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**A theoretical introduction to oxide ultra-thin films :  
intrinsic finite size effects and interaction with a metallic substrate**

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**Keywords**

Bond-breaking, charge transfer insulator, finite size effects, gap, interface band alignment, interfacial dislocations, ionicity, Madelung potential, metal substrate, Mott-Hubbard insulator, oxide thin films, polarity, quantum confinement, structural relaxation, work function.

**Glossary**

Band alignment: Relative positions of the band structures of two compounds at a heterojunction.

Iono-covalent character: Extent of valence electron sharing between anions and cations, from full localization at anions (ionic limit) to delocalization along the anion-cation bonds (covalent limit).

Madelung potential: In an ionic or a mixed iono-covalent compound, the Madelung potential is the electrostatic potential value at any atomic site due to all other charges.

Metal induced gap states: Electronic gap states at the interface between a semiconductor/insulator and a metal, due to the penetration of the metallic wave functions inside the semiconductor/insulator.

Work function: Minimum energy needed to move an electron from inside a solid to a point in the vacuum far from the solid surface.

## **A theoretical introduction to oxide ultra-thin films : intrinsic finite size effects and interaction with a metallic substrate**

### **Abstract**

The microscopic processes which control the inter-related structural and electronic characteristics of oxide thin films are discussed. Various parameters play a role, among which the ionic-covalent character of the oxide, which determines the type of structural relaxation and the resulting variations of in-plane lattice parameters, interlayer distances and gap widths. The finite film thickness may also be at the origin of sub-critical regimes with novel structural and electronic characteristics, especially for specific polar film orientations. In the case of metal-supported oxide films, the interface lattice mismatch, the interaction strength and the band alignment influence the film properties. In particular, the interface charge transfer induces a structural distortion of the oxide film and impacts its surface work function and adsorption properties. Metal substrates may also enable a stabilization of new 2D oxides with stoichiometry, atomic, and electronic structures specific to the nano-scale and qualitatively different from that of the parent bulk materials.

### **Introduction**

Due to their relevance in physics, chemistry and earth science, oxides have long been the subject of intense research work. Oxides display an impressive variety of structural and electronic properties. Aside from simple wurtzite or rocksalt structures adopted by binary compounds, corundum, fluorite, rutile, perovskite and many other, more complex structures are met. From the electronic point of view, oxides range from highly ionic insulators to semiconductors, metals and even superconductors. The origin and description of the band gap in semiconducting and insulating oxides has been much debated. One distinguishes charge transfer insulators, such as simple metal  $s$ - $p$  oxides (e.g. MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>) or transition metal  $d^0$  oxides (e.g. ZnO, TiO<sub>2</sub>, SrTiO<sub>3</sub>), from Mott-Hubbard transition metal oxide insulators (e.g. Ti<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>). The difference lies in the nature of the smallest electronic excitation: electron transfer from oxygen to cation in the former case and electron exchange between two cations in the latter (Figure 1, left). However, this separation is too radical, since, in many cases (e.g. NiO), the top of the valence band has a mixed oxygen-cation character. In charge transfer insulators, the separation between the centers of gravity of the valence (VB) and conduction (CB) bands has an ionic and a covalent contribution, whose ratio is correlated to the local cationic coordination in the structural ground state (Figure 1, right). Ionic oxides display more compact structures with octahedral cationic environment (e.g. rocksalt, rutile, corundum) while less compact tetrahedral local coordination is typical for more covalent compounds (e.g. ZnO wurtzite or SiO<sub>2</sub>).

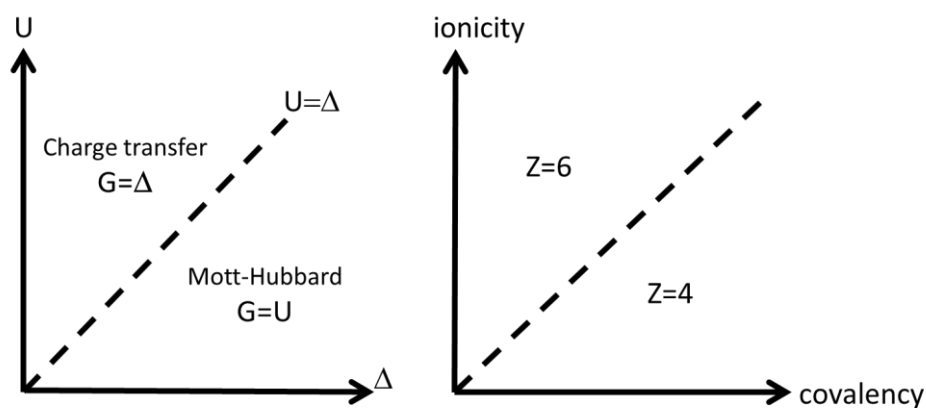


Figure 1: Left: Sawatzky-Zaanen diagram giving the nature of the insulating state as a function of the cation-cation charge excitation  $U$  and the energy for anion-cation charge transfer  $\Delta$ . Right: Phillips diagram showing how the crystal structure of binary  $sp$  compounds ( $Z$  the cation coordination number) depends on the relative degree of ionicity and covalency of the anion-cation bond.

All these properties are prone to modifications at surfaces or in thin films. While the characteristics and properties of most binary oxide surfaces are now well-established, in the last decade, in view of their numerous applications, the main focus has been on ultra-thin oxide films. Compared to bulk systems, they display specific characteristics driven by their finite thickness and/or their interactions with the substrate on which they are grown. In the ultra-thin limit (a few atomic layers), these two-dimensional (2D) oxides may exhibit structures, stoichiometries and properties different from the parent bulk crystals.

### **Intrinsic finite size effects (unsupported films)**

Local structural distortions and modifications of the electronic structure mainly take place in the direct vicinity of under-coordinated atoms at the surface of ultra-thin films. However, finite size effects may also produce modifications of the whole film structural and electronic characteristics. This is particularly true in films of polar orientations, subject to long-range electrostatic interactions.

#### **Local structural relaxation**

Bond-length contraction occurs around under-coordinated atoms, as a result of the competition between short range repulsion and the prevailing attractive interatomic forces: electrostatic in highly ionic compounds, electron delocalization in metals, or mixed ionic and covalent in oxides. In thin films, this leads to variations of distance between the outermost surface layers, but it also impacts the in-plane lattice parameters. The resulting distortion of the entire film depends on the prevailing ionic or covalent character of the compound.

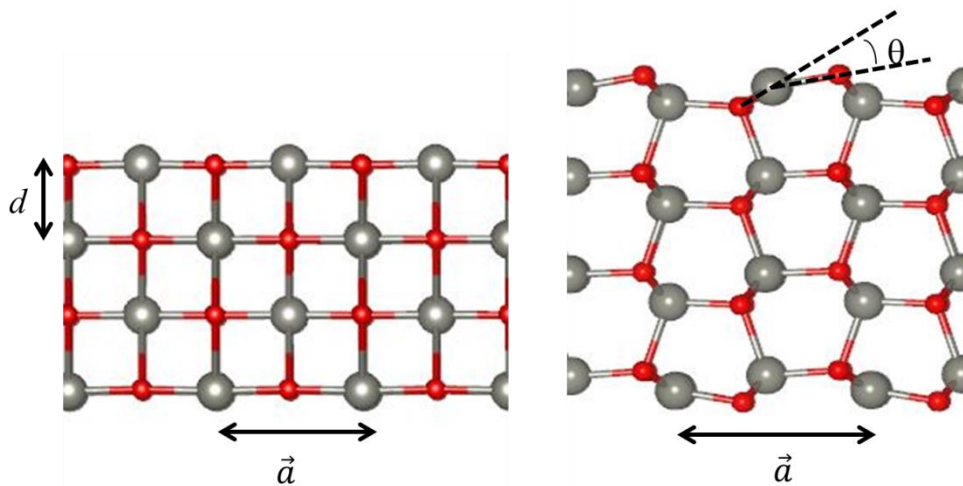


Figure 2: Left: Structural relaxation via bond contraction as exemplified in a rocksalt (100) thin film. The outermost interlayer distance  $d$  is expanded while the in-plane lattice parameter  $\vec{a}$  is shortened with respect to the bulk values. The small film rumpling in which the most polarizable surface atoms (oxygen) are pushed outwards is not visible at this scale. Right: Relaxation via bond rotation, in a wurtzite (10-10) thin film. At the surface, the bond angle  $\theta$  is decreased, inducing a layer flattening and an increase of  $\vec{a}$ . Anions and cations are represented by red and grey spheres, respectively.

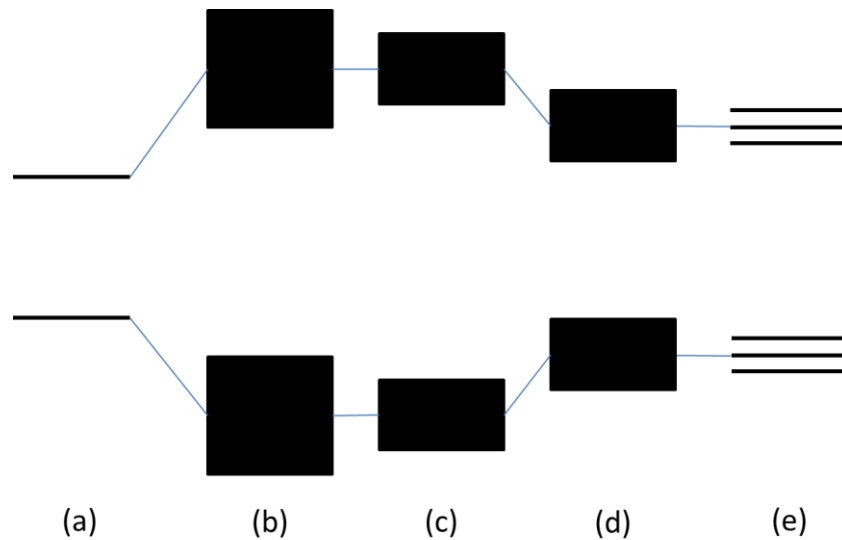
At non-polar surfaces of highly ionic rocksalt oxides like MgO in which the atoms are densely packed, the bond contraction manifests itself in a shortening of the outermost interplanar distance. At variance, in thin films, bond contraction mainly occurs within the surface layer and yields a decrease of the in-plane lattice parameters, which is stronger and stronger as the film becomes thinner. It is accompanied by a tetragonal-type distortion characterized by an expansion of the interlayer distances so as to roughly preserve the local atomic volume (Figure 2, left).

In films of more covalent oxides like ZnO, with cations in a tetrahedral environment, aside bond contraction, back-bond rehybridization also takes place, transforming the bulk-like  $sp_3$  bonding into a surface-like  $sp_2$  one, as at surfaces of elemental semiconductors. It produces a film flattening and an increase of the in-plane lattice parameters (Figure 2, right).

At the extreme monolayer (ML) limit, oxides tend to adopt flat 2D structures. Monolayer rocksalt (111) and wurtzite (0001) films display six-member rings, reminiscent of graphene, with alternating cations and anions. Corundum (0001) oxide MLs (e.g.  $Fe_2O_3$ ,  $Ti_2O_3$ ) also form honeycomb structures but with twelve member rings. Flat monolayer structures simultaneously enable a suppression of the out-of-plane dipole moment in highly ionic compounds and provide a purely  $sp_2$  bonding favoured by more covalent materials.

### Modification of the electronic structure

In oxides, structural and electronic degrees of freedom are strongly coupled. Modifications of the electronic structure are thus concomitant with the relaxation effects induced by the atomic under-coordination. Three main effects impact the electronic structure of thin films (Figure 3).



*Figure 3: Schematic representation of an oxide electronic structure: (a): the relevant atomic orbitals forming the VB and CB. (b): VB and CB in the bulk, separated by the band gap  $G$ . (c): band narrowing at under-coordinated atoms. (d): Shift of the bands as a result of the modifications of the effective atomic orbital energies. (e): quantization of states along the direction perpendicular to the film due to quantum confinement.*

The first one is a splitting and/or a shift of the effective atomic orbital energies  $\varepsilon$  (the diagonal terms of the Hamiltonian projected on an atomic orbital basis set) of which the electronic structure is built (Figure 3a-b). On the one hand, compared to the bulk, the change of symmetry of the local atomic environment lifts the degeneracy of the  $p$  or  $d$  multiplets. This concerns particularly the Mott-Hubbard insulators in which, due to the cationic  $d$  character of both the VB and CB edges, the  $d$ - $d$  electronic excitation energies depend significantly on the cation local environment. This concerns also charge transfer insulators with a pronounced covalent character, in which back-bond rehybridization changes the surface bonding from  $sp_3$  to  $sp_2$  and induces the presence of dangling bond states with energies in the gap region. On the other hand, in (highly or partially) ionic oxides whose properties are mainly controlled by electrostatic forces, the strong electrostatic (Madelung) potential  $V_i$  exerted on each ion  $i$  by its environment, shifts  $\varepsilon_i$  with respect to its value  $\varepsilon_i^0$  in the isolated neutral atom, approximately as  $\varepsilon_i = \varepsilon_i^0 - V_i - U_i Q_i$ . This Hartree-type expression involves a term associated to the ionic charge  $Q_i$  and the on-site electron-electron repulsion  $U_i$ , and a Madelung contribution  $V_i$ . In thin films, due to their lower coordination and the small film thickness, atoms are subject to a reduced Madelung potential. This brings the oxygen and cation effective levels closer to each other and, in case of charge transfer insulators, induces surface states in the gap region (Figure 3d).

As a whole, whatever the case --- Mott-Hubbard, covalent or ionic, charge transfer oxide ---, the above effects, consequence of bond breaking at the film surfaces, induce states in the gap and thus reduce its effective width. Conversely, structural relaxation, whether by means of bond length

contraction or orbital rehybridization, has an opposite effect on the effective levels and tends to reopen the gap.

The second effect induced by bond breaking is a narrowing of the local band width, which roughly scales as the square root of the atomic coordination number (Figure 3c). In Mott-Hubbard insulators, the decrease of the number of cation-cation second neighbors locally reduces the widths of both the CB and the VB. In charge transfer insulators, the local widths of the CB and VB scale with the number of cation-cation and oxygen-oxygen second neighbors, respectively. The band narrowing, on its own, tends to increase the surface band gap. However, structural relaxation and the resulting bond contraction act in the opposite direction both as regards the band and the gap widths.

Finally, quantum confinement, i.e. the quantification of electronic states propagating along the direction normal to the film, may also soundly modify its electronic structure. In particular, the discretization of bands in the direct vicinity of the VB maximum and the CB minimum produces an overall gap increase  $\delta G$  (Figure 3e). In semiconductor nanocrystallites,  $\delta G$  is of the order of  $\hbar^2 \pi^2 / 2\mu R^2$ , with  $R$  the effective radius of the crystallite and  $\mu$  the reduced electron-hole effective mass. In thin films, as a first approximation, the effect of quantum confinement scales with the square of the inversed film thickness. Moreover, since the effective mass is determined by band curvatures at the top of the VB and the bottom of the CB, it is smaller in simple metal  $sp$  charge transfer oxides than in transition metal Mott-Hubbard ones and should thus lead to larger quantum confinement effects in the former.

In thin films, these various effects induce positive or negative variations of the gap width. Their competition is driven by the nature of the oxide (charge transfer or Mott-Hubbard), its degree of ionicity, the nature (bond rotation or contraction) and the strength of relaxation effects, and the film thickness. We note however that the electronic effects due to atomic under-coordination are essentially local, so that, e.g., a gap opening at the film surface does not alter the gap of the entire film, which is determined by the fully coordinated atoms in the film core. Conversely, quantum confinement effect is global and the induced gap opening concerns the entire film.

### **Uncompensated polarity regime**

Beside the structural and electronic effects described above, the reduction of film thickness has more global consequences. This is particularly striking in thin oxide films grown along specific crystallographic orientations, classified as polar.

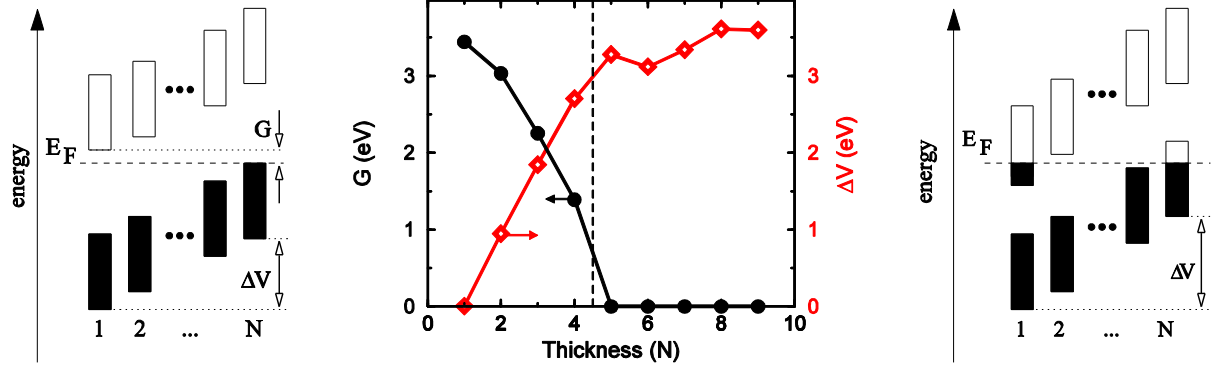


Figure 4: Schematic representation of the band shifts across a polar film and the associated electronic properties. Left/Right: band scheme in the uncompensated/compensated regimes. Middle: thickness variations of the gap width  $G$  and the jump  $\Delta V$  of electrostatic potential.

Polarity refers to the presence of a macroscopic dipole moment in a globally neutral stacking of (alternatively) charged atomic layers  $\pm\sigma$ , such as met, e.g., in (111)-oriented rocksalt films. It results in a monotonic increase of the macroscopic electrostatic potential across the film, which progressively shifts the local band structure and brings the VB maximum of one film termination closer to the CB minimum of the other one (Figure 4). The overall amplitude of the shift  $\Delta V$  scales (linearly) with the film thickness. In ultra-thin films, below a critical thickness,  $\Delta V$  may remain smaller than the width of the band gap, producing a specific “uncompensated polar”, or “subcritical” regime. In this regime, the total dipole moment of the film grows linearly with its thickness, while its band gap simultaneously decreases (Figure 4 left).

The electronic structure remains insulating up to a critical thickness  $N_c$  at which  $\Delta V$  produces an overlap between the VB and CB at opposite sides of the film. This so-called “polar catastrophe” or “Zener breakdown” is associated with an insulator-to-metal transition and a strong discontinuity of surface charges, which prevents a further increase of the film dipole moment and of the band structure shift  $\Delta V$ . In this scenario, it manifests itself by the appearance of a 2D electron/hole gas (2DEG/2DHG) at the film surface.

Beyond  $N_c$  (figure 4 right), the excess surface charge density converges towards the value  $\delta\sigma$  expected at semi-infinite polar surfaces. In the infinite thickness limit, according to the Gauss law,  $\delta\sigma = \sigma R_1/(R_1+R_2)$  is the value necessary to heal the divergence of the electrostatic potential ( $R_1$  and  $R_2$  the successive interlayer distances).

It is worth stressing that, depending upon the oxide, the environment, and the processing conditions, alternative mechanisms such as non-stoichiometric surface reconstructions, adsorption of charged species, or screening by an interface with a metal may provide the surface charge excess  $\delta\sigma$  necessary to heal the polar instability more efficiently than the surface metallization or “electronic reconstruction” described above.



## Stabilization of structures different from bulk

The reduction of film thickness may also have global consequences on the film atomic structure, beyond a mere bond relaxation around under-coordinated atoms or a change of in-plane lattice parameter. In most cases, such global structural changes with respect to that in the parent bulk crystal result from a competition between the energy cost of surface formation and that of a structural distortion/transformation of the core of the nano-objects.

If a structural transformation of the object core (whose energy cost scales as the object volume) helps to expose more compact surfaces and thus reduces its surface energy (energy gain proportional to the surface area), such transformation is thermodynamically favoured below a critical object size. Examples of such a scenario can be found in all types of materials, from metals to semiconductors or insulators. In what concerns oxides, the most documented example is probably that of  $\text{TiO}_2$  clusters. Contrary to the rutile bulk structure, small  $\text{TiO}_2$  clusters adopt preferentially an anatase structure, but brookite particles and lepidocrocite films have also been evidenced.

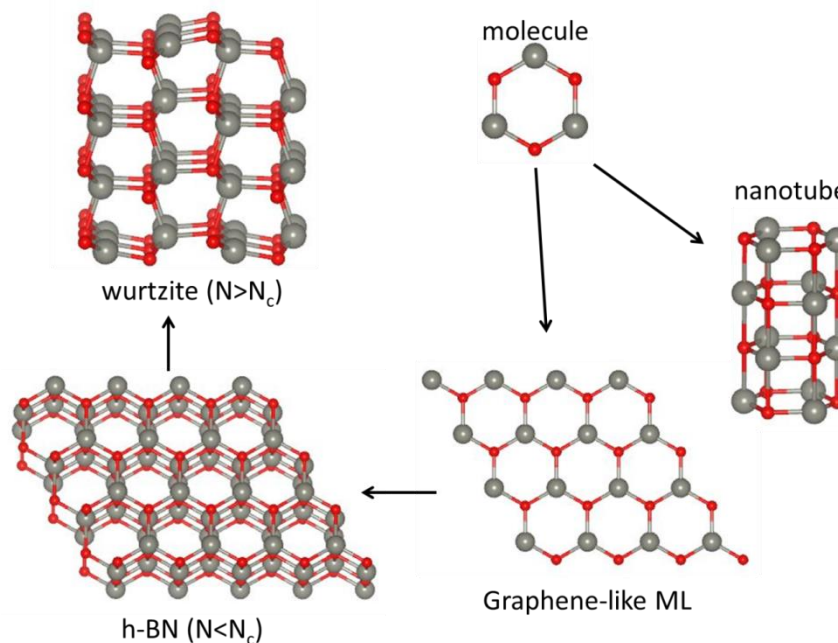


Figure 5: Low dimensional ZnO objects. At variance with the bulk wurtzite structure, a  $(\text{ZnO})_3$  molecule adopts a flat six-member ring structure. ZnO nanotubes, ZnO(0001) monolayer, and thin ZnO(0001) films with a thickness below the critical value  $N_c$  display this building unit in their most stable configurations.

In the special case of polar orientations, a structural transformation may also be driven by the gain of energy obtained by reducing or even suppressing the surface polarity. As previously, its energy cost scales with the object volume while its energy gain scales with the area of the polar termination, giving rise to the existence of a critical size below which the film structure is globally different from the bulk structure. For example, theoretical and experimental findings concur that, at low thickness, a variety of binary oxide polar films adopt a hexagonal boron nitride (h-BN) structure, which consists of a stacking of graphene-like, atomically flat six-member rings with an equal number

of cations and oxygen atoms. While the h-BN structure is only metastable in the corresponding bulk oxides, non-polar h-BN(0001) films are favoured over polar rocksalt (111) (MgO, FeO, CoO, ZnO) or wurtzite (0001) ones (ZnO, BeO) below a critical film thickness (Figure 5).

Finally, for nano-objects composed of just a few formula units, the above arguments may be of a limited use since neither a well-defined core nor well defined surfaces exists and their structural flexibility is the least constrained. For example, the smallest ZnO and MgO clusters display a variety of ring and/or tubular structures reminiscent of the h-BN structure (Figure 5).

### Interaction with a metallic substrate

With respect to the above-mentioned effects which determine the properties of unsupported thin films, additional mechanisms are at work when the films interact with a substrate, which can significantly modify their atomic and electronic structures, especially in the ultra-thin thickness regime.

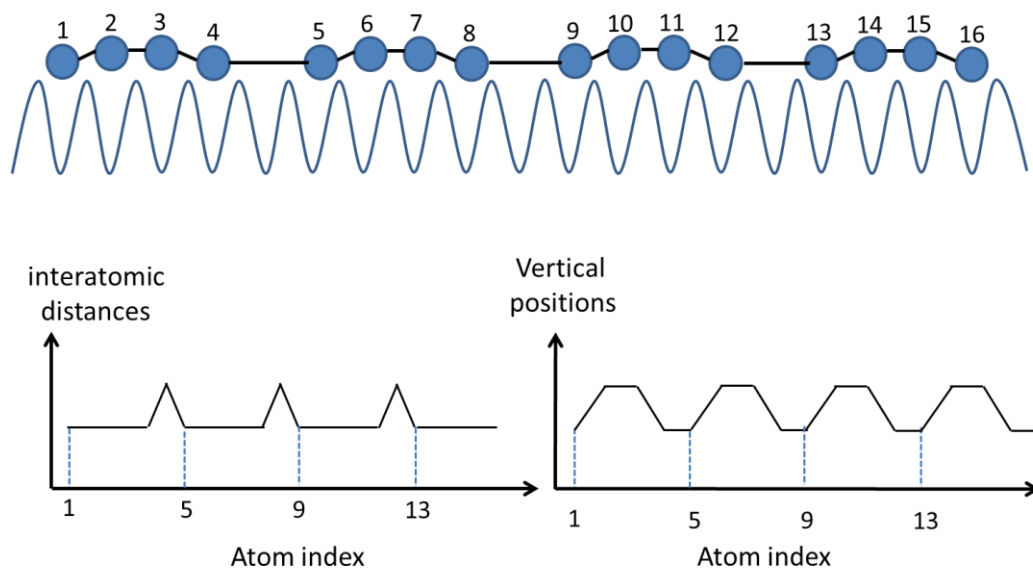


Figure 6: Top: Schematic representation in one-dimension of a film patterned by a dislocation network on a periodic substrate. Bottom: Consequences for first neighbour distances and vertical rumpling along the film.

### Structural relaxation

When a film is deposited on a substrate, mainly two energy terms enter in competition. One is the strength of interatomic forces within the film itself, which favors the (unsupported) film structure with its (unsupported) value of in-plane lattice parameter. The other is the interaction with the substrate, which favors a pseudomorphic interface with a locking of commensurability at the substrate lattice parameter. Purely pseudomorphic structures may indeed be found in a few cases, when ultra-thin flexible films strongly interact with the metal substrate. However, such a strong

interaction usually promotes metal oxidation and the formation of an interface oxide. In most cases of moderate interaction, the lattice mismatch yields an incommensurate interface, with a value of the mean film in-plane lattice parameter comprised between the substrate and the unsupported film values. Such compromise is accompanied by the formation of a periodic network of interfacial misfit dislocations which separate regions of good film/substrate matching. The dislocation network patterns the film structure. It modulates both the local anion-cation and film-substrate interfacial distances, and has consequences for its local electronic characteristics (Figure 6). A film patterning has been observed in many oxide ML films, such as FeO/Pt(111), MgO/Mo(100), etc. At small thickness, it may be used for tuning the adsorption or/and growth characteristics towards the formation of self-organized ensembles, such as, e.g., metal clusters with a particularly narrow size distribution. However, when the film thickness increases, its in-plane lattice parameters tend towards their bulk values. The density of misfit dislocations changes accordingly, and their effect on the structure of the outer film surface progressively diminishes.

### Induced polarity, rumpling

Besides the structural distortions induced by the lattice mismatch, a charge transfer exists between an oxide film and a metal substrate due to the hybridization of orbitals at the interface and/or the penetration of Metal Induced Gap States (MIGS). Its amount and sign are controlled by the relative position of the metal Fermi level and the oxide point of zero charge. Deposition of an oxide film on a metal of low electronegativity results in an electron transfer from the substrate to the film, while on more electronegative metals (transition metals of the end of the series or noble metals) electrons are transferred towards the metal.

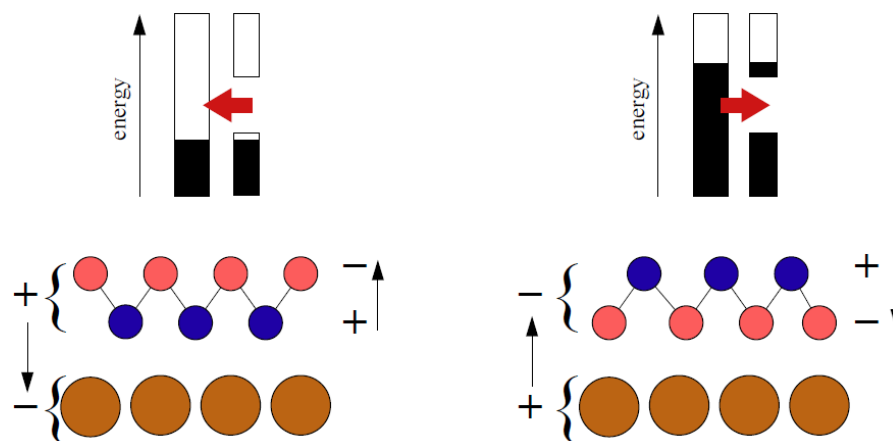


Figure 7: Top: band alignment and charge transfer at the interface between a thin oxide film and a metallic substrate. Schematic representation of the two dipoles associated to the charge transfer between an oxide film and its metal support and to the rumpling inside the oxide film (shown by arrows), for the two cases of a positive (left) and negative (right) metal charging. In the first case, oxygen atoms of the oxide film are attracted by the positive charge of the metal and pushed inwards. In the second case, they are repelled by the substrate. Cations, oxygen atoms, and metal atoms are represented as blue, red and large brown balls, respectively.

As a response to the electrostatic field produced by the interfacial charge transfer, the oxide film undergoes a structural distortion in which anions and cations are pushed in opposite directions (Figure 7). The resulting film rumpling produces a polarization which opposes and partially cancels that due to the interface charge transfer. Such electrostatic coupling between the two dipoles occurs also in thicker films but the structural distortion principally concerns the direct interface vicinity and may be limited by the film rigidity as thickness increases. The induced rumpling is also modulated by the presence of the misfit dislocations. In regions of a good matching where the film-substrate interaction is stronger, the interface charge transfer is large and so is the film rumpling. Conversely, at dislocation locations, the film-substrate interaction is weaker and induces a smaller film polarisation (Figure 8).

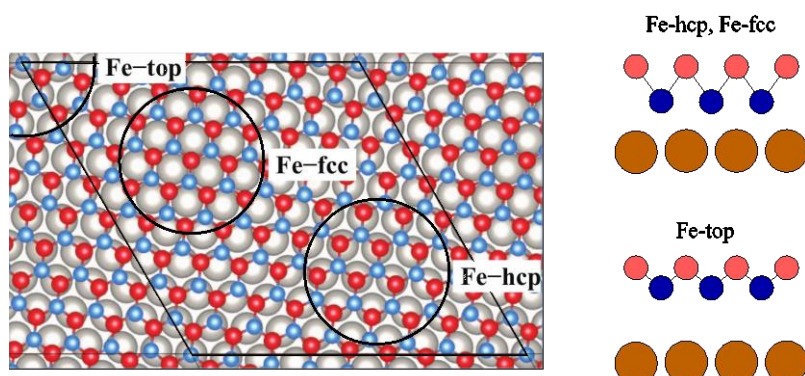


Figure 8: Left: Moiré unit cell of a FeO ML on a Pt(111) substrate. The regions of Fe-top, fcc and hcp registries are shown. Right: interfacial distance and film rumpling in the regions of the Moiré pattern of strong (Fe-hcp and Fe-fcc) and weak (Fe-top) interaction.

The interface charge transfer, the induced polarization of the oxide film, and the compression of metal electron spill-out at the oxide/metal interface determine the modification of the metal work function by the oxide film. Since the relative strength of these three contributions is sensitive to the local interface structure, a modulation of the local surface potential is observed in films patterned by interface dislocations.

### Charging of adsorbates

The modification of the metallic substrate work function induced by presence of an oxide film has a sound influence on the charge state of adsorbed species, and, as a consequence, on their growth, their self-organization and their wetting of the oxide film. The sign and amount of the charge transfer which takes place between an adsorbate and the oxide-on-metal substrate is a function of the oxide-metal work function and of the ionization or affinity level of the adsorbate. It has been demonstrated that a spontaneous adsorbate charging concerns metal atoms and clusters, as well as isolated inorganic molecules. It induces local (polaronic) distortions around the adsorbate which significantly stabilize it, especially at low film thickness (Figure 9). As in the case of substrate-induced film polarization, the dipole moment associated with the local film distortion opposes and partially compensates that due to the charge transfer. The spontaneous charge transfer and the induced distortion may enable, e.g., the incorporation of excess oxygen into ultra-thin oxide films supported on a metal, producing oxygen-rich oxide phases, with no bulk equivalent (see below).

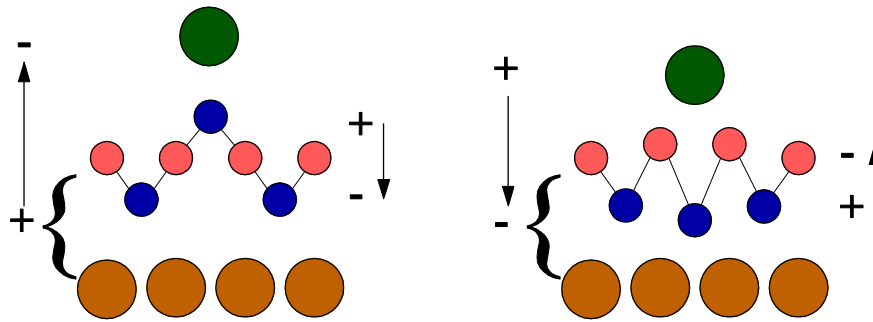
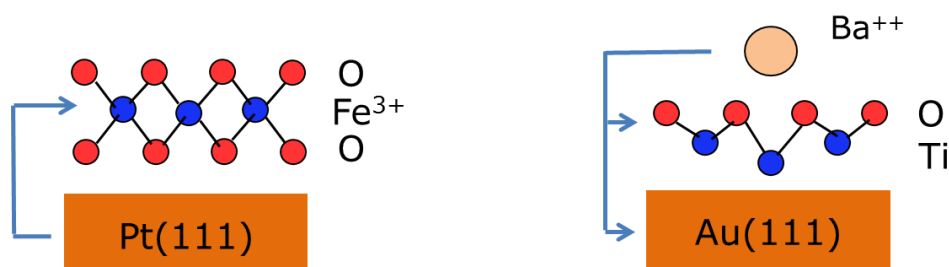


Figure 9: Schematic representation of the charge transfer between an adatom and a metal supported oxide films and the resulting polaronic distortion of the film, for the two cases of negative (left) and positive (right) adatom charging. The associated dipole moments are shown by arrows. Cations, oxygen atoms, and metal atoms are represented as blue, red, and brown circles, respectively.

### Nano-oxides with unusual stoichiometries

Unusual stoichiometries in oxide thin films result from a complex interplay between the thermodynamic conditions of preparation and the interaction with the substrate, including charge transfer and strain effects linked to the lattice mismatch. By changing the atom deposition rate, the oxygen partial pressure and the temperature, a rich variety of 2D oxide phases unknown in the bulk can be produced, such as those found for vanadium oxide  $\text{VO}_x$  on a  $\text{Rh}(111)$  substrate, manganese oxide  $\text{MnO}_x$  on  $\text{Pd}(100)$  or titania  $\text{TiO}_x$  on  $\text{Pt}(111)$ .

An emblematic example is the O-Fe-O trilayer formed by incorporation of oxygen into an FeO ML supported on  $\text{Pt}(111)$ . Even though an oxygen-rich atmosphere is necessary for the transformation to take place, it is not sufficient to explain the stabilization of an  $\text{FeO}_2$  stoichiometry which is incompatible with the +3 maximum oxidation state of Fe. The stabilization is due to a charge transfer from the Pt substrate which, although rather electronegative, provides the electrons necessary to accommodate the oxygen excess in the oxide film (Figure 10). The supported  $\text{FeO}_2$  trilayer is thus an example of a new 2D oxide, with no bulk equivalent, which cannot exist without the support on which it is grown and the thickness of which is limited to a single trilayer. Its interest comes from the relatively weak binding of the excess oxygen, which makes this nano-oxide an artificial, easily reducible material which can serve as an oxygen reservoir for, e.g., low temperature oxidation reactions.



*Figure 10 : Two examples of oxide thin films of stoichiometries unknown in the bulk. A  $\text{FeO}_2$  trilayer on Pt(111) (left) and a  $\text{Ba}_x\text{Ti}_2\text{O}_3$  layer on Au(111) (right) are stabilized thanks to an electron transfer from or towards the metallic substrate, respectively.*

The sign and the strength of the charge transfer which stabilizes the nano-oxides depends on the relative electronegativity of the metal substrate and the adsorbate. In the previous example, oxygen atoms were more electronegative than FeO/Pt(111), which led to an electron transfer from the metal substrate to the oxide film. In the case of  $\text{Ba}_x\text{Ti}_2\text{O}_3$  nano-oxides obtained by adsorption of Ba on a Au(111)-supported  $\text{Ti}_2\text{O}_3$  honeycomb ML, the strong electropositive character of Ba induces an electron transfer towards the support and the ionization of the adsorbed barium atoms. Repulsive effective interaction between Ba adsorbates drives the formation of ordered  $\text{Ba}_x\text{Ti}_2\text{O}_3$  ( $x=1/3$  or  $x=2/3$ ) phases, of stoichiometry, atomic and electronic structures which differ from those of bulk  $\text{BaTiO}_3$ .

### **Conclusion:**

The generic microscopic processes which determine the modifications, on a local or global scale, of oxide thin film structural and electronic characteristics have been presented in reference to bulk properties. Various parameters play a role, among which the film thickness, its orientation and its relative percentage of ionic and covalent character. To these intrinsic factors, the mismatch, the band alignment and the interaction strength with the substrate on which the films are grown should be added, opening a wide variety of behaviours and applications, which are exemplified in other contributions to this Encyclopedia.

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