Electronic structure of oxide thin films on metals
Altieri, Salvatore

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Summary

The existence and the properties of metal-oxide boundaries, and, more in general, metal-ceramic boundaries, play a crucial role in determining many physical processes and technological applications in a wide variety of traditional areas of the materials science and technology. Coating of oxide which function as thermal barriers or as a natural corrosion protection are of concern to the manufacturers of jet engines and equipment for power generation, who seek to improve lifetimes and efficiency. In the chemical industry, strong metal-support interactions and the performance of a metallic catalyst supported on a ceramic substrate depend on the properties of metal-ceramic interfaces, and also the electronic industry depends on the properties of such interfaces for packaging and in components such as rectifiers and MOSFETs.

In most of the traditional applications, the function of the oxide is either to protect or to support an active element or part of a device. However, oxide thin films and the interfaces with a metal, as well as oxide-oxide interfaces, may now be envisaged as a novel class of materials spanning new and yet unexplored areas of the materials science and technology. Modern fabrication and manipulation techniques, involving molecular beam epitaxy and a full range of thin film and surface characterization techniques, have provided the possibility of structuring hybrid materials on a nanometer scale, based on combinations of components with radically different intrinsic properties. The properties of such nanostructure materials can be to a large extent determined by the interfaces between the components rather than the components themselves, and can be classified as functionally gradient materials in which the properties or functionality are determined by the interfaces where the compositional gradients are large. These systems may serve as model systems in which the spins and charge densities can be controlled and the changes in properties studied, but they may also be considered as a new class of materials if the layer thickness is less than the coherence lengths of the electrons, or the collective excitations such as the magnons (magnetic excitations), excitons (important in semiconductors), and plasmons. In this case, the multilayer as a whole must be viewed as a new material with properties determined by the quantum mechanical tunneling between the components.

Thin films and multilayers of strongly correlated magnetic oxides combined with conventional metals constitute a possible example of such a kind of functionally gradient materials, which has a great potential to lead to systems exhibiting new physical phenomena and properties. Strongly correlated oxides exhibit a vast variety of very different properties with only small changes in chemical composition or structure, and are, there-
fore, very sensitive to even minor changes in environment. At surfaces and interfaces of narrow band systems such as rare earths and 3d transition metal (TM) compounds, where electron interactions are very important, large modifications are expected not only in the electronic and the magnetic structure, but also in the charge transport properties, since the propagation of electrons and holes is strongly influenced by the presence of a spin background. In systems with local magnetic moments, there is a very strong interaction between the mobile electrons and holes and the magnetic moments, providing a mechanism for long range magnetic order of some sort, but also for very strong scattering of charge carriers by the spin system itself. Since in narrow band systems these interactions may be so strong that the conduction electrons will only be able to propagate through the spin system if the spins are parallel to those of the surroundings, one may expect a very strong dependence of the conductivity on magnetic fields, as well as on the state of magnetic order in neighbouring regions, leading directly to the possibility of controlling the electrical conductivity via magnetic fields and with the compositional gradients in oxide-metal multilayer like structures, leading to what is now called spin electronics.

It is by now well recognized that the basic electronic structure, band gaps, and superexchange interactions, in transition metal (TM) oxides are mostly determined by a few fundamental quantities, and that among these, the 3d-3d on-site Coulomb interaction U and the corresponding multiplet structure, as well as the O 2p to TM 3d charge transfer energy (Δ), are of primary importance. For example, when U and Δ are larger then the electron band width, the oxide will be a magnetic insulator, for which the nature and the magnitude of the conductivity gap are determined by the relative importance of U and Δ. Therefore, if ways could be found to modify them, then spectacular changes may occur not only in the magnitude of the gap but also in the magnetic and optical properties.

The on-site Coulomb interaction U is the repulsion energy of two electrons occupying an open subshell of the same atom, and can be defined as the difference between the energy cost to remove an electron from one atom in the solid (ionization potential) and the energy gained when the electron is put back onto another atom far away from the former (electron affinity), both of these energies being referenced with respect to the ground state energy of the solid.

The charge transfer energy Δ is defined as the energy cost for charge fluctuations where one electron is transfered from a anion to a cation, and strongly depends not only on the anion ionization potential and the cation electron affinity, but also on the Madelung potential of the ionic solid. In the solid, ionization potentials and the electron affinities are effectively reduced from the the free atom values due to the high atomic polarizability of the extended ligand orbitals, and, consequently, also U and Δ in the solid have a smaller value than in the ideal case of a lattice of isolated atoms.

For ultrathin oxide films, the reduced coordination number implies a less efficient screening of the ionization potentials and electron affinities as well as a smaller value of the Madelung potential. If the thin oxide film is supported on a highly polarizable metal, however, all the ionic charges are subject to the interaction with the metal that can be described as an effective interaction with image charges appearing below the metal surface. These image charges favour polarity fluctuations by reducing the ionization potentials and
electron affinities. Therefore, if the magnitude of the image potential interaction is large enough, the presence of the metal surface can overcompensate the loss of polarization energy in the thin film, so that the Coulomb interaction $U$ and the charge transfer energy $\Delta$ in the thin oxide film on a metal may have values smaller than in the bulk phase, and, consequently, the electronic and magnetic structure film might largely differ from the bulk.

Low coordinated oxide overlayers on a highly polarizable metal substrate are also expected to exhibit modified chemical properties. For example, the reduced surface Madelung potential, together with the hybridization effect between the oxide and the metal, may result in the development of new interfacial mixed density of states, in an energy region which is relevant for various chemical interactions. The energy scales involved here are usually less than 1 to 2 eV, and fall in the gap of many insulating oxides. At the interface with the metal, however, the states of the insulator may hybridize with those of the metal and new states with energies close to the chemical potential can be formed. Moreover, the rate for various chemidissociation processes may be significantly increased in the proximity of the oxide-metal interface, due to the effective reduction of the activation energies, because of the reduced ionization potentials and increased affinity energies, originating from the interfacial image potential screening.

As discussed above, the possibility of tailoring the magnetic, electric, and chemical properties of strongly correlated oxides structured on a nanometer scale in the form of thin films and multilayers, critically depend on the extent in which $U$, $\Delta$, and the hybridization interactions can be modified in these class of systems. The main goal of the present thesis work is to experimentally explore the occurrence and the magnitude of these modifications using properly chosen model systems that can be assumed as representative of a wider class of materials. To this purpose, the in-situ preparation of suitable ultrathin oxide films on a metallic substrate by means of molecular beam epitaxy (MBE), and the structural and chemical characterization by means of various surface sensitive probes as low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), as well as various kind of electron spectroscopies, has been performed as a preliminary and fundamental subtask.

An experimental approach is necessary because the physical quantities of concern are either affected by an intrinsically high computational error ($U$), or they strongly depend on parameters whose magnitude is highly undetermined ($\Delta$). The definition of $U$ involves the difference between two energies of comparable magnitude. Therefore, no matter the accuracy of each of the separate calculation, the difference of the two calculated values will always suffer of a large inaccuracy. In a simplified model, the oxide thin film on a metal can be described as a free standing double-layer made of the oxide ionic lattice and the lattice of image charges. The total Madelung potential of such a double-layer can vary so much as a function of the double layer separation and the position of the image plane, that even the sign of the resulting potential may change from positive to negative, thus resulting in large uncertainty in the calculated charge transfer energy.

The use of model systems is necessary since the experimental determination of $U$ and $\Delta$ for correlated oxides is a difficult task, because the charge fluctuations created in such open shell systems, for instance in a spectroscopic experiment, involve not only the TM 3$d$
degrees of freedom but also transfer of charge from the O 2p to the TM 3d, therefore, the interpretation of the data is not so straightforward. With its crystal structure similar to some TM oxides, MgO may serve as a suitable model system without the complexity due to correlation effects because of its closed shell electronic structure. It allows for the direct determination of changes in U and Δ via a combined X-ray photoemission (XPS) and Auger electron spectroscopy (AES) experiment. Ag(100) was chosen as a metal substrate mainly because epitaxial MgO(100) films can be grown on Ag(100) in a layer-by-layer fashion, thereby allowing to probe the changes of U and Δ as a function of the distance from the metal surface.

As an example of strongly correlated oxide thin films on a metal, epitaxial NiO(100) films have been also prepared on the Ag(100) metal surface and studied by means of electron spectroscopy. NiO constitutes an interesting system that is traditionally used to probe the effects of electron correlation and the changes thereof. Moreover, the similarity of the crystal structure with that of MgO makes possible to use the results obtained for thin MgO films on Ag(100) as a starting point for the interpretation of the more involved results obtained for the NiO thin films on Ag(100).

In a detailed electron spectroscopic investigation of epitaxial MgO(100) thin films on Ag(100) we have found that the on-site Coulomb interaction U and the charge transfer energy Δ for thin MgO(100) films on Ag(100) are indeed reduced from the bulk MgO values, by as much as 1.8 eV and 2.5 eV, respectively, due to the presence of a very efficient image potential screening by the substrate, which more than compensates the appreciable loss in screening in the oxide itself due to the reduced coordination number. Furthermore, we have found that the MgO(100)/Ag(100) oxide-metal interface has a very peculiar electronic structure, and, in connection with this, also a rather unusual chemical behaviour. Using ultraviolet and X-ray photoelectron spectroscopies (UPS and XPS), we were able to identify the hybridized oxygen-silver bands at the interface, and show that the O 2p states strongly hybridize with the Ag 5sp and only weakly with the Ag 4d. As a result of these interactions, an appreciable density of states, with large oxygen antibonding character, is pushed above the Fermi level, thereby determining the chemical bonding at the oxide-metal interface. Using XPS and Auger electron spectroscopy (AES), we also find out that the MgO(100) monolayer on Ag(100) has a surprisingly high chemical activity towards water dissociative chemisorption. We argue that this peculiarity is determined by the fact that oxygen derived states have been moved from the high energy scales in MgO to low energy scales at the Ag interface.

We have also studied the core level and valence band photoemission spectra of NiO(100) thin films on Ag(100) and found that the electronic structure of the NiO(100) monolayer on a metal is dramatically different from that of bulk NiO. The Ni 2p XPS spectrum of the NiO(100) monolayer on Ag(100) has been analyzed in comparison with the Ni 2p spectra of an in-situ cleaved bulk NiO crystal, Ni2+ impurities dispersed in a MgO matrix, and Ni metal. Based on this comparison and the results obtained for the MgO(100) thin films on Ag(100), we argue that the electronic structure of the NiO(100) monolayer on Ag(100) is strongly shifted from 3d8 to a strong admixture of 3d9 and 3d10 configurations. As a consequence, also the local spin of the Ni ions in the monolayer might be different from the
bulk value of \( S=1 \), resulting in a peculiar magnetic structure of the NiO monolayer, very different from the bulk one. In the limit of a predominantly \( 3d^{10} \) ground state configuration, for instance, the total atomic spin would be zero and NiO(100) monolayer on Ag(100) would be diamagnetic. The validity of this idea can be verified, for instance, in a temperature dependent X-ray absorption (XAS) experiment at the Ni 2p edge.

In conclusion, the results of the present thesis work demonstrate that the electronic structure of oxide thin films on metals is largely different from that of the corresponding bulk oxides and strongly support the idea that oxide thin films on metals have also novel chemical-physical properties. In particular, thin films of strongly correlated oxides on metals are expected to exhibit new magneto-optical and transport properties, and have a great potential to span new and yet unexplored areas of the materials science and technology.