nm that might contribute to the 280 nm band. The effect is stronger for thin MgO layers, because Bremsstrahlung is more effectively produced by electron injection into the underlying metal support.}. With increasing film thickness, both bands gain intensity, whereby the low-energy band at 3.1 eV is more affected. Saturation of the total emission yield is observed for films thicker than 40 ML. As geometric and electronic tip properties slightly vary with time, the experimental set-up does not allow for a quantitative comparison of the emitted light intensity.

In the literature, the characteristic light emission from MgO surfaces is rationalized by the following mechanism. In a first step, surface excitons are formed by interactions of O\(^{2-}\) ions with photons or electrons. They are dominantly excited at 5-fold coordinated terrace sites (5C sites), simply because they represent the most abundant surface site. Excitonic modes on the MgO surface are mobile and can move away from their activation centre in a random-walk type process \cite{88, 89}. The diffusion stops when the electron-hole pair becomes trapped at defect sites (e.g. F centres) or sites with lower local coordination, such as 4-fold coordinated edge (4C) or 3-fold coordinated corner sites (3C). The trapping occurs because of the smaller Madelung potential at low-coordinated sites, resulting in a stabilization of the electron-hole pair \cite{88, 89}. Defects and low-coordinated edge or corner sites are therefore preferential recombination centres for surface excitons and dominate the emission characteristics of MgO. The relative importance of the two exciton-deactivation pathways, either via corner and edge sites or via oxygen vacancies, is heavily debated in the literature. In recent photoluminescence measurements on defect-poor MgO nanocubes, two emission bands have been identified at 3.84 eV and 3.2 eV and assigned to the radiative recombination of excitons at 4C edge and 3C corner sites, respectively \cite{81}. This interpretation is in accordance to previous data on MgO smokes \cite{84} and theoretical calculations \cite{88–90}. Slightly different results were reported by other groups, with emission bands somewhat red-shifted to 3.2 eV for the 4C and 2.7 eV for the 3C emission centres \cite{82, 85}. On the other hand, an emission band at 3.2 eV detected for MgO single crystals was claimed to originate from an emission mechanism involving F\(^+\) centres \cite{91}.

To discriminate between the two proposed mechanisms, colour centres have been intentionally introduced into the surface by exposing the MgO film to a flux (1 mA) of 300 eV electrons for 10 minutes prior to spectroscopy. Electron bombardment induces desorption of O atoms from the
MgO surface in an Auger-like process, and should thus intensify the emission channel involving colour centres [92]. However, decreasing emission intensity was observed for electron-bombarded films, pointing towards a minor role of surface colour centres in the emission process (Fig. 4.11a). The reverse approach, namely a annihilation of potential colour centres by healing MgO films in $1 \times 10^{-7}$ mbar of oxygen, led to a similar conclusion, as the emission yield was not completely quenched even after prolonged O$_2$ exposure (Fig. 4.11a).

**Figure 4.11:** a) Photon emission spectra from a 30 ML thick MgO film. Upper curve: as prepared film, central curve: after exposure to 45 Langmuir O$_2$ and lower curve: after electron bombardment (300 eV, 10 min). Neither changes in the spectral shape nor variation in intensity are observed that would be compatible with a dominant role of surface colour centres. b) Series of photon emission spectra from a 30 ML thick MgO film on Mo(001) (electron energy: −240 V, current: 1 nA, acquisition time: 60 sec). Numbers next to each curve indicate the total electron exposure time the surface has experienced during spectroscopy. The inset shows the time evolution of the total emission intensity during spectral acquisition from a freshly prepared MgO film measured with a photo-multiplier. After reaching the maximum, the photon intensity remains relatively constant over the full acquisition time of 10 min. See text for details.

For the interpretation of the optical data, the electron exposure during spectral acquisition has to be considered, too. In a typical spectrum taken with 1 nA field-emission current from the STM tip, approximately 100 electrons per second are injected into every anion site. This dosage is sufficient to induce a reasonable quantity of surface colour centres, provided that the electron energy exceeds the threshold for electron-induced O-desorption. Two observations suggest that colour centres formed during spectral acquisition are not the main cause of the light emission.
First, spectra exhibiting the distinct emission bands at 3.1 and 4.4 eV are obtained even for excitation energies below 50 eV, where electron-induced colour centre formation is inefficient [25, 92]. Second, photon yield as well as spectral characteristics of the MgO emission were found to be constant over several minutes of data acquisition (Fig. 4.11b), although the number of O vacancies and therewith the emission yield should continuously rise with acquisition time. In combination with results on intentionally electron-bombarded versus oxygen-treated films, colour centres have thus been ruled out as the dominant source of light emission from the MgO surface.

The two bands in our optical emission spectra are therefore interpreted as signature of radiative exciton decays from low-coordinated MgO sites. The emission peak at 3.1 eV agrees well with the main feature detected in previous photoluminescence experiments on cube-shaped MgO nano-crystals [81, 82]. Based on model calculations, this band has been assigned to emission centres located at 3C corner sites on the MgO surface [88, 89]. The energy of the second peak (4.4 eV) in this experiment indicates an emission pathway involving higher coordinated sites. Similar emission bands in photoluminescence spectra have been attributed to emission from 4C anion sites located at MgO step edges [81]. An unambiguous assignment of the 4.4 eV peak is not possible here due to the less-regular film morphology compared to well-defined MgO nanocubes. Beside step edges, other low-coordinated sites might be relevant for optical transitions above 4.0 eV in the MgO/Mo(001) system, such as kinks, irregular and inverse corners.

Our interpretation of the light emission as radiative decay of MgO excitons trapped at low-coordinated sites also provides an explanation for the observed dependence of the emission yield on the film thickness. The probability for a surface exciton to reach a low-coordinated step or corner after excitation on a distant terrace site depends on the lifetime of the electron-hole pair and the surface morphology. In the case of ultra-thin MgO films on Mo(001), the exciton lifetime is governed by the presence of non-radiative decay channels provided by the metal support (Landau damping). The exciton lifetime and therefore its probability to undergo a radiative recombination increase when the MgO surface is spatially decoupled from the Mo substrate via a thick oxide film. This behaviour is reflected in our experimental finding that the emission yield initially increases with film thickness but saturates for higher MgO coverage. The influence of the metal vanishes for films containing more than 40 layers, which enables a rough estimation of the interaction length between MgO surface excitons and electronic excitations in the Mo support.

Finally, we want to emphasise that structural changes in the MgO surface during electron

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MgO luminescence peaks observed in our experiment are generally red-shifted with respect to earlier photoluminescence data. A number of reasons might be responsible for this discrepancy. First, the MgO film has only limited thickness and is supported by a Mo(001) crystal. Interactions between electron-hole pair excitations in the oxide and their image in the highly polarizable metal support lead to smaller excitation energies. Second, the presence of a biased tip in close proximity to the sample surface produces a strong electric field in the oxide film that shifts optical transitions energies via the Stark effect.
injection from the STM tip cannot be excluded. Radiation- and electron-induced damage on oxide and halogenide surfaces is described in the literature in great detail [93–95]. Usually, the emergence of holes is observed in the surface layer, triggered by the electron-induced desorption of anions. Similar surface modifications are sometimes observed in the MgO films after spectral acquisition. The importance of such desorption processes for the optical characteristics is not clear at this moment and will be explored in future electro-luminescence experiments performed at smaller excitation energies.

Conclusions

Flat and defect-poor MgO films have been grown on a Mo(001) support, as revealed by STM and LEED measurements. The film morphology depends critically on the number of MgO layers and passes through different stages with increasing thickness, such as a coincidence lattice with the Mo support and a dislocation network. Optical properties of the MgO film are dominated by two emission bands located at 3.1 and 4.4 eV, which have tentatively been assigned to the radiative decay of MgO excitons at 3-fold and 4-fold coordinated sites. The local nature of the employed technique, namely stimulating light emission by electron injection from an STM tip, will hopefully lead to an atomic-scale correlation between well-defined MgO surface features and distinct optical emission bands in future.

Acknowledgments

We are indebted to Dr. M. Sterrer for many experimental suggestions and helpful discussions.
4.3 Discussion and conclusions

The growth of MgO thin films on Mo(001) produces well ordered, stoichiometric films, with a flat surface characterized by low-coordination sites responsible of the optical properties of the film and that can act as nucleation centers for metal growth.

Another important characteristic is the relaxation of the strain. We observed in STM images that for very thin films (1-5 ML) a square pattern covers the surface. Correspondingly the four-fold splitting of LEED spots along the $\langle 100 \rangle$ directions suggests the formation of regions tilted out of the (001) surface plane, the same regions that contribute to the corrugation of the surface. These tilted mosaics appear in the thickness range between 1 to 5 ML in Sec. 4.2 and for 2-12 ML in Sec. 4.1 where the relaxation of the in-plane parameter and the splitting of the LEED spots are observed. The thicknesses reported in Sec. 4.2 are smaller by about a factor 2 with respect to those reported in Sec. 4.1. This difference may be due to the calibration performed by means of STM in Sec. 4.2 that introduces an error in the results larger than in the case of XPS calibration, due to the non-uniform coverage of the film for very low MgO thickness. Therefore the values reported in Sec. 4.2 should be multiplied by 2. Furthermore the 2 ML MgO film shows not-clearly-resolved satellites in LEED (Fig. 4.4c and Fig. 4.8a), indicating to be close to the critical thickness for the transition from pseudomorphic growth (compatible with the in-plane parameter evolution shown in Fig. 4.4f within the error bar) to the relaxation (evident from the square pattern in STM, see Fig. 4.9a).

Tilted mosaics have been interpreted in the past as due to the formation of a square network of dislocations along the $\langle 100 \rangle$ directions, suggested as the most stable for such films [20, 24, 25, 96]. In this work a proof for this hypothesis is the trend in the in-plane lattice parameter with MgO thickness, consistent with the formation of dislocations at the interface that relieve the misfit strain. A picture of the surface morphology compatible with the model shown by

![Figure 4.12: Models for the surface morphology after dislocation formation.](image-url)
Dynna et al. [24] and Wollschläger et al. [25] (reported respectively in Fig. 1.12 and 1.13) is the presence of pyramids covering the surface with tilted areas like in Fig. 4.12a. The square pattern on thin films reported in this work seems to confirm the pyramid formation, that could give a contrast similar to a Moirè pattern in STM images and can be associated to the formation of the $\langle 100 \rangle$ dislocations. The bright areas in the square pattern on STM images, however, are due to electronic effects, therefore enhanced by the bias used, that depend on the atomic vertical displacements in the outermost layers [87]. Thus the contrast in the STM images is not so strictly related to dislocation lines or topographic features, such as the top of the pyramids, even if there is some kind of correspondence.

For increasing thickness, STM images show lines aligned along the $\langle 100 \rangle$ directions (Fig. 4.9c). On the contrary LEED images indicate a rotation of the crosses around the spots, and therefore of the tilted areas, by $45^\circ$. This can be caused by the rotation of the dislocation lines along the $\langle 110 \rangle$ directions. Even if this configuration is less stable than the formation of $\langle 100 \rangle$ dislocation lines in a bulk, both accommodations are possible [20]. The energy for the dislocation formation in fact does not depend only on their cost per unit length, but also on the cost to create a monatomic step at the surface and the energy gain for the relief of the misfit strain. Additionally dislocations require an activation barrier for their nucleation and are subject to reciprocal interactions. Therefore in thin films the energy balance can be different from that of a bulk and the observed dislocations are not necessarily those with the lowest energy, but for example those with the lowest activation barrier. In this case the lines in STM images would not be related to dislocations but simply to island edges. An alternative explanation can involve the surface deformation without changes in the dislocation alignment. Additionally the surface is far enough from the interfacial dislocations to experience an attenuated strain field, so that the effective tilting is along a $\langle 110 \rangle$ direction, intermediate between two $\langle 100 \rangle$ directions on the almost rectangular islands.

The difference in the LEED spot splitting along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions for the various thicknesses can be related to the different surface morphology. The presence of a well-defined square pattern on thin films is an indication of a definite tilting angle of the surface, giving rise to distinct satellites in LEED. On thicker films the surface is less regular, with the film characterized by inhomogeneous rectangular islands. This leads to less regular tilted surfaces, where a wider range of tilting angles is present. This is reflected in the broader crosses observed in LEED.

Another proof of the presence of tilted regions is the comparison of the Full Width Half Maximum (FWHM) of the $0^\circ$ peak in PDMEE scans of Mg KLL along the [100] azimuth with the ones measured on the MgO/Ag(001) system, reported in Fig. 4.13a. These values are meaningful only if considered together with the anisotropy of the considered peak (Fig. 4.13b), that is a direct indication of the crystal quality of the film. The FWHM is clearly decreasing for increasing MgO thickness for both systems, approaching the value measured for a bulk
MgO. Before annealing the FWHM for MgO/Mo is systematically larger than for MgO/Ag and a poorer order is observed also in LEED and in the peak anisotropy (Fig. 4.13b). After annealing the FWHM for the MgO/Mo system decreases. At 2 ML, when the mosaics are not yet completely formed (no distinct spots in LEED, Fig. 4.4c), the error bar on the PDME width is large, therefore the comparison of the FWHM between the two systems is difficult. When mosaics are clearly formed in LEED images (5-12 ML), the corresponding FWHM in PDME IADs points out the significant enlargement of the MgO/Mo peak with respect to the MgO/Ag one. The difference in the FWHM cannot be explained only by the reduced crystalline order, as the 0° peak anisotropy is comparable for the two systems (see Fig. 4.13b). The formation of tilted regions can play an additional role, since it occurs at higher thickness when MgO is deposited on Ag (see Sec. 5.2) and mosaics are less organized on a long range scale. If the models shown in Fig. 1.12, 1.13 and 4.12 are chosen to explain the dislocation formation, then the accommodation of a higher strain requires a smaller coincidence distance and if a monatomic vertical displacement is assumed, then the tilt angle must be higher and therefore also the LEED spot splitting larger. The tilted regions contribute to the PDME plots by adding a component to all the peaks shifted by the tilt angle in all the (100) directions. Since the tilt angle is small and peaks large, the two components cannot be deconvolved and only an enlargement in the peak is visible. Therefore the difference in width of PDME peaks can be ascribed to the presence of mosaics, more evident in the case of MgO/Mo(001) than on MgO/Ag(001). This further evidence highlights the hypothesis of the formation of tilted regions on the surface of MgO films grown on Mo(001) and their correlation to the film relaxation supports the explanation of dislocation formation.
Chapter 5

The Fe/MgO(001) system

The interest for metallic nanostructures on oxide surfaces is motivated by interesting applications in different fields, such as for example information storage technology and catalysis. Simple epitaxial metal/oxide films and nanostructures are studied as model systems in order to unravel the interplay among electronic and magnetic properties, morphology and atomic scale structure. The Fe/MgO system in the form of thin films and multilayers has been widely investigated in the last decade under structural, morphological, magnetic and catalytic aspects [56, 57, 97–103]. These studies show that Fe has a good epitaxial quality [99, 100] and that it forms islands, whose size decreases as the temperature is increased [98, 99, 101]. Most studies, however, focus on Fe amounts significantly higher than 1 ML, while the sub-monolayer coverage range has rarely been investigated [98]. Additionally the sharpness of the interface is never investigated into details. MgO in fact has been chosen as a substrate because it is inert, insulator and non magnetic. Theoretical calculations predict that it does not interact with the metal on top [56], proving that MgO is the ideal substrate for the growth of quasi free standing metal structures on which the effects of reduced dimensionality on the electronic properties of the metal can be studied.

For all these reasons the first purpose of this chapter is to present in form of a paper that the Fe/MgO interface is not affected by chemical processes like oxidation-reduction reactions and intermixing that often involve the metal-oxide interfaces [104–107] and that would influence the overlayer properties (Sec. 5.1).

The reduction from 2D to 1D and 0D is a very interesting topic since the modifications of Fe 3d band induced by spatial confinement can be responsible for changes in important properties, such as for example an increased magnetic moment per atom [56, 102], out of plane magnetization [97] and increased catalytic activity [103]. Thus the second purpose is to employ the dislocation network of MgO to induce the self-organization of metal clusters on MgO films. Therefore first of all the substrate patterning of the MgO/Ag(001) film is briefly discussed (Sec. 5.2) and thus the Fe/MgO morphology is analysed (Sec. 5.3).
5.1 Absence of oxide formation at the Fe/MgO(001) interface

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Abstract
We present a study focused at the atomic level characterization of the Fe/MgO(001) interface by means of X-ray photoelectron spectroscopy, X-ray photoelectron diffraction and X-ray absorption spectroscopy. The data show a good crystalline quality of the Fe films grown on MgO(001) at room temperature. The films have a bcc structure with the Fe(001) // MgO(001) and Fe[110] // MgO[100] orientation. The Fe growth in the 1-10 ML thickness range proceeds by the formation of islands covering a fraction of the MgO surface. The oxidation of Fe and the consequent reduction of MgO can be excluded, thus proving that the interface is locally abrupt, with a very weak interaction between the two sides. The interface is stable with temperature up to 670 K.

Introduction
Magneto-electronic devices, such as spin valves or magnetic tunnel junctions (MTJs), are composed of alternating layers with different magnetic properties and thickness in the nanometer range. The importance of the quality of the interfaces for their performance has been widely recognized [108–112]. In MTJs, for example, the tunnelling current between two ferromagnetic layers through the non-magnetic layer has been shown to be strongly affected by the presence of magnetic oxides or nonmagnetic metal layers at the interface [112]. These aspects stimulated an interest towards the investigation of the quality of the interfaces [78, 113–116]. The non-magnetic barrier is typically an amorphous or polycrystalline oxide [109, 117]. The recent interest in the use of epitaxial layered systems for this kind of applications is motivated by their reproducibility and by the fact that their transport properties can be modelled theoretically [118, 119]. Since the operating temperature of real devices is higher than room temperature, the search for interfaces which are stable in temperature, so that their characteristics are not modified by use, is also a crucial aspect.

At the interface between a metal and an oxide, in the absence of kinetic constraints, at thermodynamic equilibrium, a reduction of the substrate oxide is expected when the heat of formation of the most stable oxide of the deposited metal is more negative than the one of the substrate oxide [120]. In practice, when dealing with ultrathin film growth, kinetic constraints, such as diffusion, adhesion, formation of mixed oxides and epitaxial constraints, come into play, so the phases formed at the interface can be rarely predicted. Accurate studies for each specific case are therefore necessary.
MgO is suitable to be used as a tunnelling barrier in MTJs due to its high band gap and good chemical, mechanical and thermal stability. Furthermore the compound is rather easy to grow, because of the low melting temperature and high oxygen affinity of magnesium. The relatively small lattice mismatch between MgO and Fe (3.8%) allows to obtain Fe/MgO/Fe junctions with a good epitaxial quality and high tunnel magnetoresistance [79, 121, 122].

MgO is also commonly used as a non-magnetic and non-interacting support for Fe structures in magnetic studies [97, 123, 124]. Theory, in fact, predicts a very weak interaction between Fe and MgO with negligible charge transfer [56].

Growth [98, 116], structure [99, 100] and magnetic properties [56, 97, 124] of the Fe/MgO(001) system have been widely investigated in the last two decades, though the interface properties are rarely taken into consideration. Though most studies report the formation of islands at the first stages of the Fe growth at room temperature [98–100], Suzuki et al. [116] show that 0.8 ML Fe is located in the first layer without significant vertical stacking. The investigation performed by Suzuki et al. by means of coaxial impact-collision ion scattering spectroscopy is, to our knowledge, the only one which studies also the possibility of intermixing at the interface, reporting no Fe interdiffusion in MgO. However the investigation is limited to 0.8 Fe ML deposited at room temperature and annealed to 1070 K. The heat of formation of MgO is more negative than the one of the most stable Fe oxide [125], so thermodynamics does not predict the occurrence of an oxidation-reduction reaction at the Fe/ MgO interface. However recently Meyerhiem et al. [78, 113] observed that at the opposite interface, MgO/Fe(0 01), the presence of MgO induces an unexpected oxidation of the Fe substrate with the formation of a FeO layer at the interface. De Masi et al. showed that a 5 ML MgO buffer layer prevents the NiO reduction at the Fe/NiO(001) interface [104]. The study, however, does not investigate the Fe oxidation at Fe/MgO interface, focusing rather on the effects of the MgO layer on the NiO side of the interface after the growth of a 5 ML Fe film.

Given the conflicting literature results and the lack of an experimental study focused at the Fe/MgO(001) interface characterization, in terms of the chemical state of the two constituents, in this work we present our study of this widely used system by means of a multi technique approach. The stability of the interface with temperature is also investigated. X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD) are used to obtain a first indication of the structure, the chemistry and the growth mode of the interface. X-ray absorption spectroscopy (XAS) is then used to investigate the chemical state of Mg and Fe. XAS is in general more sensitive than XPS to the chemical state of the excited atom, since the XAS lineshape depends not only on the chemical shift of the core level, but also on the site and symmetry projected density of final states.
Experimental

For the experiments here described we used MgO substrates in the form of thin films (10 ML) grown on Ag(001) in order to avoid the charging problems expected with highly insulating bulk MgO samples. MgO films on Ag(001) have been previously shown to have a strained rock-salt structure which relaxes to the bulk one at the used coverages [12, 13]. The Ag surface was prepared by Ar\textsuperscript{+} sputtering (0.6 keV, 1 µA/cm\textsuperscript{2}) and annealing (670 K) cycles in ultra-high vacuum chamber with a base pressure of 6×10\textsuperscript{−11} Torr. MgO was grown by evaporating Mg from a Knudsen cell with a rate of approximately 1 Å/min in an O\textsubscript{2} partial pressure of 4×10\textsuperscript{−8} Torr, keeping the Ag(001) substrate at a temperature of 460 K to enhance surface diffusion. Fe was subsequently grown at room temperature from an electron beam evaporation cell, which allowed to keep the pressure lower than 3×10\textsuperscript{−10} Torr during evaporation. Care has been taken to measure the samples immediately after Fe growth (within approximately 1 min) in order to avoid Fe contamination due to residual gases in the chamber. For this purpose the Fe evaporator was mounted in the XPS measuring chamber. The Fe and MgO thickness were estimated from the deposition rate measured by a quartz micro-balance. A 1 ML Fe/10 ML NiO/Ag(001) sample has been used for comparison with the 1 ML Fe/10 ML MgO/Ag(001) sample. The NiO film has been grown using the same procedures used for the growth of MgO.

The MgO substrate and the Fe films were analyzed on campus by XPS and XPD. The measurements were performed using a non-monochromatized X-ray source and a hemispherical analyzer operating at a normal take-off angle. The analyzer was operated at its lowest angular resolution (\(\Delta \theta = \pm 10^\circ\)), in order to partly average out possible intensity modulations due to photoelectron diffraction. The overall energy resolution was estimated to be \(\pm 1\) eV. Al-K\(\alpha\) photons were used to excite Mg 1s core level, while for Fe 2p spectra we used Mg-K\(\alpha\) photons rather than Al-K\(\alpha\) ones in order to have lower kinetic energy electrons with a higher surface sensitivity. The bulk Fe 2p XPS spectrum was measured on a 35 ML thick Fe film. The background [126] subtracted XPS spectra have all been normalized in intensity in order to compare the lineshapes at the different thicknesses. XPD measurements were performed by rotating the sample in front of the hemispherical analyzer, in this case operating in the angle resolved mode (\(\Delta \theta = \pm 1^\circ\)). Polar scans along symmetry azimuths were performed with a step of 2\(^\circ\), measuring the area of the selected photoemission peak at each polar angle. The displayed spectra have been normalized to have the height of the 0\(^\circ\) forward focusing peak proportional to the anisotropy (defined as \((I_{\text{max}} - I_{\text{min}})/I_{\text{ave}}\) where \(I_{\text{max}}, I_{\text{min}}\) and \(I_{\text{ave}}\) are the maximum, minimum and average intensity of the peak, respectively) of the measured spectra.

Fe L-edge and Mg K-edge XAS measurements were performed at the BEAR beamline [127] of ELETTRA synchrotron radiation facility. The beamline provides bending magnet radiation monochromatized by a plane grating-plane mirror monochromator. The geometry used for XAS measurements was with the photon beam at 45\(^\circ\) from sample normal and the electric field in the growth plane. The spectra were collected in drain current mode without any bias.
applied to the sample. The samples for XAS measurements were prepared in situ using the same procedures used for sample preparation in the laboratory. When we heated the sample the heating temperature was kept for 30 min in order to reach a stationary state. A nonlinear background, fitting the higher and lower energy sides of the edges, was subtracted to the Fe XAS spectra, while no background subtraction was necessary for the Mg spectra, being on a rather flat region of the absorption spectrum. All of the XAS spectra were normalized to the edge jump. It has to be underlined that the photon energy of Mg K-edge (1303 eV) is difficult to be obtained, since it falls near the upper energy limit of grating monochromators and is typically too low for usual single crystal ones. It is remarkable, however that, despite the low available photon flux at the limit of operation of the monochromator, the Mg K-edge XAS spectra could be measured and gave the required information.

**Results and discussion**

The epitaxial quality of the Fe/MgO interface, in terms of film structure and orientation, was first checked by means of XPD on a 5 ML Fe film. Fig. 5.1 shows O 1s, Mg KLL and Fe 2p intensity as a function of the polar angle along the [100] and [110] substrate symmetry azimuths. The O and Mg intensities show angular modulations typical of a rocksalt structure with forward focusing peaks along the [101] ([100] azimuth) and [111] ([110] azimuth) atomic chains. The
features in between the main peaks are due to superposition of higher order diffraction and forward focusing from less packed atomic chains. Since the kinetic energies of Mg KLL and of O 1s electrons are significantly different (950 eV and 724 eV, respectively), the Mg and O XPD spectra are not identical. In particular the intermediate structures are more affected than forward focusing peaks by differences in the kinetic energy. A significant change in the shape of the [111] peak on the [110] azimuth can be detected. In the case of O in fact the peak has the so called volcano-shape, a multiple scattering effect typical of low energy electrons scattered by atoms with a low scattering factor [128]. The Fe 2p angular modulation, instead, presents a strong forward focusing peak at 55° along the substrate [100] azimuth and one at 45° along the substrate [110] azimuth. These indicate the formation of a bcc(001) film rotated in plane by 45° with respect to the MgO substrate, as expected on the basis of the lattice parameter mismatch, which is rather low (3.8%) when considering the Fe bcc side (2.87 Å) and the Mg-Mg nearest neighbour distance (2.98 Å). The high anisotropy of the Fe forward focussing features, comparable to the one of the Mg and O peaks of the substrate, indicates the good crystalline order of the Fe films.

Figure 5.2: (a) XPS Mg 1s spectra excited by Al-Kα photons of the clean MgO substrate (dashed line) and after the deposition of Fe films of different thickness. (b) XPS Fe 2p spectra excited by Mg-Kα photons of Fe films of different thickness and for a bulk Fe sample (dashed line).
In order to have a preliminary information on the chemical environment of Fe and MgO at the Fe/MgO(001) interface we performed an XPS analysis of Fe films of different thickness. Fig. 5.2a shows Mg 1s photoemission spectra for the MgO substrate after coverage by Fe films of increasing thickness. It has to be noted that, since the kinetic energy of Mg 1s photoelectrons excited by Al-K\(\alpha\) photons is as low as 180 eV, the sensitivity to the uppermost MgO layers of such probes is enhanced as compared to the one of the other core level photoelectrons or Auger electrons. Non-oxidized Mg\(^0\) atoms have a 1s photoemission peak at 1303.2 eV binding energy [129], 0.6 eV lower than Mg\(^{2+}\) ions. A shoulder towards the lower binding energy side is therefore expected if a fraction of Mg\(^{2+}\) ions are reduced to Mg\(^0\) as a consequence of the possible oxidation of the deposited Fe. The absence of any Mg 1s lineshape broadening gives a first indication that no detectable MgO reduction is present at the interface. To exclude the occurrence of any interfacial reaction, however, also the Fe 2p lineshape was investigated. Fig. 5.2b shows Fe 2p XPS spectra in the 1-10 ML range. While for coverages larger than 5 ML the spectra show a bulk like shape, as can be seen by comparison with the bulk Fe lineshape also shown in Fig. 5.2b, the 3 and 1 ML spectra show a slight broadening of the 2p\(_{3/2}\) peak towards higher binding energies, though the peak positions and the spin-orbit splitting correspond to those measured at higher coverages. The broadening can be possibly ascribed to a contribution by oxidised Fe atoms, whose 2p photoelectrons are expected to have a higher binding energy [130], but it can also be due to the correlation satellites observed in core level photoemission lines when the dimensionality of the systems is reduced [37]. The Mg 1s and Fe 2p XPS measurements were repeated after heating the 5 ML thick Fe sample to 670 K, without detecting measurable changes in the lineshapes (spectra not shown).

The XPS measurements presented up to this point are not conclusive concerning the chemistry of the interface. At the related Fe/NiO(00 1) interface an oxidation reduction reaction has been shown to take place [105, 106, 131]. MgO and NiO both have a rock-salt structure and a similar lattice parameter (\(a_{\text{MgO}} =4.210\) Å, \(a_{\text{NiO}} =4.186\) Å), and Fe grows epitaxially on both substrates. Therefore we grew a 1 ML Fe/10 ML NiO/Ag(001) sample and compared its Fe 2p XPS lineshape with the one of a 1 ML Fe/10 ML MgO/Ag(001) (Fig. 5.3). When the film is deposited on NiO the Fe 2p peaks show a much larger broadening and a slight shift of the binding energy towards higher values, at least partly induced by Fe oxidation, concomitant to NiO reduction [105, 106, 131]. Thus the differences between the two lineshapes of Fig. 5.3 can be ascribed to less important oxidation at the Fe/MgO interface, but they can also be a consequence of the different growth mode of Fe on the two substrates. A lower surface wetting when 1 ML Fe is deposited on the MgO surface would give rise to a lower fraction of oxide formation at the interface, which could explain the differences in the lineshape. The higher surface free energy of Fe (2.9 J/m\(^2\)) with respect to the one of MgO (1.1 J/m\(^2\)) and of NiO (1.1 J/m\(^2\)) favours island formation on the two oxide surfaces, observed in the first stages of the growth at room temperature on both MgO(001) [98, 116] and NiO(001) [106, 131]. In the case
of the NiO(001) surface we estimated a fractional coverage of 50% (±10%) of the NiO surface by 1 ML Fe [131]. In order to have an estimate of the fractional coverage for the MgO(001) surface, we measured the attenuation of the Mg 1s signal for a 1 ML Fe nominal thickness (i.e. the thickness estimated from the growth rate, corresponding to the real thickness if the surface coverage is complete, to the average thickness otherwise). The measured value is smaller than the one expected in the case of a layer by layer growth (the inelastic mean free path for Mg 1s photoelectrons has been estimated to be ∼ 10 Å [46]). This might indicate either that the deposited Fe atoms form islands and/or that they diffuse into the substrate. Since the possibility of a significant intermixing can be excluded, based on the analysis of the XAS data reported below, we can conclude that the slow attenuation of Mg 1s signal is due only to a non-complete wetting of the substrate by Fe atoms. The experimental attenuation is fairly well reproduced by assuming a fractional coverage of 60% (±10%) of the MgO surface (the ±10% error bar includes the experimental errors on the evaluation of Mg 1s intensity, due to small fluctuations in the stability of the XPS source and electron analyzer and those on the nominal Fe thickness). The wetting of the MgO(001) and the NiO(001) surface by 1 ML Fe is approximately the same, so the presence of oxidized Fe atoms at the interface should have the same weight in the two cases and the difference in the 1 ML Fe 2p lineshape is possibly ascribed to a more metallic character.
5.1 Absence of oxide formation at the Fe/MgO(001) interface

In order to have a definite and reliable picture of the Fe/MgO(001) interface, we measured X-ray absorption spectra on the Mg K-edge and Fe L-edges of Fe/MgO samples. In this case we expect remarkable differences in the Fe and Mg XAS lineshapes in samples with different oxidation state and local environment, as reported in the literature [13, 107]. Mg K-edge spectra for the MgO clean substrate and after the growth of Fe films of increasing thickness in the 0.7-10 ML range are shown in Fig. 5.4a. The signal to noise ratio of the spectra is large enough to exclude the presence of significant differences in the Mg chemical state with increasing Fe thickness. It has to be noted however that the XAS signal comes from the full MgO film thickness, smaller than the secondary electrons escape depth, therefore the presence of a fraction of reduced MgO at the interface layers may be too small to give marked changes in the spectra. Fig. 5.4b shows Fe L-edge XAS measurements of the Fe films of different thickness, in comparison with a bulk Fe spectrum taken from Ref. [107]. The 10, 2 and 1.4 ML films have a bulk-like lineshape with the same energy positions and width of the $L_3$ and $L_2$ peaks. We then focused
on the 1.4 ML film and oxidized it on purpose to have a reference sample also at reduced dimensionality. Fig. 5.5 reports the 1.4 ML spectrum of the as grown 1.4 ML sample, the spectrum obtained after heating the sample up to 670 K and the one after exposing it to $10^3$ L of O$_2$ (assumed to be the saturation exposure) at 670 K. The difference between the as grown spectrum and the one measured after heating is within the noise level. A clear narrowing and shift to 1.7 eV higher photon energy of the L$_3$ peak can be detected after high temperature oxygen exposure of the sample. The L$_2$ edge is broadened and also shifted to higher photon energy, in agreement with the formation of a Fe oxide film after the high temperature oxygen exposure, as can be seen by comparison with the spectra from Fe$_3$O$_4$ and Fe$_2$O$_3$ sample (taken from Ref. [107]). If a part of the "as grown" film were oxidized to Fe$_3$O$_4$ or Fe$_2$O$_3$, we would expected a shoulder in the L$_3$ peak at approximately 1.7 eV higher binding energy. The shape of the measured spectrum allows to limit the possible oxidation to within the noise level at that energy, i.e. approximately 1/10th of the oxidized line intensity. This demonstrates that the Fe/MgO

**Figure 5.5:** Fe L$_{2,3}$ XAS spectra of a 1.4 ML Fe film after growth, after heating to 670 K and after heating to 670 K during exposure to an oxygen dose of $10^3$ L. The figure also shows the Fe L$_{2,3}$ XAS spectra of a Fe$_3$O$_4$ and a Fe$_2$O$_3$ sample (taken from Ref. [107]) for comparison.
interface, as predicted theoretically [56], is non-interacting and stable up to temperatures higher than normal device operation ones.

**Conclusions**

This work confirms the expected good epitaxy and good crystal quality of Fe films on MgO(001). Furthermore it demonstrates that the Fe/MgO(001) interface is sharp at the atomic level with a very weak interaction between Fe and MgO, an aspect which was predicted theoretically, but never carefully proved experimentally. This makes the Fe/MgO interface ideal for the growth of almost free standing Fe films and low dimensional structures, interesting both for the applications and for basic physics studies. We also demonstrate the thermal stability of the interface: Fe keeps its metallic character despite the presence of nearby oxygen atoms up to a temperature of 670 K, higher than the normal operating temperatures of the devices. Fe, in the low coverage range, forms islands on the MgO surface. This should not be a problem for the applications, since the thickness of the Fe layer used is typically above the coalescence limit.

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5.2 MgO structure and morphology

Once the stability of the interface has been proved, the growth of self-assembled nanostructures is the following aim of this work. Therefore first of all in this section a brief discussion about the preparation of the substrate is reported, in order to choose the best substrate to induce the nanostructure organization.

The structure of MgO films grown on Ag(001) has already been extensively reported in literature [11–14, 25], as described in Ch. 1. However the morphology has never been analysed for coverages higher than 8 ML. In particular it has never been investigated with an approach similar to the one described in the previous chapter for MgO/Mo(001). The reason is mainly connected with the high insulator character of the oxide, and features related to strain relaxation are expected to be observed on even thicker films. For technical limits in the imaging of thick MgO films by means of a RT STM, we present here only the characterization by means of LEED. Parallel to the study presented in Ch. 4, we try to correlate the LEED features to the formation of dislocations, following the approach described in Ch. 4.

![LEED patterns of MgO films on Ag(001)](image)

Figure 5.6: LEED patterns of (a) clean Ag(001) and (b) 3 ML, (c) 7.5 ML, (d) 10 ML, (e) 15 ML and (f) 22 ML MgO films on Ag(001) (Ep=163.5 eV). The crystallographic directions of MgO films are indicated, together with the main spots.
For this purpose we have prepared MgO films of increasing thickness in the same conditions described in the experimental part of the previous section. The LEED patterns on the as grown films in the range 3-22 ML are reported in Fig. 5.6 for a primary beam energy of 163.5 eV. The chosen primary energy is a maximum for the (1,0) I(V) of MgO. It can be observed that spots are sharp and form a simple (1×1) till a thickness of about 10-15 ML is reached. Then the appearance of a weak cross around each spot is evident and reaches a maximum contrast at 22 ML MgO thickness. These crosses are aligned along the [100] direction of the MgO film, as in the case of the features observed on MgO/Mo(001) (Fig. 4.4e and 4.8b). In the present case, however, the crosses are more faint and distinct satellites could not be resolved. In Fig. 5.7 the

![Figure 5.7](image)

Figure 5.7: (1,0) spot profiles along the [100] (solid line) and [110] (dotted line) directions taken on some LEED images of Fig. 5.6 (Ep=163.5 eV). The x-axis has been scaled to the MgO first Brillouin zone (Bz). Curves have been normalized to the peak height.

profiles along the two main surface azimuth [100] and [110] of the (1,0) spot are shown for some of the LEED images of Fig. 5.6. The profiles are reported with the parallel component of the scattering vector scaled to the MgO first Brillouin zone (Bz). At the lower coverages the [100] and [110] profiles coincide. At 15 ML a small difference between the two azimuths at around 10%
of Bz can be observed. This variation is larger on the 22 ML profile, even though no additional spots can be resolved and a deconvolution including three Lorentzian components is ambiguous. We can therefore only give a qualitative description of the film structure. The appearance of these features is already reported in literature [25, 132] and assigned to the formation of interfacial dislocations along the [100] direction. This creates tilted mosaics in that direction with an initial tilt angle of about 3°, that decreases with increasing thickness. In Ref. [25] these crosses appear at a lower thickness, due possibly to a different calibration of the deposition rate. The use of a SPA-LEED allowed the authors to deconvolve the various contributions to the spots and to determine into details the surface morphology. However here the scope is to find the actual thickness in our system where the crosses have a maximum contrast and to use the film for Fe growth.

Figure 5.8: LEED patterns of 22 and 40 ML MgO films on Ag(001) as grown and after annealing at 720 K (Ep=163.5 eV). The inset show a zoom of the (1,0) spot of each LEED pattern, together with the lines of the profiles shown in Fig. 5.9.

What has never been observed before on MgO films is the LEED reported in Fig. 5.8. Annealing the 22 ML MgO film at 720 K produces a change in the spot shape, varying from
almost square aligned to the [100] direction to round. The profiles before and after annealing are reported in Fig. 5.9a for the two different azimuths. The [100] profile is unchanged, while the [110] becomes slightly larger with annealing. This indicates the appearance of an additional component aligned along the [110] direction. The same effect is even more evident on a 40 ML thick film, where before annealing the spot is almost round while after annealing the spot becomes square and aligned along the [110]. In fact the [110] profile does not change and the [100] sharpens, indicating the disappearance of extra structures in the [100] direction (Fig. 5.9b). This suggests a modification of the mosaics whose tilt direction rotates by $45^\circ$ from the [100] to the [110], favored by the increase in the temperature and in the thickness. The same effect has been observed and described in Sec. 4.3 for MgO/Mo(001) and seems therefore typical of MgO, rather than of the specific system here considered. The influence of the substrate is related to the different mismatch, higher in the case of Mo(001), that induces more defined structures in the MgO film. On the contrary MgO/Ag(001) system does not show a definite spot splitting, that can be assigned to the formation of mosaics with a definite tilting angle. Here the spots are broad with a four-fold symmetry, suggesting the presence of a wider range of tilting angles. Also the critical thickness for mosaic formation, related to the strain relief, is lower for MgO films on Mo due to the larger lattice mismatch.

The interpretation we suggest is similar to the one discussed in Sec. 4.3 for MgO/Mo(001). We expect the formation of interface dislocations to relieve the strain, that starts at about 10 ML and is completed at 20 ML for MgO/Ag(001) [12, 13]. These dislocations form along the ⟨100⟩ direction, as reported previously for a glide system $\frac{1}{2}\langle 110 \rangle \{110 \}$ [24, 25, 96]. This creates steps at the surface and regions tilted of a certain angle. In this case it is hard to say if the surface is covered by pyramids (Fig. 4.12a) or by linear steps (Fig. 4.12b and c), because no STM images are available for such thicknesses. The wide range of the tilt angles for MgO/Ag(001) is evident from the absence of distinct spot splitting as compared to MgO/Mo(001) and is due to the smaller mismatch and therefore to the larger thickness at which the strain is relieved, determining a weaker elastic deformation of the surface. Furthermore this can induce also a lower degree of order in the dislocation network. Increasing the thickness or the temperature the mosaics move towards the ⟨110⟩ directions, due possibly to a change only in the surface deformation or to a modification in the glide system to one less energetically favoured for a bulk, but maybe more stable for a film, as already discussed in Sec. 4.3. Regions tilted along the ⟨110⟩ directions are observed also on another rocksalt oxide, namely CoO, deposited on Ag(001) [133].

Therefore we expect that, like in the case of MgO/Mo(001), the surface morphology is influenced by the presence of this dislocation network. One way to see it indirectly is to investigate the possible induced organized growth of metals on top via the deposition of Fe on a suitably chosen MgO film. For this reason different Fe films have been grown on 22 ML MgO, the thickness where the crosses are more distinct, and imaged by STM.
5.3 Fe nanostructure growth on MgO/Ag mosaics

Scanning tunnelling microscopy (STM) measurements were performed at room temperature on the as-grown Fe samples to investigate the Fe morphology and organization. The STM was operated in constant current topography (CCT) mode at room temperature using a bias between +1.8 and +3.0 V on the sample with the tip grounded and 0.1 nA tunnelling current. The STM images have been processed by means of SPIP 4.3.2.0 program [134]. In order to extract the average lateral island dimension a grain size analysis has been performed on five $100 \times 100$ nm$^2$ different areas for each Fe nominal coverage. The cluster size is certainly influenced also by the tip shape. However here the trend in the cluster diameter is the main point of the discussion.

Fe was grown using a Knudsen cell, calibrated by a quartz microbalance. In the following we will refer to the different samples studied in terms of the nominal amount of deposited Fe in monolayers (1 ML=1.435 Å). These numbers do not have to be considered as a proper thickness of the Fe layer, since Fe atoms actually organize into islands rather than into a continuous film, as will be shown.
5.3 Fe nanostructure growth on MgO/Ag mosaics

It was very difficult to obtain good images for sub-monolayer Fe coverages, where large uncovered MgO areas prevented to obtain stable tunnelling conditions, due to the wide band gap of the oxide. The lowest coverage which gave a good image was 2 ML. In Fig. 5.10 representative STM images obtained for 2, 3, 5 and 15 ML Fe on 22 ML MgO are shown. At 2 ML nominal coverage Fe forms very small islands with an average diameter of 5 nm. The average height of such clusters appears to be 2 nm. It has to be noted that, at least at low coverages, the measured value of the cluster height may be altered by the different electronic structure of MgO and Fe. At 3 ML the clusters are larger and reach an average width of approximately 8 nm and a height of 2.2 nm. After 5 ML Fe deposition a 11 nm average width and 2.2 nm average height were measured. At 15 ML the clusters are further enlarged in size reaching 12 nm average diameter,
while their height is 2.1 nm in average. At all thicknesses the clusters are rather regular in size and tend to have a square or polygonal shape. The trend in the cluster size is reported in Fig. 5.11b. The diameter increases rapidly between 1 and 5 ML, saturating then to 12 nm.

![Figure 5.11: Average Fe cluster diameter as a function of (a) underlying MgO thickness and (b) nominal Fe thickness. The error bar is the standard deviation of the size distribution averaged over five 100×100 nm² STM images.](image)

In some areas of the sample clusters line up along the [100], the direction where alignment is expected if driven by mosaics on MgO surface, as shown in Fig. 5.10b. However a regular distribution cannot be observed on the whole sampled areas. The effect of the thickness of the underlying MgO film on Fe clusters shape and size was found to be negligible, providing the MgO thickness to be larger than a few monolayers (Fig. 5.11a).

It can be seen in Fig. 5.10c and d that increasing the Fe thickness from 5 to 15 ML the size distribution of the clusters enlarges, leading to less homogeneous clusters. This reflects in the larger error bar of the Fe cluster diameter for 15 ML Fe compared to the lower Fe thicknesses. Furthermore the homogeneity in the cluster size together with a tendency in the [100] orientation, at least for low enough thicknesses, suggests that the dislocation network may provide preferential nucleation centres for Fe clusters. This network however is not very regular, as already revealed by the faint structures in LEED. Therefore the crossing points of dislocations are possibly enough to nucleate clusters of a determined size, but the dislocations lines and thus the surface steps are not straight and long enough to induce well-organized lines of clusters. Additionally the possible coexistence of two different orientations of the tilted regions can complicate further the situation.

Additionally the deposition rate and temperature can play an important role. Since the substrate organization is not very regular, the use of low deposition rates (and consequently larger adatom diffusion length) and of higher temperature can help the cluster arrangement.
The stability of the lattice adsorption sites (on top of O atoms) may be comparable to the one of surface defects like steps introduced by mosaics. Therefore the good epitaxy of Fe on MgO could prevent the organized growth. This effect has been taken into consideration by depositing Fe on CoO/Ag(001). CoO is also a rocksalt oxide with a small lattice mismatch with Ag (4.5%) and it has been shown to form mosaics after a critical thickness is reached [133]. Deposition of crystalline Fe (the mismatch between CoO and Fe is about 5%) on top of this mosaic surface leads to the formation of clusters with a square symmetry along the \(\langle 100\rangle\) oxide directions. Thus it cannot be considered as a general statement that epitaxy prevent the nucleation on the dislocation network.

Last but not least the presence of a high amount of defects on the surface (low-coordination sites, oxygen vacancies, etc.), energetically comparable to special sites induced by mosaics, could create further nucleation centers which prevent an organization due to the dislocations. Annealing of the MgO surface does not improve the LEED quality but only changes the mosaics orientation. This suggest that a small mobility has been given to the oxide atoms, maybe not enough to improve the surface morphology. For this reason it would be interesting to repeat the same kind of experiments on MgO/Mo(001), where there are some more favorable conditions (possibility to treat the film at high temperatures and therefore better defined surface features at lower MgO thicknesses) and a more complete characterization of the surface morphology is available.

5.4 Conclusions

In the present chapter we have investigated the Fe/MgO system as prepared by deposition on Ag(001).

First the absence of chemical reactions and strong electronic interactions at the interface has been proved by means of XPS and XAS, together with the thermal stability up to a temperature of 670 K. The good Fe crystal quality was also confirmed by means of XPD.

Then the morphology of the system has been studied, starting from the morphology of MgO films grown on Ag(001). These films show the appearance of mosaics aligned along the [100] direction at about 15 ML, becoming evident at 22 ML. The increase in MgO thickness or the sample annealing induces the rotation of mosaics to the [110] direction. The presence of mosaics due to an interfacial dislocation network has been observed in the past to induce a self-organized growth of metal clusters [28, 29]. Therefore we have grown increasing Fe amounts on 22 ML MgO and investigated the morphology by means of STM. For low Fe coverages the atoms aggregate into islands with nanometric lateral size where Fe atoms have an average atomic coordination very different from the bulk. This may imply different electronic and magnetic properties for Fe/MgO low dimensional systems, interesting for data storage technology, which will be subject of further investigation.
Clusters homogeneous in size line up in chains, but a strong alignment is not evident. The oxide patterning is therefore not regular enough to strongly influence the Fe growth.

5.5 Future perspectives

Though it was not possible to image sub-monolayer Fe coverages, already at 1 ML the Fe islands are formed by Fe atoms which, in average, have a local atomic environment markedly different from the one of Fe atoms in the bulk. Therefore their valence band is expected to have a different empty and filled states structure with changes in the related properties compared to bulk Fe. Based on the STM images measured, a dominantly bulk-like situation for Fe atoms is expected to be reached between 3 and 5 ML nominal coverage.

A further improvement of the oxide patterning by changing the growth conditions (deposition temperature or employ of atomic oxygen) or using MgO/Mo(001), and a deeper surface characterization by means of X-rays (GIXD - Grazing Incidence X-ray Diffraction), together with a study of the deposition parameters of Fe can help to induce a more evident nanostructure organization.

Additionally other metals can be employed (Au, Ni), not only to investigate the self-organization, but also the variations in the electronic, magnetic and optical properties.

Furthermore a reduction of the dimensionality of the system is expected to enhance electronic correlations. In previous experiments this has been shown, however, only for systems where metals have been used as substrates, with non negligible hybridization between overlayer and substrate states. Therefore self-assembled Fe nanostructures on MgO(001), both as a film or as a stepped surface, can be the proper system to study the modifications of the electronic structure as a function of Fe local atomic coordination and dimensionality.
Chapter 6

Comparison with metals on NiO(001) systems

In previous chapters a study of patterned MgO bulk and films and successive Fe deposition has been presented. The importance of the system in various fields, like magneto-electronic devices and catalysis, both for the films and the nanostructures was underlined. The sharpness and the stability of the interface allow to consider the Fe overlayer as almost free-standing and its properties as related only to the reduced dimensionality and not to the interactions with the substrate.

Another rather similar and interesting subject is the deposition of metals on NiO films. NiO has the same rocksalt structure of MgO and is an insulator, even if the band gap is smaller (3.6 eV) than for MgO. It has a small lattice mismatch with Ag(001) (2.1%) and it has been extensively characterized in the past [25, 135–137]. NiO films show features very similar to MgO, relieving the misfit strain between 10 and 20 ML [136, 138], with a surface morphology that for thin films shows square islands exhibiting [110] polar edges [139]. Furthermore LEED patterns show the presence of crosses aligned with (100) directions for film thickness between 5 and 18 ML [25] and, as discussed in the case of Fe/MgO, the presence of mosaics could influence the overlayer morphology. Nothing is however reported for thicker films to my knowledge.

In addition NiO is an antiferromagnet (AFM), therefore interesting for the magnetic properties of the oxide itself and especially after the deposition of a ferromagnet (FM) like Fe. FM-AFM interfaces attract wide interest due to the exchange bias and its possible applications for spin-valves [111, 140].

In this case the interface is not sharp, leading to chemical reactions and interdiffusions at the interface. In view of a comparison with the previous system, the aim of the work presented in this chapter is to deepen the knowledge of the chemical processes (presented in Sec. 6.1 in form of a paper) and the structural and morphological characterization at the interface (Sec. 6.2). In fact metal-oxide interaction can strongly influence the electronic and magnetic properties of Fe.
films and nanostructures on NiO.

The same characterization is discussed also in the case of Au/NiO, where an unexpected chemical interfacial interaction is present. The system, interesting for catalytic applications, can highlight the dependence of electronic properties of Au in connection to the interaction and defectivity of the substrate. First the chemical and morphological investigation is reported in Sec. 6.3 in form of a paper, and then a brief discussion of the Au film structure is presented (Sec. 6.4).

This work will therefore help future investigations to compare the properties of these similar but basically different systems: metals on NiO and on MgO.
6.1 Chemical reactions and interdiffusion at the Fe/NiO(001) interface

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Abstract

The interaction between Fe and NiO(001) surface for increasing metal deposition at RT was studied by means of X-ray photoelectron spectroscopy and X-ray photoelectron diffraction. NiO reduces to an extent that depends on the amount of deposited Fe, up to a maximum of 1 ML for Fe deposition of 5 ML or larger. The overlayer initially grows in a 3D island mode, with partial intermixing between the deposited Fe atoms and the metallic Ni atoms resulting from the reduction process. The intermixed region extends up to about 3 ML. For 5 ML Fe deposition, the islands coalesce into a continuous film.

Introduction

Metal-metal oxide multilayers are of fundamental importance in many applications, including microelectronic devices, gas sensors, heterogeneous catalysts, electronic packaging and metal-ceramic bonding. Interfacial interactions often determine the overall properties of the metal-oxide system. In this context, Fe-NiO films play a prominent role as prototype systems to study the magnetic behaviour of a ferromagnetic-antiferromagnetic (FM-AFM) interface, in particular as far as the exchange bias coupling is concerned [111, 140]. Although theoretical models of different FM-AFM systems often assume an abrupt interface, experimental studies showed that their magnetic behaviour is extremely sensitive to the details of the interfacial roughness, diffusion, chemical state and geometrical structure [111, 140]. NiO is a very appealing AFM material for several reasons, including the quite easy and well controlled epitaxy of this oxide on Ag(001) [25, 135–137] and the large Néel temperature (523 K). Fe is a FM material showing a good epitaxy on NiO [105, 106]. However, clear evidences of oxidation-reduction reactions at the interface between Fe and NiO(001) have been reported in the literature [105–107]. A decrease of the Fe magnetic moment at the interface with NiO have been observed and ascribed to the disorder at the interface with the formation of intermixed regions and the appearance of additional, magnetically relevant actors like FeO [141]. Oxidation-reduction processes and formation of complex interfaces were also observed for Fe deposition on different metal oxides like CoO(001) [107, 142], TiO$_2$ (110) [143] and Si native oxide [144], and for different transition metals like Co [105, 145] and Mn [105] on NiO(001). The formation of a Fe oxide layer has also been reported for NiO [146] and MgO [78, 113] growth on Fe(001).

The main objective of this work is to provide a better understanding of the processes oc-
currying at the Fe-NiO interface, to describe the details of the chemical interaction, the species redistribution and the growth mode. These phenomena are expected to directly influence the interaction and ordering of interfacial spins and therefore to be of crucial importance for the explanation of the magnetic effects observed for this system [141, 147]. For several relevant aspects, e.g. (i) the (initially) three-dimensional overlayer islands growth, (ii) the formation of an (at least locally) ordered, epitaxial Fe-Ni mixed layer, (iii) the confinement of the oxidation-reduction process to the very outermost substrate layer (only one NiO ML involved), the picture of the Fe/NiO interfacial processes reported in this paper significantly deviates from the previously reported results [105–107].

Experimental

The NiO substrate used for the subsequent Fe deposition was in the form of a 10 ML film on a Ag(001) single crystal. The details of the preparation procedure used for NiO films are described elsewhere [136]. Fe films were deposited at room temperature on top of the NiO films, at a deposition rate of about 0.5 ML/min. The Fe atoms source was an electron bombardment evaporation cell, calibrated by a quartz microbalance.

XPS measurements were performed to investigate the composition of the growing film and the chemical processes occurring at the interface. The spectra were collected with an energy resolution of 1 eV at a take-off angle of 10° with respect to the surface normal. The take-off angle was integrated over ±10°, to ensure diffraction effects from the ordered substrate and overlayer to be smeared out. Selected spectra were also collected at 50° and 65° take-off angles. Angle-resolved X-ray Photoelectron Diffraction (XPD) measurements were performed to determine the chemical resolved, local environment of the different atomic species in the growing film and in the interfacial region. Polar scans, with an angular resolution of ±1°, along the [100] substrate azimuth of the (001) surface of the NiO film, were measured by rotating the sample in front of the analyser by steps of 2°. All the measurements were performed at room temperature. Simulations of XPD spectra to obtain anisotropy values were performed by means of MSCD code developed by Chen and Van Hove [44]. The code performs multiple scattering calculations, in this case up to 8th order events. The cluster used is defined as a semi-ellipsoid with circular basis of radius constant to 10 Å and depth variable with the number of layers involved.

Results

Fig. 6.1 shows the Ni 2p spectrum of the clean NiO film and for increasing Fe deposition. The Ni 2p spectrum of a pure Ni film is also shown for comparison. The substrate spectrum exhibits a bulk-like lineshape indicating that the 10 ML NiO film is a good mimic of a bulk NiO. The deposition of Fe induces relevant changes in the substrate spectrum, reflecting the occurrence of significant chemical bonding modifications in the outermost substrate layers. Beside the
6.1 Chemical reactions and interdiffusion at the Fe/NiO(001) interface

characteristic NiO lineshape, additional features appear on the low BE side of the $2p_{1/2}$ and $2p_{3/2}$ features, whose energy positions strictly agree with the BE of the corresponding peaks in the metallic Ni spectrum. These additional features become more and more intense for increasing Fe deposition, clearly indicating the occurrence of a Fe-induced chemical reduction of nickel cations (Ni$^{2+}$) with the formation of an increasing amount of nickel atoms in a metallic state (Ni$^0$), as already reported on this system [106, 107]. Changing the take-off angle from near-normal to grazing, as shown in the figure for the 8 ML Fe case, the Ni$^0$ contribution to the spectrum significantly increases, indicating that the reduction process is localized in the outermost region of the substrate layer.

Figure 6.1: Ni 2p XPS spectra for the 10 ML NiO substrate (bottom curve) and for increasing Fe deposition. The 2p spectrum of pure Ni metal is shown for comparison (top curve). The spectra are collected at $10^\circ$ take-off angle. For 8 ML Fe deposition, a spectrum collected at $65^\circ$ take-off angle is also shown (dotted line). All the spectra have been background subtracted using a Shirley algorithm.

The driving force for the NiO reduction process is the thermodynamically favourable Fe oxidation with respect to Ni oxidation, due to higher oxygen affinity of Fe. Therefore concurrent with substrate reduction, oxidized states are observed for the metal overlayer. In the photoelectron spectra recorded at the Fe low deposition stage, additional intensity appears on the high
Comparison with metals on NiO(001) systems

BE side of the Fe 2p lines, with respect to the metallic Fe spectrum (Fig. 6.2). This contribution can be ascribed to the presence of a certain amount of Fe atoms in a Fe$^{2+}$ state on the basis of the lineshape of the difference spectrum (Fig. 6.2, bottom curve) [130]. Formation of FeO has already been suggested when the only source of oxygen was the adjacent NiO layer [107]. The relative weight of the Fe$^{2+}$ contribution to the overall Fe 2p spectrum does not depend significantly on the take-off angle (Fig. 6.2, top curves). This means that FeO is rather homogeneously distributed within Fe overlayer. The misfit between Fe and FeO is small enough (about 6%) to be consistent with the presence of FeO microaggregates dispersed in the growing bcc Fe matrix. Outdiffusion of oxygen through the grain boundaries of the growing overlayer must be assumed to explain the in-depth distribution of Fe oxide [105]. From the relative spectral weights of Fe$^{2+}$ and Fe$^{0}$ components the fraction of the deposited Fe atoms that is oxidized can be roughly estimated for each Fe deposition (inset of Fig. 6.2).

![Figure 6.2: Fe 2p XPS spectra collected at 10° and 65° take-off angle (top curves) for 5 ML Fe deposition. The 2p spectrum of pure Fe metal is shown for comparison (dotted curve). The difference spectrum between XPS spectrum for 5 ML Fe deposition and the pure Fe one is also shown (dashed curve). All the spectra have been background subtracted using a Shirley algorithm. The inset shows the number of oxidized Fe layers as a function of Fe deposition.](image)
In order to quantify the extent of the reduction reaction, a simple evaluation of the relative weight of the Ni\(^{2+}\) and Ni\(^0\) components of the Ni 2p spectra can be misleading, because the interface morphology must be also taken into account. In particular the possible growth of Fe in form of separate islands, already suggested for the initial stage of the Fe deposition on a number of oxide substrates [98, 101, 143], is expected to largely affect the quantitative approach. In fact the reduction reaction only involves the fraction of the substrate covered by Fe islands. Possible Fe-Ni alloying at the interface should also be taken into account.

The actual interface morphology and species distribution have been obtained by XPD measurements (Fig. 6.3a). Previous XPD measurements of the Fe/NiO interface [105] were focused on the Fe overlayer signal intensity angular distribution (IAD). However more detailed information can be extracted from the IAD of XPS signals of other species involved in the oxidation-reduction process, in particular the chemically resolved Ni\(^{2+}\) and Ni\(^0\) components of the Ni 2p spectrum (shown separately in Fig. 6.3a). The O 1s and Ni\(^{2+}\) 2p IADs are very similar, both reflecting the symmetry of the rocksalt structure of the NiO substrate along the selected [100] azimuth. It is noticeable that the metallic Ni signal intensity oscillates in strict agreement with the Fe signal intensity, indicating a bcc local atomic environment for the interfacial metallic Ni. This suggests the formation of a bcc Ni-Fe alloy at the interface. A further evidence for the formation of an alloyed region is given by the angular dependence of the Fe 2p/Ni\(^0\) 2p intensity ratio. The data are shown in the inset of Fig. 6.4 for 5 ML Fe coverage. The intensity ratio has a nearly constant value for near-normal and grazing take-off angles, as expected for the formation of an intermixed layer (dashed curve). On the contrary the angular behaviour expected for the case of a sharp interface between an outermost Fe layer and an underlying metallic Ni layer (continuous line) does not account for the measured values. Although the possible formation of a M-Ni (M=Fe, Co) alloy has been already mentioned [106, 107, 141], in previous papers [105–107] the interface was always modelled assuming the Ni atoms layer to remain confined in the substrate topmost region. The XPD results of Fig. 6.3a on the contrary suggest that some degree of Fe-Ni intermixing actually occurs and must be considered in the interface modelling for a reliable quantification of the oxidation-reduction process. In the following, we assume this alloy to have an average Ni concentration of 25% (the maximum Ni concentration for which bulk Fe-Ni alloys are stable in a bcc structure). The dependence of the final results on this assumption was also checked (see later).

The strength of the oscillations in the Fe and Ni\(^0\) IAD also gives information on the overlayer growth mode, necessary to go on towards the quantification of the reduction effects. The anisotropy values\(^1\) of the [001] peak at 0° in the Fe IAD have been measured as a function of Fe deposition and are shown in Fig. 6.3b (open dots). The anisotropy values obtained by multiple scattering-based simulations [44] in the assumption of a layer-by-layer growth mode, also shown

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\(^1\)The anisotropy is defined as \(2(I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}})\), where \(I_{\text{max}}\) is the maximum of the intensity and \(I_{\text{min}}\) is the average value of the two intensity minima for the considered peak.
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Figure 6.3: (a) Intensity distribution of the Ni$^{2+}$ and Ni$^{0}$ 2p, O 1s and Fe 2p as a function of the polar take-off angle along the [100] substrate azimuth, for 5 ML Fe/NiO. The spectra have been normalized to the intensity of the [001] peak. (b) Measured (•) (the dot dimensions are representative of the error bars in the vertical direction) and calculated (○) anisotropy of the [001] peak at 0° and fractional coverage (▲), deduced from the comparison between experimental and calculated anisotropy values, as a function of the Fe deposition.

In Fig. 6.3b as full dots, largely deviate from the measured ones in the low deposition range. In particular the non-zero anisotropy of the [001] peak measured for 1 and 2 ML deposition cannot be fully explained by assuming the formation of an alloy at the interface. In fact the effective metallic layer thickness would be increased by one third of its nominal value if only intermixing is considered. In order to explain the discrepancies between the measured and calculated anisotropy values a three dimensional islands Fe growth has also to be called into play. The fractional coverage has been determined for each deposition step by comparing the measured and calculated anisotropy values, previously normalized to their saturation values, and is shown
in Fig. 6.3b (triangles, right axis). For 1 ML deposition, a continuous film model suggests the Fe atoms to be distributed in a 1.3 ML thick Fe-Ni alloy, however the measured anisotropy indicates that the alloy aggregates in 2.6 ML thick islands covering 50% of the substrate. A complete NiO surface coverage is only obtained for 5 ML Fe deposition. This is to our knowledge the first report on three-dimensional metallic island formation on NiO induced by Fe deposition.

**Figure 6.4:** Ni$^0$ and Ni$^{2+}$ 2p intensity as a function of Fe deposition (the dot dimensions are representative of the error bars in the vertical direction). The lines represent the best fit of the intensities calculated in the exponential attenuation model, assuming the fractional coverage deduced from XPD results of Fig. 6.3b and the formation of a Fe-Ni alloy. The inset shows the Fe 2p/Ni$^0$ 2p intensity ratio as a function of the take-off angle measured on a 5 ML Fe film (triangles) and calculated in the assumption of a sharp interface between the Fe overlayer and a pure metallic Ni layer (solid line).

Moving back to the quantification of the reduction process, in Fig. 6.4 we report the intensity of the Ni$^{2+}$ and Ni$^0$ components of Ni 2p XPS spectrum as a function of Fe deposition. The Ni$^{2+}$ intensity shows a decrease with Fe overlayer thickness due to both the attenuation effect and to the additional decrease of the number of Ni$^{2+}$ atoms caused by the reduction process. The presence of a fraction of Fe-O aggregates within the overlayer has been taken into account by simply including an additional layer of appropriate thickness (see the inset of Fig. 6.2) with the same attenuation efficiency of the Fe-Ni alloy. The Ni$^0$ component behaviour is determined by the competing effects of the reduction process, that progressively increases the number of metallic
Ni atoms in the sampled region, and of the attenuation induced by the growing Fe overlayer. The Ni\(^{2+}\) and Ni\(^0\) intensity behaviour have been modelled in the exponential intensity attenuation approach assuming the formation of a Fe-Ni alloy with an average Fe concentration of 75%, covering the fraction of the surface previously determined by XPD, and using the number of reduced NiO layer as fit parameter. Satisfactory fits of both the Ni\(^{2+}\) and Ni\(^0\) intensity curves have been obtained (continuous curves in Fig. 6.4). The best-fit parameter values are reported in Fig. 6.5. The amount of NiO affected by the reduction process increases with the amount of deposited Fe, however the reduction rate decreases (Fig. 6.5a). The process stops for Fe deposition larger than 5 ML, when the surface coverage is complete. This indicates that the strength of the interfacial reactions is controlled by the uncovered fraction of the NiO surface.

Figure 6.5: Best fit parameters of Fig. 6.4. (Panel a): number of reduced NiO layers as a function of Fe deposition (▲); data by Refs. [106] (□) and [107] (○) are also reported for comparison. A sketch of the interface is shown in the top part. (Panel b): thickness of Ni-Fe alloy and of pure Fe as a function of the Fe deposition (the dot dimensions are representative of the error bars in the vertical direction).

Fig. 6.5a also shows the results of similar studies [106, 107]. The number of reduced NiO
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Layers are systematically larger than the one obtained in the present study. This discrepancy is possibly ascribable to the simplified model used in Ref. [106, 107], where the alloy formation and the islanding growth mode were not included.

The inset of Fig. 6.5a shows a picture of the proposed arrangement of the Fe/NiO interface. The thickness of the Fe-Ni alloy layer and the thickness of the outermost metallic Fe layer are shown in Fig. 6.5b for each Fe deposition stage. Up to 3 ML deposition, all the deposited Fe atoms take part in the intermixed phase. For larger Fe deposition, the thickness of the intermixed phase still increases with a reduced rate and part of the Fe atoms starts to form a pure metal overlayer.

A final, open question is to what extent the assumption of an average Ni concentration of 25% in the alloy would affect the reported results. Changes of this concentration in the 15-35% range still enable to satisfactorily fit both the experimental attenuation curves of Fig. 6.4 with very similar sets of fitting parameters. This indicates that the relevant quantitative results of this investigation, namely the number of the reduced NiO layer and the relative extension of the intermixed region and of the pure Fe layer (Fig. 6.5), does not depend significantly on the assumptions on the alloy composition.

Conclusions

In conclusion, this work provides detailed and quantitative evidences of the fact that Fe/NiO(001) interface is far from sharp. An interfacial intermixed Fe-Ni bcc phase is formed as a consequence of the NiO reduction process, promoted by Fe atoms deposition. In the initial Fe deposition stage three-dimensional islands form. Both the fractional coverage and the amount of reduced NiO increase with Fe deposition. Interfacial reactions stop after 5 ML Fe deposition, corresponding to a complete coverage of the surface. It is noticeable that these reactions do not prevent the formation of an epitaxial and well ordered Fe overlayer. Both the Curie temperature and the magnetic moment of the ferromagnetic overlayer are expected to become lower as the interfacial intermixing occurs, due to the decrease of Fe concentration in the Fe film [141, 148]. The presence of Fe-O aggregates in the overlayer is expected to give a further contribution to the Curie temperature reduction [148]. Dichroic and MOKE measurements are in progress to determine the detailed effects of the interfacial processes on the magnetic behaviour of Fe/NiO system.

Acknowledgments

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6.2 Structure and morphology of the Fe/NiO interface

In Sec. 6.1 some information about the Fe film structure has been given (Fig. 6.3). In this section we want to deepen the study of the interfacial structure, in order to better understand the configuration of the mixed Fe-Ni layer.

![LEED patterns](image)

**Figure 6.6:** LEED patterns of (a) clean Ag(001) (Ep=120 eV), (b) 10 ML NiO and (c) 5 ML Fe (Ep=170 eV). (d) Fe in-plane parameter as a function of Fe deposition as determined by means of LEED. The references values for bulk Fe, Ag and NiO (in the two latter cases the value of the half diagonal \(d/2 = a \cdot \sqrt{2}/2\)) are reported.

First of all the in-plane parameter \(a\) has been measured from LEED patterns. To determine the evolution of the lattice parameters, the distance between diffraction beams has been measured, averaged over the distances between different equivalent spots. They have been compared with a known standard sample, in this case the clean Ag(001) surface. Images have been taken at an energy of 170 eV, since this energy corresponds to a maximum in the I(V) of the (1,1) spots of Fe and to a minimum in the I(V) for Ag and NiO spots. The values obtained are reported in Fig. 6.6d, together with lines representing the bulk Ag, NiO and Fe values. The 10 ML NiO film shows an \(a\) value comparable to that of the bulk Ag within the error, in accordance to previous results [136, 138]. Fe thin films are pseudomorphic to the substrate, as expected.
Increasing the thickness, Fe lattice parameter reaches its equilibrium bulk value for about 5 ML ($a = (2.85 \pm 0.04) \text{ Å}$), due to the small mismatch. This is valid at least for the superficial layers, that for 5 ML are constituted by pure Fe. No information can be argued for the interfacial mixed layers, even if we can suppose a gradient from a parameter corresponding to the NiO substrate to the Fe bulk value. In fact bulk and films of Ni$_{0.25}$Fe$_{0.75}$ alloy at this concentration show the lattice parameter of pure bulk Fe [149].

![Figure 6.7](image)

**Figure 6.7:** Measured IAD of the Ni$^0$ 2p (○) and Fe 2p (□) as a function of the polar take-off angle along the (a) [100] substrate azimuth and (b) [110] substrate azimuth for 5 ML Fe/10 ML NiO. The spectra have been normalized to the intensity of the [001] peak. The solid lines are the best-fit simulations obtained with the MSCD code. See text for details.

To get more information about the Fe-Ni interfacial layers we have determined the lattice parameters $a$ and $c$ from the Ni$^0$ 2p XPD plot for the 5 ML Fe film reported in Fig. 6.7. To do this the Ni 2p spectra have been deconvolved in the two Ni$^0$ and Ni$^{2+}$ components and the IAD of the metallic part has been considered, since it is more sensitive to the alloy structure. 5 ML were still enough to have signal from the interface and gives a high signal to noise ratio, determining clear features in the IADs. We have compared XPD measured plots with simulations performed by means of the MSCD code developed by Chen and Van Hove [44]. The code performs multiple scattering calculations, in this case up to $8^{th}$ order events. The cluster used is defined as a semi-ellipsoid with circular basis of radius constant to 10 Å and depth variable with the number of
layers involved. For further details see Sec. 2.1. The cluster used for the simulations was made by 2 ML of pure Fe on 4 ML of Ni$_{0.25}$Fe$_{0.75}$, as determined in previous section. The presence of oxygen has been discarded, due to its negligible contribution to the final IAD in the considered model. The position of O has been determined in another work by means of EXAFS at the Fe K-edge, more sensitive to the variations in the local atomic environment of Fe [150]. On the other side, EXAFS is not sensitive to the difference between Ni and Fe scattering atoms. Therefore it was not possible to determine the lattice parameters for the alloy in Ref. [150].

![Graph showing R-factor values as a function of in-plane and out-of-plane parameters of Fe.](image)

**Figure 6.8**: R-factor values as a function of (a) in-plane and (b) out-of-plane parameters of Fe. The minimum values and the associated errors are reported in both cases. The equilibrium values for bulk Ag and Fe are indicated by arrows.

The in-plane parameter has been determined to test the possible differences with LEED. In the model cluster the out-of-plane parameter has been fixed to the bulk Fe value and the in-plane parameter (the same for all the layers in the cluster) has been varied from 2.5 Å to 3.4 Å in steps of 0.1 Å. In Fig. 6.8a the R-factor as a function of $a$ has been shown for Ni$^0$ 2p IAD, averaged over the two azimuths. The minimum in the R-factor is given by $a = (2.96 \pm 0.10)$ Å. The value found with XPD simulations is larger than the result obtained from LEED. This could be due to an expanded lattice cell at the interface with NiO, that is not sampled by LEED, while XPD is sensitive to the average in-plane parameter within the sampling depth. Thus a gradient of the in-plane lattice parameter within the depth of the film is probably present. Anyway it is consistent within the error with the value obtained by LEED. The MSCD code does not permit the introduction of different in-plane parameters for the different layers of the cluster. Therefore we set the in plane parameter of the whole cluster and the out-of-plane parameter of the 2 ML of pure Fe on top to the bulk value.
Then the Ni$^0$ 2p IAD has been simulated varying the out-of-plane parameter $c$ in the 4 ML of Ni-Fe alloy. The R-factors as a function of $c$ are reported in Fig. 6.8b averaged over the two azimuths. The best-fit value is $c = (2.64 \pm 0.10)$ Å and does not depend substantially on the $a$ value. The simulation of Fe 2p IAD is in accordance with these results. The value found for $c$ indicates that the alloy is compressed. Since it is located at the interface, it could be subject to a gradient in the lattice parameters. This can have possible influences on the magnetic properties of the system, especially for thin Fe films. The presence of strain in fact can modify the magnetic properties of the Fe atoms in the mixed layer, in analogy with the results obtained in Ref. [151] for Co films on Mo(110). The best-fit simulations are reported for both IADs along both azimuths as solid lines in Fig. 6.7. The agreement is good and the simulated and measured plots show the same features. There is a larger deviation in the Fe 2p simulated IADs, due to the limited cluster that cannot have more than 300 atoms. This limitation introduces an approximation, especially on complex clusters like an alloy. Therefore differences in the features anisotropy can be observed, more evident on Fe. Also for this reason the determination of the lattice parameter is more reliable on the Ni 2p IAD.

![STM images of Fe deposition on NiO film](image)

Figure 6.9: CCT 100×100 nm$^2$ STM images of (a) 1 ML Fe, (b) 2 ML Fe and (c) 5 ML Fe on 10 ML NiO on Ag(001) (I=0.5 nA, $U_{\text{sample}} = +1.5$ V).

STM images of Fe deposition on NiO film have also been acquired (Fig. 6.9). The film grows in the form of islands as already revealed by XPD and XPS analysis in previous section. The cluster size increases from 3.8 nm for 1 ML Fe to 4.8 for 5 ML. The grain analysis has been performed as already described at page 80 [134]. The cluster height, together with the average roughness, decreases from about 1 nm at 1 and 2 ML to 0.5 nm at 5 ML. The reduced island height indicates the coalescence of the islands and the increase in the fractional coverage of the oxide at 5 ML, in accordance with XPS-XPD results reported in previous section.

Comparing the images to those obtained on the Fe/MgO system (Fig. 5.10), it is evident
that in the present case the clusters are smaller by a factor of about 2. The thermodynamical contribution of the surface free energy can be ruled out, since it is the same for the two oxides (1.1 J/m$^2$). Other possible explanations can be connected to the kinetic of the system growth. The interfacial interaction can reduce the diffusion length and increase the nucleation points. Therefore it decreases the island size and favours the coalescence at lower metal thickness (on Fe/MgO no evidence of island coalescence was observed at 5 ML Fe). In the limiting case of a very strong interfacial interaction this would lead to a layer-by-layer growth, where every point on the oxide surface acts as nucleation center. This is in agreement with results reported in literature, where the sharpest metal-oxide interfaces (the non interacting ones) are characterized by a stronger island growth of the metal. On the contrary an almost layer-by-layer growth is observed when a strong interaction is observed [152].
6.3 Morphology and chemical activity at the Au/NiO interface

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Abstract

We have grown Au films of different thicknesses, ranging from 1 to 30 MonoLayers (ML), on 10 ML of NiO deposited on Ag(100) single crystal. XPS and STM measurements were performed in order to study the chemical activity at the interface and the morphology of the system. The Au growth on the NiO film starts in a 2D mode and becomes a 3D island growth after the formation of an almost complete layer. After Au deposition, the formation of about 0.3 ML of metallic Ni (Ni⁰) is observed. The absence of significant attenuation of the PE signal of Ni⁰ after successive Au depositions indicates that Ni does not remain confined to the interface between Au and NiO. The density of defects at the surface of the NiO film is shown to be fundamental in determining the chemical activity at the Au/NiO interface.

Introduction

Metal-oxide interfaces are considered very promising candidates for the development of new devices for applications in many fields including heterogeneous catalysis, gas sensors production and photocatalysis [153–156]. Within this wide class of systems, thin deposits of Au on oxide substrates have been surprising for their catalytic activity in contrast with the inert behaviour of bulk Au [157, 158]. The formation of small Au clusters on the oxide surface during the Au growth, together with the clusters size, have been individuated as the fundamental parameters in determining the catalytic properties of the Au. The structure and growth mode of Au is thus responsible for its unusual reactive behaviour. As a consequence, the study of the parameters that influence the Au overlayer formation, such as defects at the oxide surface (steps or oxygen vacancies) and growth conditions (deposition rate and temperature), are of great relevance.

If Au/oxide systems have been intensively studied (in particular Au on TiO₂), the literature is scarce on the structure and morphology of the Au/NiO system. Nevertheless, a recent work reports an unexpected chemical reaction between Au and NiO: Au deposition on NiO film gives rise to the formation of a small amount of metallic Ni [105]. In this study we address the growth mode of Au overlayer deposited on NiO and the chemical activity at the Au/NiO interface.

Experimental

The sample used as substrate was a silver (001) single crystal. Under UHV conditions, the sample was cleaned by cycles of Ar⁺ ion bombardment (at 600 eV of KE) at room temperature, followed by annealing at 710 K for 30 min. NiO films were prepared by evaporating Ni on the
clean Ag surface in $1 \times 10^{-7}$ Torr of oxygen pressure. During the growth of NiO the temperature of the substrate was kept at 460 K. A detailed description of the NiO preparation and the film characterization has been reported elsewhere [159]. Au films of different thicknesses, from 1 to 30 ML, were evaporated at room temperature from a Knudsen cell. The typical evaporation rate, measured with a quartz crystal balance, was about 1 Å/min for NiO, while Au was evaporated at different rates ranging from 0.15 to 1 Å/min.

The XPS measurements were made using a non-monochromatized Mg-Kα X-ray source. In our system the X-ray beam forms with the direction of electrons collection a fixed angle of 45°. The experimental chamber is equipped with an hemispherical electrostatic analyser with an angular acceptance of ±8°. The overall energy resolution, dominated by the width of the Mg-Kα line, is about 1 eV. The morphology of the Au films was investigated by in situ STM, working in constant current mode, with the W tip kept grounded and a bias voltage applied to the sample.

Results and discussion

We performed STM measurements on a sample with three different regions: 7 ML NiO/Ag(100), 1 ML Au/NiO/Ag(100) and 9 ML Au/NiO/Ag(100). The images were recorded in constant current mode with low current values (~0.1 nA). The NiO film presents a surface with small round clusters with an average width of 4 nm and height ranging from 0.5 to 2 nm (Fig. 6.10a). After 1 ML of Au deposition we observe the presence of large Au islands (Fig. 6.10b). The width of the Au islands is between 8 and 20 nm, while their average height is about 2 nm. In this image the fraction of uncovered NiO (the darker areas in which smaller cluster are visible) is 20%. Unfortunately it was not possible to perform STS measurements on the different structures of Fig. 6.10b due to the strong interaction between the tip and the surface above 2 V of tip bias voltage. To overcome this limitation CCT images of the same area at different voltages were recorded. In panels (d) and (e) of Fig. 6.10, the same area has been recorded with 0.5 and 1 V of tip bias, respectively. The two images present the same topography, but the line profiles (panel f) show that at 1 V of tip bias the height of the clusters is reduced in average by 0.1 nm. The same effect of cluster height reduction is also observed when tip bias is increased from 1 to 2 V. Previous studies concerning thin films of NiO and MgO on Ag(100) [17, 160] have shown that the height of the oxide islands increases with the tip bias voltage. In the present case, in which Au is deposited onto an oxide substrate, increasing the bias voltage leads to a reduction of the height of the clusters, thus supporting the picture that the observed clusters have metallic character.

Regarding the high values of the Au cluster height with respect to the nominal Au thickness of 1 ML, the images at different bias voltages demonstrate that the difference in the electronic structure between the regions covered by gold and the NiO surface has a strong influence on the measured cluster heights. After the deposition of the first layer, Au grows in a 3D mode, as
shown in Fig. 6.10c. The Au clusters of this strange worm-like shape have lateral dimensions ranging from 15 to 90 nm (depending on the direction considered) and heights from 3 to 5 nm. The surface of these Au clusters occupies 81% of the analyzed area. From our STM images it is not possible to directly determine if there is still uncovered NiO in the space between Au clusters or if a thin Au layer covers the entire substrate surface. Nevertheless the Au cluster heights (from 3 to 5 nm) are overestimated with respect to the nominal thickness of the deposited Au (about 2 nm) at this coverage as well, suggesting the presence of uncovered NiO between Au clusters.

The growth mode of Au on NiO appears to be in a Stranski-Krastanov-like mode, with the formation of an almost complete layer (≥80% of fractional coverage) and successive 3D island growth. Making the comparison with other studies on the growth mode of gold on oxide surfaces, we note that Au on TiO$_2$ grows in a Volmer-Weber (3D) growth mode [161, 162]. In those studies the authors observe a transition from 2D to 3D growth at about 0.1/ 0.2 ML of Au deposition.
In this initial growth stage, Au nucleates at defects like steps and oxygen vacancies, forming 2D islands of 2 nm of diameter [161]. In our experiment the NiO film grown on Ag(100) presents a much bigger density of defects with respect to the TiO$_2$(110) single crystal employed in [161]. Thus the same mechanism of Au growth (a nucleation of 2D flat islands of 2 nm diameter at defects) will result, on our NiO film, in a large fraction of substrate coverage even at 1 ML.

![Figure 6.11: PE intensity of Au 4f (full squares) and Ni 2p (open circles) plotted as a function of Au coverage, together with the exponential curves (continuous and dashed line) representing PE intensities in case of an ideal layer-by-layer growth.](image)

We performed XPS experiment on Au films of different thicknesses deposited at room temperature on 10 ML of NiO on Ag(100). The integrated PE intensities of the Au 4f and the Ni 2p lines, recorded at normal emission as a function of Au coverage, are shown in Fig. 6.11, after the subtraction of a Shirley-like background. The intensities shown in the figure were normalized to 1 taking as a reference the intensity of the Ni 2p of the bare NiO and the intensity of the Au 4f of a thick deposit of 30 ML. Plotted in the same figure are the exponential curves (i.e., $e^{-d/\lambda}$ and $1 - e^{-d/\lambda}$) representing the expected behaviour of the substrate and overlayer PE intensities in the case of ideal layer-by-layer growth. We assumed EAL (Effective Attenuation Length) values for photoelectrons originating from Au 4f and Ni 2p shells, to be 6 and 10 Å, respectively [163]. The behaviour of the PE intensities is in good agreement with the STM measurements: the points up to 1 ML lie on the exponential curves, and at 9 ML, the Ni 2p intensity is 21%, corresponding to the STM image which shows 81% of the surface covered by thick Au clusters. Moreover, if we assume that at 9 ML of Au deposition the NiO surface is 81% covered by Au clusters of 11 ML of height and uncovered in the remaining area we will obtain 21% of the bare Ni 2p intensity and 72% of the bulk Au 4f intensity; a pure S-K growth mode at 9 ML of Au would lead to 16% for Ni and 74% for Au. Even if the difference between these
two configurations is of a few percent of the PE intensities, our data (21% for Ni 2p and 66% for Au 4f at 9 ML of Au coverage) suggest that a small fraction of NiO film is still uncovered.

**Figure 6.12:** Ni 2p XPS spectra of 10 ML NiO/Ag(100), 9 and 14 ML Au/10 ML NiO/Ag(100) (continuous line) and of 7 ML Au/NiO(100) and NiO(100) single crystal (dash-dotted line), are presented after linear background subtraction. The bulk Ni 2p reference (dashed line) is also shown. The spectra were collected at 65° of emission angle with respect to the surface normal. In the inset the PE intensity ratio of Ni\(^0\) 2p /Ni\(^{2+}\) 2p (open triangles) and Ni\(^0\) 2p /Au 4f (full circles) plotted as a function of Au thickness.

Spectra of Ni 2p at 65° of emission angle (relative to the surface normal) were also recorded. In these spectra, a shoulder on the low binding energy side of the Ni 2p\(_{3/2}\) photoemission peak appears after Au deposition and increases as a function of Au thickness (Fig. 6.12). This shoulder corresponds to the binding energy of the metallic Ni and confirms the previous observation of chemical activity at the Au/NiO interface [105]. We have fitted the Ni 2p\(_{3/2}\) peak for all the Au depositions using a linear combination of the Ni 2p\(_{3/2}\) of the bare NiO film and of Ni bulk
Comparison with metals on NiO(001) systems recorded in the same experimental conditions (Fig. 6.13). From the relative intensities of Au

![Photoemission intensity (arb. un.) vs. Binding Energy (eV)](image)

**Figure 6.13:** Ni 2p_{3/2} photoemission peak from 9 ML Au/10 ML NiO/Ag(100) sample (open circles). Continuous line represents the fit obtained by the sum of Ni 2p_{3/2} line of bare NiO (dotted line) and metallic Ni (dashed line). In the inset the PE intensity ratio of Ni^{0} 2p/Ni^{2+} 2p (open triangles) and Ni^{0} 2p/Au 4f (full circles) as a function of the emission angle with respect to the surface normal.

4f and Ni^{0} 2p (weighted for their relative cross sections) at 0.5 ML of Au thickness, we have evaluated the quantity of Ni^{0} to be about 0.3 ML. Although the complex growth mode of Au does not allow us to interpret the ratios of the PE intensities in terms of simple exponential attenuation (as a function of the Au thickness or emission angle) some qualitative information about the process of Ni^{2+} cations reduction can be obtained from this analysis. To summarize the main experimental findings: the Ni^{0} absolute intensity is almost constant as a function of Au coverage and the ratio between Ni^{0}/Ni^{2+} increases as a function of the Au thickness while the Ni^{0}/Au 4f steadily decreases until reaching a constant value at about 7 ML (see inset of Fig. 6.12). Moreover, at 9 ML of Au deposit, the Ni^{0} signal increases as a function of the emission angle with respect to both Ni^{2+} and Au 4f (see inset of Fig. 6.13). We explain this behaviour as follows: after the formation of a small quantity of Ni^{0}, successive depositions of Au does not cover this fraction of metallic Ni. Thus the observed variation in Ni^{0}/Ni^{2+} and Ni^{0}/Au 4f with Au coverage is due to Ni^{2+} signal attenuation and Au 4f signal growth as a function of Au coverage. The angular dependence only means that metallic Ni is located in a near surface region. Although the surface free energy of Ni is larger than the one of Au (1.94 and 1.41 J/m² respectively [164]), the Ni^{0} PE intensity as a function of Au coverage and emission angle led us to consider the idea that metallic Ni acts as a surfactant floating on top of the Au cluster. Following this hypothesis we have exposed the 9 ML Au sample to 5 L of O₂ but no
change in the metallic Ni shoulder was detected. If metallic Ni is not located at the interface between NiO and Au or on top of Au, the only possibility left is that metallic Ni is embedded in gold clusters. The formation of an ordered stable alloy between Au and Ni is unlikely since Au and Ni are immiscible at room temperature [165]. Nevertheless, at the nanoscale, deviations from the bulk behaviour are frequent and alloying phenomena at the Au/Ni(110) interface has previously been observed [166]. Our conclusion is that metallic Ni is possibly diluted in the Au clusters. The growth of an overlayer by MBE on a substrate kept at room temperature can be strongly influenced by kinetics [167]. Although this study is not focused on the effect of kinetics on Au growth, we performed Au evaporations at different rates ranging from a maximum of 1 down to 0.15 Å/min. Those attempts show that low evaporation rates favour the reduction of Ni\textsuperscript{2+} cations. We repeated the same XPS experiment as a function of the Au thickness, evaporating gold on the (100) surface of a NiO single crystal. The sample was cleaved in air and successively annealed in vacuum at 650 K at a pressure of 1.5×10\textsuperscript{−7} Torr of oxygen for 60 min. The previously observed shoulder on the Ni 2p\textsubscript{3/2} peak corresponding to formation of metallic Ni was not visible at any coverage up to 7 ML (see Fig. 6.12). The Ni 2p photoemission spectrum of the NiO film is fully consistent with the bulk NiO and a previous study confirms the epitaxial growth of NiO on Ag(100) [159]. Thus, the absence of a reaction between NiO and Au on the crystal surface suggests that the roughness of the NiO film and, as a consequence, the increased density of low coordination sites is the origin of the unusual chemical activity at the Au/NiO interface.

Conclusions

The growth mode of Au on NiO film has been investigated by means of STM and XPS. Both scanning probe microscopy and electron spectroscopy indicate that Au initially grows on NiO film in a 2D mode, covering a large fraction (about 80%) of the surface at 1 ML of Au deposit. Subsequently, the Au growth takes place in a 3D mode, forming elongated clusters several nm wide. The Au deposition on the NiO film determines the formation of a small quantity (about 0.3 ML) of Ni\textsuperscript{0}. The fraction of metallic Ni does not remain confined at the interface between Au and NiO but is possibly diluted in the Au. The Ni\textsuperscript{2+} reduction does not take place when Au is deposited on the surface of a NiO single crystal, strongly supporting the picture that low coordination sites at the surface of the NiO film are responsible for the observed reaction between Au and NiO.

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6.4 Structural analysis of the Au/NiO interface

After the study of the growth mode, interactions and morphology of the Au/NiO interface, we present here briefly the analysis of the structure of the Au film. From the small mismatch between Au (fcc) and NiO lattice parameters (2.2%) we would expect the epitaxial growth of the film.

LEED images show a (1×1) pattern up to about 9 ML, reproducing the substrate. From 9 ML on, a ring appears and coexists with the (1×1) pattern (Fig. 6.14). The ring indicates the presence of rotational domains. Part of the film forms crystalline islands with a lattice parameter slightly different from the substrate one, but randomly oriented, in analogy with the results reported for NaCl films deposited on Cu(111) in Ref. [168]. The (1×1) is originated from part of the surface that is epitaxial to the substrate.

Figure 6.14: LEED pattern of 30 ML Au on 10 ML NiO on Ag(001) (Ep = 135 eV).

To confirm this hypothesis we have measured XPD plots of the Au 4f\(_{7/2}\) as a function of the azimuthal and polar emission angle. In the first case (not reported here), the IAD is isotropic with no relevant features, confirming the LEED observations. The polar scans are made along the two main azimuths of the NiO (001) surface: [100] and [110] (Fig. 6.15a and b respectively). These plots show similar features on the two main azimuths for both 9 and 30 ML, namely three peaks at about 21°, 38°-41° and 57° respectively. These features do not correspond to forward focusing from the atomic chains of Au(001) single crystal (simulated spectra in Fig. 6.15, dashed line), where we expect the main peaks at 45° for the [100] and 55° for the [110] azimuth. Since we have deduced from LEED that the film is made by randomly oriented crystallites, we have simulated also an average plot over all the azimuths between [100] and [110] (the remaining are symmetric). The average plot, shown in Fig. 6.15, is more similar to the experimental ones, confirming our hypothesis. It has in fact two pronounced features at 19° and 42°.
6.5 Conclusions and future perspectives

In this chapter we have shown that the deposition of metals on NiO films produces the formation of interfaces less sharp than in the case of metal deposition on MgO. This property depends in some cases (such as for Fe growth) to the lower oxide heat of formation for the substrate than for the overlayer, in other cases to the fact that NiO is in form of a film, therefore more defective than a bulk (such as for Au deposition).

Another possible explanation for the interfacial reactivity could be a charge transfer from the Ag substrate to the metal overlayer, as already predicted by Pacchioni et al. for noble metal atoms deposited on MgO/Mo(001) [169]. In the present case this could play a role in the Au/NiO/Ag(001) system, where the effect is present only on thin NiO films and not for a bulk oxide. The thick oxide layer however could prevent the charge transfer, due to the too large tunneling barrier. On the contrary in the case of Fe/NiO/Ag(001) system the possible charging effect does not play the major role, since the modifications in the XPS lineshapes occur to the same extent also for Fe films grown on bulk NiO.

Figure 6.15: XPD plots of Au 4f<sub>7/2</sub> along the (a) [100] and (b) [110] azimuth of 9 and 30 ML Au (solid lines) compared with simulated plots for bulk Au(001) (dashed line) and an average plot over the (001) plane (dotted line). See text for details.
This defectiveness and interdiffusion at the interface is expected to strongly influence the electronic and magnetic properties of the metals deposited on top.

In the case of Fe, future studies will investigate the influence of the alloy on the ferromagnetism of the metal, in particular for the interfacial layers. Magnetic phenomena like the exchange bias are in fact correlated to the interaction at the interface and therefore deeply influenced by the intermixing, as already shown in the case of Co films on oxides for the study of magnetic tunnel junctions [170]. However, since the alloy involves only up to the fourth layer, the magnetic properties of thicker films could be independent on the intermixing.

Therefore the investigation of the exchange bias both for Fe films and nanostructures is one of the next steps in the study of this system.

In the case of Au, the reduced size of the clusters and the presence of defects on the oxide film can determine changes in the electronic and therefore catalytic properties of Au, as already shown in the cases of Au on MgO and TiO$_2$ [155, 157, 171].
Conclusions and future trends

In this work rocksalt oxides have been prepared for the successive growth of metal films and nanostructures.

In particular MgO has been investigated in various forms.

Bulk MgO has been used for the preparation of stepped oxide surfaces. Through a polishing and annealing procedure in controlled atmosphere a regular surface with a periodic array of steps has been obtained, suitable to be used as a template for the growth of one-dimensional metal nanostructures.

MgO in form of a thin film has been grown on Mo(001) and Ag(001). Various aspects of the MgO/Mo(001) system have been extensively investigated, demonstrating the good stoichiometry, crystal quality and morphology of the oxide film. Additionally optical properties have been studied and discussed, showing that MgO films emit light from the recombination of excitons at low coordinated sites like steps and corners. This can be useful for the successive deposition of metal clusters and the study of their possible nucleation on these defect sites.

Besides, on the more-studied MgO/Ag(001) system the formation of mosaics in the oxide film has been investigated. Already reported by Wollschläger et al. [25], mosaic formation occurs when the film relaxes its structure to relieve the misfit strain with the substrate. This induces the formation of a network of dislocations that deforms the surface of the oxide film. The same phenomenon has been observed and discussed for MgO/Mo(001) and the presence of an elastic strain field on the surface can be used as a template for the growth of well-ordered metal nanoparticles, as already reported for different metals and supports [28, 29]. This self-organization induced by the substrate has been tested on the Fe/MgO/Ag(001) system for a MgO thickness where the presence of the mosaics is more evident. Only a weak organization of clusters aligned along the ⟨100⟩ directions is present, together with the homogeneity in the cluster diameter distribution. This could be due to the reduced order in the dislocation network, because of the small mismatch between MgO and Ag and the consequently high thickness at which the mosaics appear.

More appealing is the case of MgO/Mo(001), where this pattern appears at lower coverages and is more defined, due to the 5% lattice mismatch between MgO and Mo. This will be a future perspective of this work, together with the determination of the electronic and magnetic...
properties of the Fe clusters, with or without the ordered array. The lateral confinement itself can in fact determine a change in the properties.

Finally the same kind of studies has been developed also for more reactive oxides, like NiO, grown in form of a thin film on Ag(001), in parallel to what already discussed for MgO. In this case the oxide is less stable and antiferromagnetic. The proved presence of an intermixing at the interface, both after deposition of Fe and Au, evidences that NiO, particularly in form of thin film, is quite reactive. This can have strong influences on the catalytic properties of Au and on the magnetic properties of Fe clusters and thin films. In fact the ferromagnet-antiferromagnet interfacial coupling can lead to a shift in the hysteresis loop typical of the overlayer. The presence of a mixed phase at the interface can modify the extent of this coupling, both for thin and thick films, since, even if the mechanism is not yet completely clear, it is strongly dependent on the interfacial conditions.
Bibliography


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Curriculum and list of publications

Stefania Benedetti
Born in Sassuolo (Modena), Italy, on 26/04/1979.

Course of study
2004-2007: PhD in Physics at the University of Modena and Reggio Emilia

2003: Diploma degree in Physics at the University of Modena and Reggio Emilia, discussing the thesis: “Processi di ossidoriduzione e riorganizzazione strutturale in sistemi di interesse magnetico: l’interfaccia Fe/NiO(001)” (Oxidation-reduction reactions and structural order in systems of magnetic interest: the Fe/NiO(001) interface), Supervisors: Prof. Sergio Valeri, Dr. Paola Luches.


Scientific experiences and interests

• Characterization of metal-oxide interfaces by means of XPS, AES, XAS measurements to study chemical reactions, while LEED, PDME and XPD are employed to analyse crystal structure. Simulation of XPD data by means of MCD code. XMCD and XMLD measurements performed to study magnetic properties of thin films and bilayers. In my diploma work I started the study of the of the Fe/NiO system, comprising both a chemical aspect and a structural part. This led to the completion of this work during my PhD in Physics and to the publication of a paper on Surface Science (Sec. 6.1).

The same kind of analysis has been carried out for the Fe/MgO system. The investigation of the interface has been performed mainly in situ and at the beamline BEAR (ELETTRA, Trieste), with the collaboration of Dr. I. I. Pronin (A.F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, Russia)
and Prof. F. Boscherini (INFM and Dipartimento di Fisica, Università di Bologna, Italy). This work has brought to the publication of the paper on Surface Science, shown in Sec. 5.1.

The third interface investigated is the Au/NiO. The related results have been published on Surface Science and presented in Sec. 6.3. The study of the structural part is not yet finished and here only the preliminary results are given.

- Growth and preparation of oxide vicinal surfaces, studied by means of STM, AFM, XPS, XPD, PDMEE and LEED. Growth and characterization of metallic nanowires on oxide vicinal surfaces. For the perspectives we have a collaboration with Prof. M. P. Pileni for the preparation of Au preformed clusters on these stepped surfaces.

- Study of thin oxide films on metals and surface patterning. For the MgO/Mo(001) system this has been done in collaboration with Prof. H.-J. Freund, Dr. N. Nilius and H. M. Benia at the CP Department of the Fritz-Haber-Institut of the MPG (Berlin, Germany), that has led to the publication of a paper on Chemical Physics Letters (Sec. 4.2). The collaboration with this group and with Dr. G. Renaud in Grenoble will give further insight into MgO/Mo structure. For this purpose a beamtime is scheduled in November 2006 at ESRF and a proposal is submitted for 2007.

- First stages of metallic growth on oxide surfaces: cluster deposition and nucleation by means of STM and AFM, magnetic and electronic properties (MOKE, XMCD, electronic spectroscopies). About the electronic properties measurements have been performed at the beamline ALOISA (ELETTRA, Trieste) and a paper has been submitted to Surface Science, but not discussed in this work. For the magnetic properties a beamtime is scheduled in December 2006 at the beamline APE (ELETTRA, Trieste).

**List of publications**


Conference contributions

- IWOX-5, January 7th to 12th 2007, Lake Tahoe (USA) (Oral)
- NANSEOA, July 2nd to 6th 2006, Aix-en-Provence, France (Oral)
- ICSOS-8, July 18th to 22nd 2005, Munich, Germany (Poster)
- MMD-Meeting, June 22nd to 25th 2005, Genova, Italy (Poster)
- IWOX-4, January 4th to 8th 2005, Torino (Italy)-Aussois (France) (Poster)
- ECSCD-8, July 18th to 21st 2004, Segovia, Spain (Poster)

Languages

Italian (mother-tongue)
English
German