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Oxide Films at the Nanoscale: New Structures, New Functions, and New Materials

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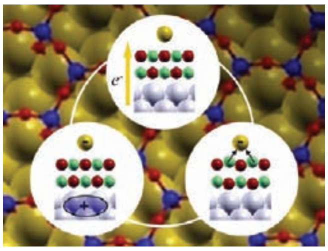

We all make use of oxide ultrathin films, even if we are unaware of doing so. They are essential components of many common devices, such as mobile phones and laptops. The films in these ubiquitous electronics are composed of silicon dioxide, an unsurpassed material in the design of transistors. But oxide films at the nanoscale (typically just 10 nm or less in thickness) are integral to many other applications. In some cases, they form under normal reactive conditions and confer new properties to a material: one example is the corrosion protection of stainless steel, which is the result of a passive film. A new generation of devices for energy production and communications technology, such as ferroelectric ultrathin film capacitors, tunneling magnetoresistance sensors, solar energy materials, solid oxide fuel cells, and many others, are being specifically designed to exploit the unusual properties afforded by reduced oxide thickness.

Oxide ultrathin films also have tremendous potential in chemistry, representing a rich new source of catalytic materials. About 20 years ago, researchers began to prepare model systems of truly heterogeneous catalysts based on thin oxide layers grown on single crystals of metal. Only recently, however, was it realized that these systems may behave quite differently from their corresponding bulk oxides. One of the phenomena uncovered is the occurrence of a spontaneous charge transfer from the metal support to an adsorbed species through the thin insulating layer (or vice versa). The importance of this property is clear: conceptually, the activation and bond breaking of adsorbed molecules begin with precisely the same process, electron transfer into an antibonding orbital. But electron transfer can also be harnessed to make a supported metal particle more chemically active, increase its adhesion energy, or change its shape. Most importantly, the basic principles underlying electron transfer and other phenomena (such as structural flexibility, electronic modifications, and nanoporosity) are now largely understood, thus paving the way for the rational design of new catalytic systems based on oxide ultrathin films. Many of the mechanisms involved (electron tunneling, work function changes, defects engineering, and so forth) are typical of semiconductor physics and allow a direct link between the two fields.

A related conceptual framework, the "electronic theory of catalysis", was proposed a long time ago but has been largely neglected by the catalytic community. A renewed appreciation of this catalytic framework, together with spectacular advances in modeling and electronic structure methods, now makes it possible to combine theory with advanced experimental setups and meet the challenge of designing new materials with tailored properties. In this Account, we discuss some of the recent advances with nanoscale oxide films, highlighting contributions from our laboratory. Once mastered, ultrathin oxide films on metals will provide vast and unforeseen opportunities in heterogeneous catalysis as well as in other fields of science and technology.

Introduction

Oxide ultrathin films are essential components of several modern technologies. For instance, ultrathin silicon dioxide films represent an unsurpassed material in the design of metal oxide field effect transistors, and the microelectronic revolution would have not been the same without the excellent properties of thin SiO_2 films grown on silicon. But oxides at the nanoscale (typically up to 10 nm in thickness) are used also in many other systems and devices: corrosion protection of metals by passive films,[1] ferroelectric ultrathin film capacitors,[2] tunneling magnetoresistance sensors,[3] and solar energy materials.[4] Sometimes, the possibility to growth ultrathin films is essential to improve performances: for instance, for solid oxide fuel cells to operate at low temperature ultrathin films of yttria-stabilized zirconia would be needed.[5]

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Oxide ultrathin films have large potentialities also in a completely different field: catalysis. The active phase of many heterogeneous catalysts is not the bare metal surface but, rather, a thin oxide layer which forms under reactive conditions.[6] Also oxide supports, often considered as inert materials, start to exhibit new phenomena when their dimensionality enters in the nanometer range. About 20 years ago, chemists started to grow oxide films on metals in order to use electron spectroscopies and scanning tunneling microscopies (STM) to better understand heterogeneous catalysts.[7−11] Several techniques were developed to grow epitaxial oxide films, deposit metal nanoparticles, and study their chemistry.[12] Indeed, significant advances have been done in the understanding of oxide catalysis. It is only in the past few years, however, that it became evident that besides oxide thin films that closely resemble the corresponding bulk phases, also new systems exist, sometimes with unexpected properties either related to the morphology and nanostructure of the films or to their structural flexibility. But, probably, the most exciting developments are related to the possibility to modify in a desired manner the chemical properties of molecules or metal nanoparticles deposited on oxide films with nanometer thickness and below.

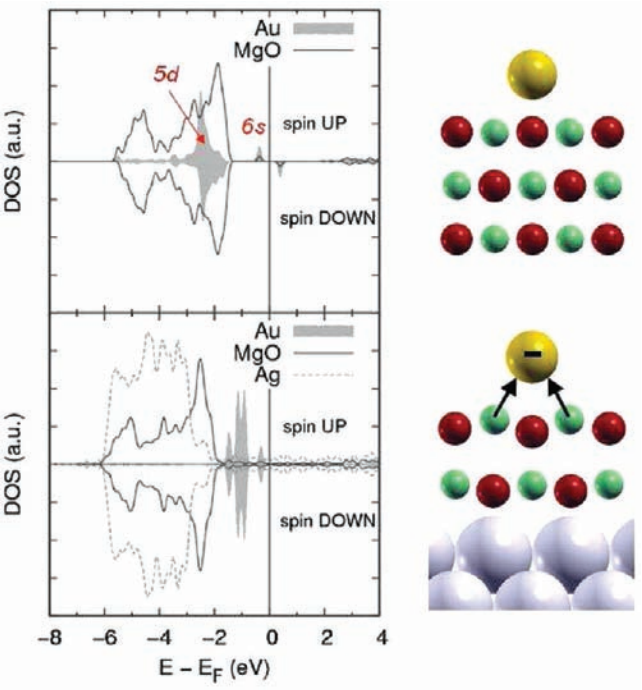

FIGURE 1. Left: spin resolved density of states (DOS) curves for Au_1/MgO(100) (on top of O adsorption) and Au_1/MgO/Ag(100) (on top of Mg adsorption). Right: adsorption geometries of Au_1/MgO and Au_1/MgO/Ag(100) showing the polaronic distortion.

Charge Flow through Oxide Ultrathin Films

Our first observation of the anomalous behavior of ultrathin oxide films was accidental. Using density functional theory (DFT) calculations, we compared the properties of transition metal atoms adsorbed on a prototypical bulk oxide, MgO, or on few layers (L) of MgO deposited on Mo(100). Only minor differences in the adsorption properties were expected mainly due to the slightly different lattice parameters in MgO(100) or MgO(2L)/Mo(100). Indeed, almost identical characteristics were found for Pd atoms adsorbed on the two systems.[13] The surprise came when we adsorbed a Au atom: in fact, gold exhibits completely different adsorption properties on bulk MgO or on a thin MgO film (Figure 1). It took some time to realize that this was not an artifact of the calculations, and to identify the reasons for the different behavior of Pd and Au.[9,13] While Pd remains neutral and forms covalent bonds with the oxide, Au has a different nature in the two cases: neutral on MgO(100) and negatively charged on MgO/Mo(100) or MgO/Ag(100). In fact, on the ultrathin film a net charge transfer takes place from the metal support to Au through the MgO thin dielectric barrier. In the absence of defects or grain boundaries (the computed films are ideal and defect free), a possible mechanism is electron tunneling, provided that the film thickness remains below the mean-free paths of electrons. The charging effect was then observed by low-temperature STM experiments,[14] *providing a clear proof that oxides at the nanoscale may exhibit completely different properties from their bulk phases*.

Since then, other examples of charge flow have been reported.[15,16] DFT calculations showed that O_2 adsorbed on MgO/Mo(100) films forms superoxo radical anions, O_2^-,[16] and indeed the presence of O_2^- on MgO/Mo(100) films has been detected by low temperature electron paramagnetic resonance (EPR) spectra,[17] which show that the intensity of the EPR signal decreases with the number of layers and disappears for a 15L MgO film, in full agreement with the proposed model of electron tunneling.[9,13,14,18] The analysis of the g-tensor has shown unambiguously that the MgO film undergoes a polaronic distortion in response to the formation of the O_2^- species, *an effect which is essential for the stabilization of the charged admolecules* and which is absent on bare MgO (Figure 1). This distortion is indicative of easy deformability, another typical property of oxide ultrathin films.

The spontaneous electron flow through an ultrathin oxide film can be exploited for the activation and dissociation of admolecules. A similar mechanism was proposed long time ago by Cabrera and Mott to explain oxidation of

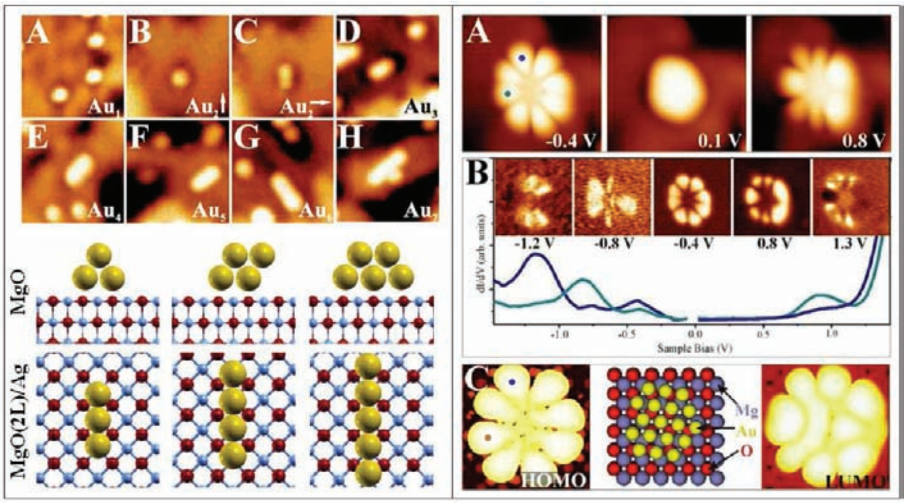

FIGURE 2. Top left: STM topographic images of (A) Au monomers, (B,C) upright and flat Au dimers, and (D–H) Au_3–Au_7 chains on MgO/Ag(100). Bottom left: DFT calculated Au clusters for bulk MgO(100) or MgO (2L)/Ag(100) films. (Adapted from ref 22. Copyright American Physical Society 2008.) Right: (A) Topographic and (B) d*I*/d*V* images of Au_{18} on MgO/Ag(100). The corresponding d*I*/d*V* spectra are shown. (C) Calculated HOMO and LUMO shape. (Reproduced with permission from ref 23. Copyright American Physical Society 2009.)

metals:[19] the presence of an adsorbate (e.g., O_2) with empty states below the metal Fermi level stimulates electron tunneling through the thin insulating layer. The Cabrera and Mott model is restricted to native oxide films, while the results described above extend the phenomenon to any thin dielectric on a conducting support.

There are several interesting consequences of the charge transfer. One is the possibility to prepare supported metal particles whose properties can be tuned by varying the thickness of the oxide support. In fact, the probability of electron tunneling decreases exponentially with the thickness of the oxide film: beyond a given thickness, typically 10 ML, the behavior of a bulk oxide surface is recovered.[18] According to DFT calculations, a Au_{20} cluster has a completely different shape when deposited on ultrathin or thick MgO films:[20] on bulk MgO, Au_{20} keeps the tetrahedral shape it has in gas-phase, while on a MgO(2L)/Mo(100) film a planar 2D isomer is largely preferred.[20] The change in shape is a consequence of the charge transfer from Mo to gold. The extra charge localizes at the Au–MgO interface and reinforces the interaction so that the cluster rearranges and "wets" the surface. The effect has been demonstrated by depositing Au atoms on 3L and 8L MgO films on Ag(100) and by stimulating cluster aggregation by thermal annealing at 300 K.[21] The STM images clearly show that on 3L MgO two-dimensional gold islands are formed, whereas on 8L films the Au clusters grow three-dimensional.[21] This effect is present also for smaller clusters: on MgO/Ag(100), Au clusters grow linear up to Au_7 at variance with MgO(100) (Figure 2).[22] While a single electron is transferred to a Au atom,[13] multiple electron transfer occurs on Au clusters. By studying with STM the nodal structure of the wave function of a flat Au_{18} cluster on MgO/Ag(100) (Figure 2), it has been possible to demonstrate that four electrons have been transferred to gold by this mechanism.[23] Similar effects have been observed for Au clusters on alumina/NiAl(110).[24]

The change in shape and the extra charging have direct consequences on the reactivity of the supported gold clusters. Gas-phase, mass-selected Au_{20} clusters have been soft-landed on MgO/Ag(100) films, and the oxidation of CO to CO_2 has been studied as a function of the MgO film thickness.[25] CO_2 forms at two different temperatures for Au_{20} deposited on 1L–3L or on 10L MgO films, showing that the oxide support has an important role in the reaction.[25] Recent studies show that the change in cluster properties as a function of film thickness is related also to the presence of trapped electrons at grain boundaries of the film.[26]

So far we have seen that electrons can flow from the metal to adsorbed species. Furthermore, the reported examples refer to a single oxide, MgO. So, several questions emerge. Is a charge transfer in opposite direction also possible? What is the behavior of other oxides? Why does the charge transfer occur in some cases (Au) and not in others (Pd)? In order to answer these questions, other substrates have been considered. One is FeO/Pt(111). The detailed structure of this system has been determined only recently.[27] The film consists of one atomic layer of Fe atoms at direct contact with the Pt(111) surface, and an external layer of O atoms. Density of states (DOS) curves and scanning tunneling spectra (STS) show that Au atoms deposited at 5 K on the FeO/Pt(111) film adsorb on-top of O and that the Au 6s level is empty, above the Fermi level (E_F).[28] This means that Au^+ has formed and a charge transfer from the adsorbate to the substrate has occurred, opposite to the Au/MgO/Ag(100) case.

Another example is Au deposition on $SiO_{2.5}$/Mo(112) films consisting of a single layer of SiO_4 tetrahedrons with three of the O atoms forming Si−O−Si bridges in the plane and the fourth one binding to the Mo underneath.[29] The tetrahedrons are arranged in a honeycomb structure made of six-membered −Si−O− rings. Au atoms interact extremely weakly (the binding energy is <0.1 eV), and no charge transfer takes place, at variance with the MgO/Ag(100) and the FeO/Pt(111) cases.[30]

So, why does the same atom, Au, behave so differently when deposited on MgO, FeO, or $SiO_{2.5}$ films? The answer is that when a species is adsorbed on an oxide film its HOMO or LUMO may be at different energies with respect to metal Fermi level; this creates a potential difference which may induce a spontaneous electron tunneling through the thin dielectric barrier. In particular, if the adsorbate HOMO is above E_F, electrons can be transferred to the metal/oxide interface. This is the case of K atoms on MgO/Ag(100).[31] Alkali metals have low ionization potentials (typically 4 eV), which are further reduced to 2−3 eV by the interaction with an oxide support.[32] Since the E_F of most metals is between 4 and 5 eV below the vacuum level, alkali metals are easily ionized on ultrathin oxide films. This has nothing to do with what happens on bulk MgO where ionization occurs by transferring the valence electron to specific defects (oxygen vacancies, grain boundaries, hydroxyl groups, etc.).[33] On an ultrathin film, the electron tunnels through the oxide insulating layer and is transferred to the metal support *even in the absence of defects*.

If the HOMO or LUMO levels of the adsorbed species are close to E_F, the potential energy difference may be too small to induce a spontaneous tunneling and the adsorbate remains neutral, as for Au/$SiO_{2.5}$/Mo(112)[30] or Pd/MgO/Mo(100).[13] In this case, the film behaves essentially as a bulk oxide.

The last case is when the LUMO of the adsorbate falls below E_F. This is only possible for species with high electron affinity (EA), such as O_2 (EA = 0.45 eV), NO_2 (EA = 2.23 eV), or Au (EA = 2.31 eV). Here the condition $EA_{adsorbate} > E_F$ is met and electrons can flow from the metal support toward the adsorbate (Figure 3). The induced image charge in the metal substrate and the polaronic-like distortion of the ionic lattice contribute to stabilize the charged adspecies (Figure 3).

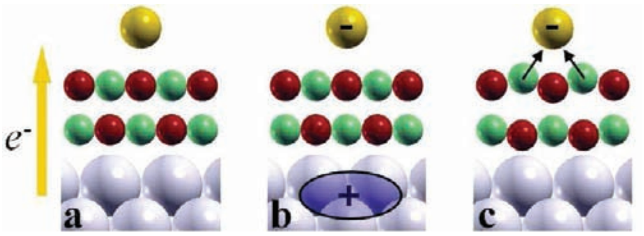

FIGURE 3. Electron transfer phenomena through an oxide thin film: (a) electron tunneling, (b) polarization of the metal substrate (image charge), and (c) polaronic-like distortion of the oxide. Electron tunneling in the opposite direction can also occur.

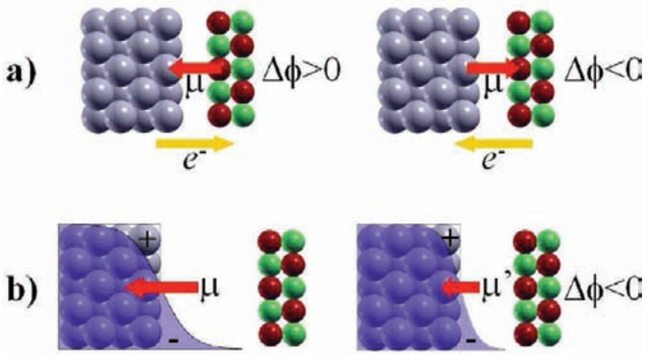

FIGURE 4. Two major contributions to the change in work function Φ induced by an ultrathin dielectric layer on a metal. (a) Charge transfer at the interface; (b) compressive electrostatic effect.

Thus, charge transfer on ultrathin dielectric films is governed by the position of the frontier orbitals of the adsorbate, and of the metal Fermi level. Since this latter depends on the nature of the metal/oxide interface, it provides an important way to tune the properties of the support. The direct measure of E_F in a metal is the work function Φ_m, the energy needed to move one electron from E_F into the vacuum. Therefore, Φ_m becomes a central quantity in this discussion as it determines the direction of the electron flow on oxide thin films.

Tuning the Work Function in Oxide Thin Films on Metals

The formation of chemical bonds at the metal/insulator interface can create a dipole, μ, due to the charge displacement, and a shift in the position of the metal Fermi energy (Figure 4). Thus, the effective work function, $\Phi_{m/d}$, may differ substantially from that of the pure metal, Φ_m (Table 1).[34,35] According to the classical picture of Kingdom and Langmuir[36] and Gurney,[37] a negative charge above the metal generates an image charge and a dipole layer which the emitted

TABLE 1. Work Functions (Φ) of Metal and Oxide Thin Films on Metals from DFT Calculations

	Φ_m, eV	$\Phi_{m/d}$, eV
FeO/Pt(111)	5.8	5.8−6.4
TiO_2/Pt(111)	5.8	5.6
$SiO_{2.5}$/Mo(112)	4.2	4.9
NiO/Ag(100)	4.3	3.9
MgO/Ag(100)	4.3	3.0
BaO/Au(100)	5.1	2.3
MgO/Mo(100)	4.2	2.1
BaO/Ag(100)	4.3	2.0
BaO/Pd(100)	5.2	2.0

electron must pass through; this leads to an increase of work function, $\Delta\Phi > 0$ (and vice versa for positive adsorbates). For instance, in $SiO_{2.5}$ films grown on Mo(112), charge flows from Mo toward the O atoms at the interface and Φ increases from 4.2 to 4.9 eV (Table 1).[34]

However, strong work function changes can occur also when the charge transfer at the interface is negligible, like for films of ionic materials (MgO, NaCl) which can induce a reduction of Φ of up to 2 eV (Table 1). This shift has an electrostatic origin.[38] Due to the exchange or Pauli repulsion, the dielectric layer pushes the electronic charge that spills out from the surface back into the metal, thus changing the surface dipole (Figure 4). While bond polarity at the interface dominates the work function change for oxide films with strong chemical interactions with the metal, the electrostatic or "compressive" effect is dominant for films of highly ionic materials.[34,35]

Accurate work function measurements for thin dielectric films support this view. Field emission resonance studies of NaCl islands on Ag(100) induce a reduction of Φ of 1.3 eV;[39] MgO films on Ag(100) reduce Φ by 1.1−1.4 eV, according to Kelvin probe force microscopy, contact potential difference curves, and field emission resonances.[40] These values are in excellent agreement with DFT estimates ($\Delta\Phi = -1.3$ eV).[34,35]

Oxide Films as Molecular Sieves

Another important property of oxide ultrathin films is related to their porous structure. Today there is an increasing interest in porous materials such as zeolites and metal−organic frameworks for their gas storage properties. Recently, 2D counterparts for 3D porous materials have been prepared,[29,41] such as the already mentioned $SiO_{2.5}$/Mo(112) film.[29] A related structure, SiO_2/Ru(0001), consists of a SiO_2 bilayer weakly interacting with a Ru(0001) support.[41] These silica structures have two common aspects: (1) they are chemically completely inert, and (2) they present openings in the surface which provide access to nanopores located at the metal−silica interface. This offers the opportunity for metal atoms and small molecules to diffuse through the pores and to modify the chemical activity of the film.[30,42] Theory has been quite helpful in predicting which atoms have the right size and valence structure to allow penetration through the porous films (Figure 5).[43]

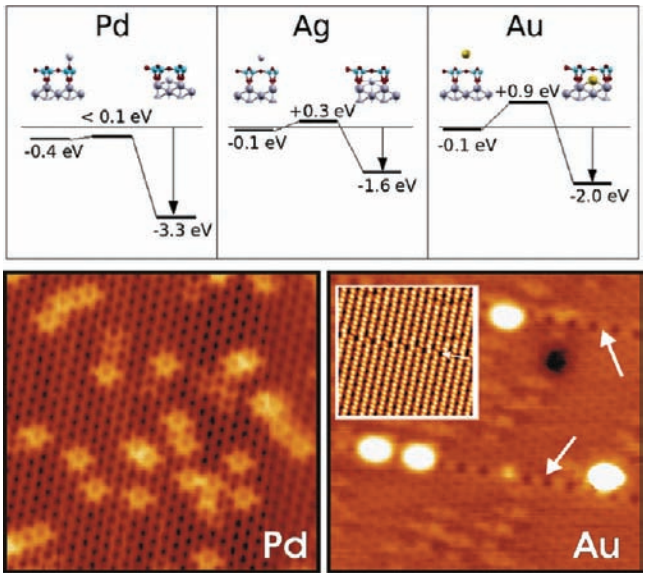

FIGURE 5. Pd, Ag, and Au atoms adsorbed on $SiO_{2.5}$/Mo(112) films. Top: Energy profiles for Pd, Ag, and Au insertion into the film (energies with respect to a gas-phase atom). (Adapted from ref 43. Copyright Elsevier 2009.) Bottom: STM images. (a) Pd atoms are imaged as bright stars due to diffusion through the silica rings. (b) Au particles are formed by Au atoms which diffuse and aggregate along line defects. (Adapted from ref 42. Copyright Wiley-VCH 2008.)

While Pd (and to less extent Ag) can penetrate into the pores of $SiO_{2.5}$/Mo(112) by overcoming a tiny energy barrier and become stabilized at the interface, Au is too large. The barrier for diffusion cannot be overcome by an increase in temperature, as this will lead to lateral diffusion rather than to incorporation into the film. The behavior of $SiO_{2.5}$/Mo(112) as molecular sieve has been proven by depositing Pd and Au atoms. STM images (Figure 5)[42] clearly show that Pd atoms cannot be detected on the surface of the silica film while Pd-related features are imaged with starlike shapes showing penetration of Pd atoms through the silica holes and their attachment to Mo at the interface.[42] On the contrary, no Au adsorbates are found on the defect-free silica surface, confirming that Au atoms are unable to pass the holes in the −Si−O− rings. Instead, small Au aggregates form along extended defects which act as nucleation sites.[42,43]

The observation that some atoms can penetrate below the oxide thin film opens new perspectives for the functionalization of these otherwise inert surfaces. If atoms with the

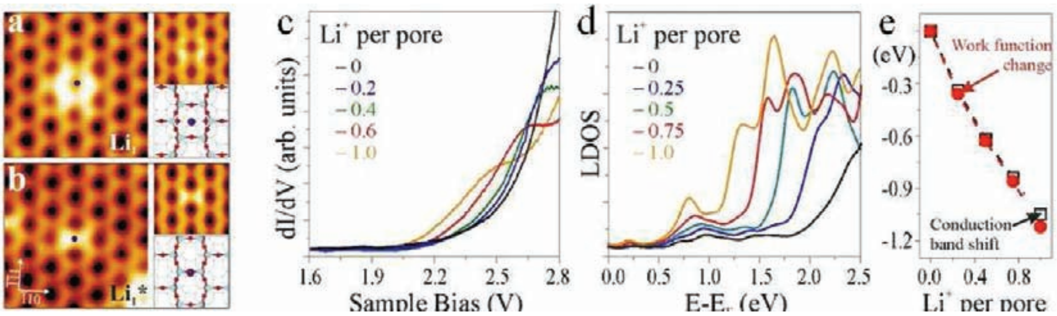

FIGURE 6. (a, b) Experimental and simulated (inset) STM images of a Li atom bound to two different sites at the $SiO_{2.5}$/Mo(112) interface. (c) Differential conductance spectra for different amounts of incorporated Li. (d) Calculated DOS (conduction band region) for various Li coverages. (e) Correlation between work function decrease and conduction band shift as a function of Li coverage. (Reproduced with permission from refs 46 and 47. Copyright American Physical Society 2009.)

right size (e.g., Pd) are predeposited and incorporated into the nanopores, they act as nucleation centers for dimers and possibly larger aggregates.[44] Another interesting possibility is to stabilize single magnetic atoms. Exploiting the porous structure of the $SiO_{2.5}$/Mo(112) film, a thermally stable ensemble of Fe monomers which partly retain their magnetic behavior has been obtained.[45] This has a number of advantages with respect to conventional atom deposition onto flat surfaces: the Fe atom is stabilized against diffusion and desorption even at elevated temperature; aggregation of the Fe is prevented; the Fe atom is protected by the silica cage from molecules from the surrounding gas-phase. Encapsulation of magnetic atoms into porous ultrathin films is thus a promising route to fabricate a dense ensemble of magnetic entities for potential storage applications.

Doping and Defects Engineering

There is another, conceptually very important reason why film nanoporosity can be useful: modification of the film chemical properties. We have seen that silica films are chemically inert and that the occurrence of a charge transfer through the film depends on the value of the work function, $\Phi_{m/d}$. The work function of metals can be substantially reduced by adsorption of K or other alkali metals which, donating the valence electron to the surface, form K^+ and induce a surface dipole that lowers Φ. The same can be expected if K is adsorbed on $SiO_{2.5}$/Mo(112) or related systems.[31] The problem is that K is too big to penetrate spontaneously into the pores of the film, and will remain adsorbed on the surface, where diffusion and aggregation with other adsorbed species can occur, thus destroying the effect. However, smaller alkali metals like Li are able to diffuse through the pores and penetrate below the oxide surface.[46] Upon adsorption, Li becomes cationic and induces a coverage dependent reduction of the work function (Figure 6) as calculated by DFT and measured by STS spectra.[47]

The decrease in work function is not large, up to 1.2 eV depending on the coverage (Figure 6), but sufficient to change radically the adsorption properties of Li-doped silica: deposition of Au atoms and small Au clusters[47] shows now stabilization of these species on the flat terraces, at variance with the clean silica film. This is due to a spontaneous charge transfer with formation of negatively charged gold species.[47] The shape, stability, and electronic properties of gold deposited on clean and Li-doped silica supports are thus completely different. By incorporation of alkali atoms, it has been possible to convert the inert silica film into an active support.

What is reported above is an example of oxide doping by interstitial atoms. But the concept of doping and defects engineering is more general. Take as an example a classical defect in oxide materials, the O vacancy in MgO (F center) (Figure 7). F centers can exist in three charge states: F^0, F^+, and F^{2+} with two, one, and no associated electrons, respectively. F centers result in impurity levels in the band gap of MgO, with the F^0 state lying at mid gap and the F^+ state closer to the valence band (Figure 7a).[48] On an ultrathin MgO film, the contact with the metal support can determine spontaneous charge transfers depending on the position of the F^0 and F^+ energy levels with respect to the metal Fermi level: on MgO/Mo(100), where Φ is $\approx$2 eV, only F^0 centers are stable as the corresponding state lies below E_F (Figure 7b). An F^+ center, if created, becomes immediately filled by one electron from the substrate and transforms into F^0. On the contrary, on MgO/Ag(100) ($\Phi \approx 3$ eV), the F^0 state lies at the Fermi level (Figure 7c) and only F^+ states are expected to be stable (Figure 7d).[49] The stability of a given charge state depends also on factors such as the film thickness or the position of the defect in the film (surface, interface,

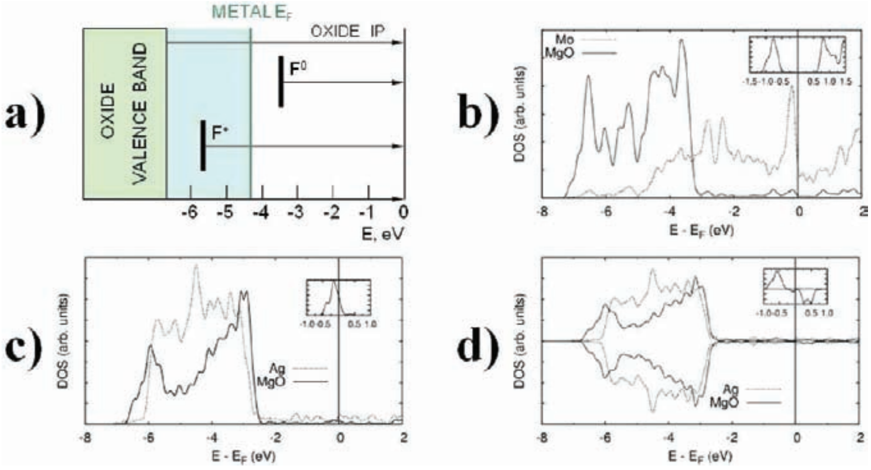

FIGURE 7. (a) Position in MgO band gap of F^0 and F^+ centers energy levels.[50] The position of the Fermi level of a metal support is also shown. (b) DOS curves of F^0 center on MgO/Mo(100). (c) DOS curves of F^0 center on MgO/Ag(100). (d) DOS curves of F^+ center on MgO/Ag(100). The inset shows an enlargement of the F center gap states. (Adapted from ref 49. Copyright American Chemical Society 2008.)

or internal layers). So far the prediction of the possibility to control the charge state of point defects in oxide films lacks experimental verification. However, this could provide new routes to tune adsorption and catalytic properties on demand.

Structural Flexibility and Chemical Reactivity of Oxide Thin Films

Compared to the surface of a bulk oxide, ultrathin oxide films are structurally more flexible. As mentioned above, the occurrence of spontaneous charging is accompanied by a significant polaronic distortion.[17] The ability to respond with a structural relaxation to changes in the electronic structure is peculiar of the nanodimensionality of the film and can have important chemical consequences. FeO/Pt(111) films can undergo a complete structural rearrangement with direct impact on catalytic reactions such as CO oxidation. While at low O_2 pressures ($<10^{-3}$ mbar) FeO/Pt(111) films are essentially inert toward CO and O_2, at higher pressures the films reconstruct and form a new phase of FeO_2 stoichiometry. O_2 molecules stimulate the flipping of the Fe atoms from their original positions at the interface with Pt(111) to the surface where they bind, activate, and dissociate O_2 (Figure 8). The consequence is that a new film forms where a layer of Fe ions is between two O layers, one at the interface and one at the surface (Figure 8). The top oxygen layer is very reactive so that gas-phase CO can bind an O atom from the surface of FeO_2 to form CO_2 and an O vacancy; the vacancy is then filled by ambient O_2, and the reaction proceeds according to a classical Mars–Van Krevelen mechanism.[51,52] The FeO/Pt(111) system is catalytically more active than Pt itself,[51] reinforcing the view that often the active catalyst phase in oxidation reactions is a thin oxide layer which forms under reactive conditions.[6] This example also shows two additional characteristics of ultrathin films: (1) the formation energy of oxygen vacancies can differ substantially in thin films and bulk oxides; (2) on thin films, it is possible to stabilize uncommon metal oxidation states.[10,12] Both of these effects have direct consequences on the surface reactivity.

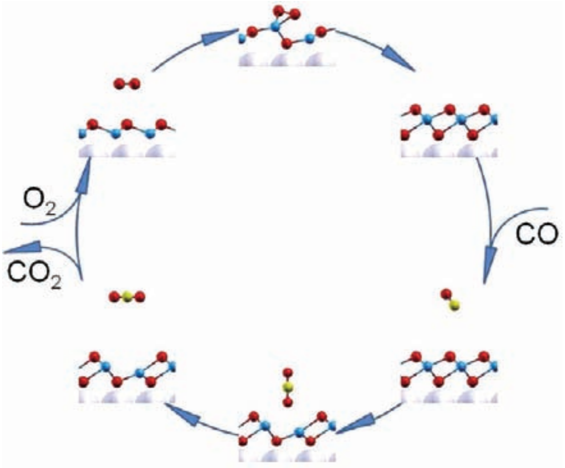

FIGURE 8. Individual steps in forming the active FeO_2/Pt(111) phase starting from FeO/Pt(111), and its reaction with CO to form CO_2, as revealed by DFT calculations.[52] Fe: blue; O: red; Pt: grey; C: yellow.

Concluding Remarks

Oxide ultrathin films may exhibit unusual phenomena and chemical properties. Electron transport through the thin dielectric barrier, nanoporosity, and structural flexibility are all aspects that make these materials interesting and unique, paving the way for their use as catalytic materials but also in sensors and electronic devices. What is fascinating about these systems is that their chemical properties can be related to concepts and notions typical of semiconductor physics: electron tunneling, work function changes, doping, defect engineering, and so forth. The potential of these concepts was understood long time ago by a Russian theoretical chemist, F. F. Vol'kenshtein, who in 1966 wrote:[53] "if the thickness of the [oxide] film is small, then the adsorption and catalytic properties can be shown to depend on the thickness of the film and on the properties of the metal substrate: the film behaves as if it were 'translucent' to the characteristics of the metal (...). By varying the thickness of the coating it is possible to control the catalytic activity (...) due to the fact that the position of the Fermi level depends on the thickness of the film". These prophetic statements did not find their way in the catalytic community mainly because they were too revolutionary for the time when they were formulated. Vol'kenshtein was also concerned about the fact that "the experimenter cannot expect from the electronic theory predictions of the numerical values of various physical quantities: he can expect the theory to discover the physical mechanisms of the observed rules".[53] Today, nearly 50 years after Vol'kenshtein's paper, we are on the way to learn how to meet the challenge to design new interfaces using the full arsenal of modeling and theory combined with very sophisticated and advanced experimental setups. Once mastered, ultrathin oxide films on metals will provide vast and unforeseen opportunities in science and technology.

BIOGRAPHICAL INFORMATION

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FOOTNOTES

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