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Theoretical approach to interfacial metal-oxide bonding

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Abstract. — This paper reviews existing theoretical calculations of the electronic characteristics and of the adhesion energy at a metal-oxide interface, in the context of non reactive adhesion processes and two- or three-dimensional metal growth processes. Emphasis is put on the competition between metal-cation and metal-oxygen interfacial interactions, on the resulting charge transfers and on the Fermi level position. Aside from the well-known image force and van der Waals contributions to the adhesion energy, the importance of kinetic and electrostatic terms associated with the Metal Induced Gap States and the interfacial dipole is stressed.

1. Introduction.

Understanding the nature and strength of the chemical bond between an insulating oxide and a metallic overlayer is of key importance in different areas of applications such as heterogeneous catalysis, electronics, anticorrosion and antithermic coating industry, confinement of liquid metals... This explains why numerous studies have been devoted to this question, either at a macroscopic level (measurement of wetting angles, adhesion energies, shear strengths..) or, more recently, at a microscopic level (spectroscopic methods, low energy ion scattering, electronic, tunneling or force microscopies..) [1].

It is the purpose of this paper to stress the main theoretical advances done in the field of metal-oxide interface electronic structure, and non-reactive adhesion, with special emphasis on the approach recently proposed by the authors. In this paper, we refer to non-reactive adhesion either when the free enthalpies of reaction ΔG (solubility, intermetallic compound formation or reduction of the oxide by the metal) are large and positive, or when the reactions are infinitely slow (low temperature). The paper is divided into two main parts : in the first one, we focus on the modifications of the electronic states at the interface, which includes 1) an analysis of the first stages of deposition of metal atoms, 2) the description of the metal induced gap states (MIGS), when the metallic overlayer is thick, 3) the determination of the Fermi level position, related to the Schottky barrier height, the index of interface behaviour and the discussion of core level shifts, and finally 4) a quick discussion of the role of surface states or defect states in changing the Fermi level position. In the second part, we recall some trends

found in adhesion energy measurements and wetting angles : we then consider the adhesion energy as a sum of elementary contributions : kinetic, electrostatic, short range and exchange and correlation, and for each of them we indicate, when it is known, the tendencies as a function of the metal characteristics and the ionocovalent character of the oxide.

2. Electronic structure at a metal-oxide interface.

Depending upon the thickness of the metallic overlayer, various theoretical approaches have been used. In the two following sections, we focus respectively on the first stages of metal deposition and on the interface between a thick overlayer and an oxide surface.

2.1 FIRST STAGES OF DEPOSITION OF METALLIC ATOMS. — Due to the importance of transition metal clusters as catalysts, an increasing number of studies is devoted to the first stages of deposition of metallic atoms, and to the determination of growth modes of clusters as a function of various parameters, such as the temperature, the surface treatments... The main relevant questions concern i) the characteristics of the chemical bond formed between one adsorbed metal atom and the oxide, i.e. the competition between oxygen-metal and cation-metal bonding as a function of the electronegativity of the atoms, the charge transfer and the nature of the adsorption site. The analysis of core level photoemission peak shapes and positions, low energy electron losses or Auger parameters has recently brought information on systems like Cu on MgO(001) [2, 3] and ZnO(10 $\bar{1}$ 0) [2], Pd, Cu, Ni, Cr on α -Al₂O₃(0001) and (10 $\bar{1}$ 2) [4]; ii) the discrimination between cluster (Volmer Weber) or bidimensional growth (Stranski Krastanov or Franck van der Merwe) [5], thanks to Auger parameter measurements, low energy ion scattering or electron microscopy. Cu [6, 7], Fe [8, 9], Cr [6], Pt [10], Rh [11] on TiO₂(110), Pd on MgO(100) [12], Cu, Ni, Fe, Cr on tungsten oxide films [13], Cu, Ni, Cr on Al₂O₃ [14, 4] are among the systems which have been analyzed. Most of these studies emphasize the metal-oxygen bond formation. Yet, the Pd clusters [12] grow epitaxially with the Pd atoms above the Mg surface sites, and on Al₂O₃ [4] the Pd atoms are located above the surface cations. This restores an Al environment closer to that of bulk ions, and induces the disappearance of Al-type surface states in the gap. As concern the growth modes for the various metal overlayers quoted above, there remains considerable controversy in the literature.

Several theoretical studies have been performed, of the adsorption of a single metal atom on clusters simulating an oxide surface, such as : Fe, Ni, Cu, Ag on a sapphire (0001) surface [15], Pt on α -Al₂O₃(0001) ending either by an aluminium or oxygen plane [16], Pt and Ru on SiO₂ and Pt on TiO₂ [17, 18]. These studies highlight the formation of the metal-oxygen bonding and antibonding states, these latter being completely filled in the case of noble metals (Cu, Ag) and only partly filled otherwise. In the case of Pt on α -Al₂O₃(0001) the calculation [16] reveals an electron transfer from the platinum to the aluminium atom, unexpected from the electronegativity difference between these atoms.

To our knowledge, there has been no quantum mechanical calculation of the electronic structure of supported metallic clusters, nor quantum simulation of the growth mode. Yet, several calculations consider the deposition of one or several monolayers of metallic atoms on an oxide surface, which may happen either in the case of Stranski-Krastanov (one monolayer then tridimensional clustering) and Franck van der Merwe (monolayer by monolayer) growths or in the case of low temperature deposition, where the diffusion of the metallic atoms on the surface is inhibited. In the case of Nb, Zr, Mo, Ru, Pd on α -Al₂O₃(0001) [19, 20], the results display the formation of a partly occupied metallic band of *d* character in the gap of the oxide and some mixing of the metallic states with the valence band, revealing the formation of a metal-oxygen bond : as the atomic number of the transition metal increases in a series, the

filling of the antibonding states at the interface increases, in complete analogy with the cluster results [15]. Similar features are found when metallic atoms of the first transition series form a three-layer thick film on top of the same alumina surface [21] ending with O^- atoms. The metal-oxygen bonding energy displays a uniform decrease from 5 to 1 eV per interfacial oxygen atom, while the charge transfer to the O^- surface ions varies in a non monotonous way from 0.45 to 0.72 electrons. Adsorption of Cu on the $(10\bar{1}0)$ face of $\alpha\text{-Al}_2\text{O}_3$ was also studied showing preferential coupling of the copper atoms to the surface oxygens [22]. In the case of Ag-MgO(001) [23, 24] there is preferential adsorption of Ag atoms above the surface oxygen and little charge transfer ; yet the formation of the Ag-O bond induces some density of states of oxygen character at the Fermi level.

Although it is too early to derive general trends, a rough correlation may be found between the oxygen affinity of the metal, the charge transfer at the interface and the growth mode : when the oxygen affinity of the metal atoms increases, a stronger metal-oxygen bond is expected, with larger charge transfer. This favors the metal spreading, i.e. a change from Volmer Weber to either Stranski Krastanov or Franck van der Merwe growth modes. Such arguments were given e.g. in reference [8], to rationalize the results on Cu, Fe, and Cr on $\text{TiO}_2(110)$. Yet, studies of the metal deposition on reduced surfaces [4] show that the change in the growth mode due to surface treatments depends upon the metal, the surface reduction inducing either an increase or a decrease in the spreading. This suggests the importance of metal-surface cation interactions, with possible charge transfer and bond formation. We will see in the second part of this paper that this interaction is indeed considered in the thermodynamic model of adhesion which makes use both of the enthalpy of formation of the metal-oxygen bond (related to the oxygen affinity of the metal), but also of the enthalpy of infinite dilution of the cation in the metal (which has some relationship with the metal cation bond strength).

2.2 ELECTRONIC STRUCTURE OF THE INTERFACE BETWEEN A THICK METALLIC OVERLAYER AND AN INSULATING OXIDE. — In the case of a simple metal deposition on an insulating oxide, we have developed a quasi-analytical approach to describe the modification of the electronic states at the interface [25, 26]. This model retains only the more relevant features of the metal and of the oxide, which are the following :

The oxide is described by a one-electron Hamiltonian involving a single orbital per site, of energy ϵ_A for the anions and ϵ_C for the cations, and an isotropic hopping term β between neighbouring sites. For simplicity, two crystal structures have been considered, namely the rocksalt and the zincblend ones. The dispersion relation is calculated at a given K_{\parallel} taken relatively to the (100) or (110) surfaces, respectively for the two crystal structures. With the above assumptions, we prove that the gap width is equal to $(\epsilon_C - \epsilon_A)$. By varying the parameter $(\epsilon_C - \epsilon_A)/\beta$ from zero to infinity, we are able to account for very covalent as well as for highly ionic oxides. This parameter fully characterizes the percentage of ionic and covalent character of the oxide.

The metal is represented by a jellium, which eigenstates are plane waves. All the metallic characteristics thus depend upon the electron density and the position of the bottom of the conduction band with respect to the vacuum level. Assuming an abrupt interface, valid for example in the case of an ideally flat oxide surface and non-reactive adhesion, a matching between the metallic plane waves and the oxide states is performed. This matching is of particular interest in the gap energy range, since only evanescent waves, characterized by a complex wave vector, are available on the oxide side. These waves are calculated by an analytical Green's function method, and shown to behave roughly as an oscillatory damped exponential function. It should be noted that, due to the presence of the metal, which acts as a

source of waves, these damped waves represent new states, in a small region of space on the oxide side. They are called Metal Induced Gap States (MIGS). The MIGS are not specific of interfaces with a simple metal. They also show up in the Ag-MgO interface [24]. The spatial dependence of the MIGS density of states $n(E, z)$ depends upon the energy value : close to the band edges, the oscillatory behaviour of $n(E, z)$ is weakly damped, indicating that the MIGS gradually transform into the propagating valence or conduction states. At midgap, on the contrary, the amplitude of the oscillations is small and the damping length ℓ_p of the MIGS is minimum, typically of the order of the interplanar distance : ℓ_p is found to decrease when the gap width increases and to be nearly independent on the metal electron density. The amplitude n_0 of the MIGS at the interface ($z = 0$) and at midgap is little dependent upon the oxide characteristics, but is fixed by the metal properties. Typical behaviours of n_0 and ℓ_p are displayed in figure 1a, b.

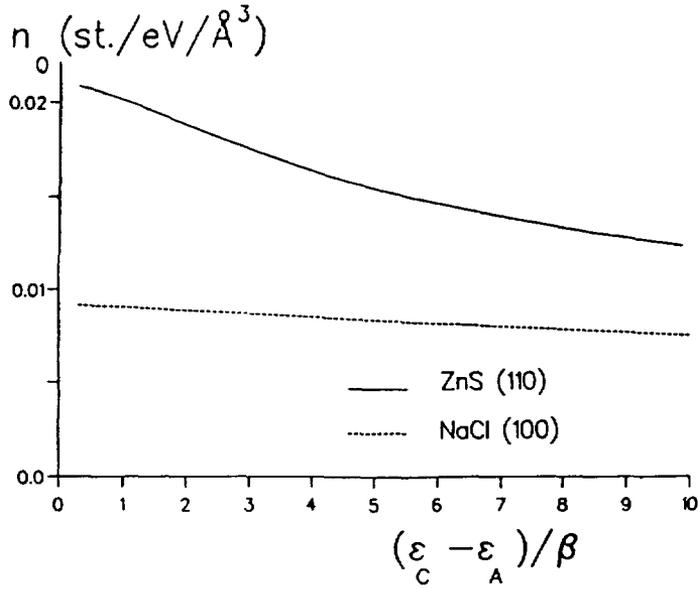
2.3 FERMIL LEVEL POSITION AND CHARGE TRANSFER. — On the insulating side of the interface the existence of the MIGS is correlated to a decrease of the state number in the valence and conduction bands (compared to bulk values). The MIGS are built from valence band-like states in the lower part of the gap, and of conduction band-like states in the upper part of the gap. A special energy E_{ZCP} called the Zero Charge Point separates these two ranges. This energy is located at mid-gap in the simplified band structures that we have considered. Charge neutrality occurs if the MIGS are filled up to E_{ZCP} .

In most of the cases, the metal Fermi level E_F does not coincide with E_{ZCP} so that charge transfer occurs at the interface, inducing an interface dipole potential, which bends the bands. To evaluate the charge density in the metal and in the insulator in a self-consistent way, we make a Thomas-Fermi approximation for the screening, and use a simple exponential form of the MIGS density of states at midgap : this allows to solve exactly the Poisson equation and thus to obtain an analytical expression for the dipole potential $V(z)$:

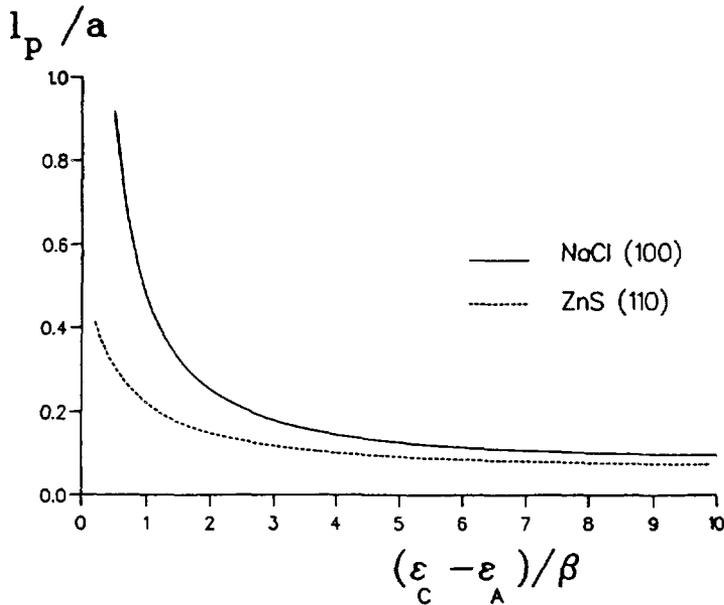
$$eV(z) = (E_{ZCP} - E_F) \left(1 - \frac{I_0(2\ell_p \exp(-z/2\ell_p)/\ell_1)}{I_0(2\ell_p/\ell_1) + (\ell_m/\ell_1) \varepsilon_i I_1(2\ell_p/\ell_1)} \right). \quad (1)$$

In equation (1), I_0 and I_1 are the two first modified Bessel functions, ε_i is the insulator dielectric constant, and ℓ_m and ℓ_1 are respectively the metal and insulator Thomas-Fermi lengths ($\ell_m = \sqrt{\varepsilon_0/e^2 n_m(E_F)}$ and $\ell_1 = \sqrt{\varepsilon_0 \varepsilon_i/e^2 n_0}$). $V(z)$ is proportional to the electrostatic perturbation at the interface ($E_F - E_{ZCP}$), but this perturbation is screened in a way which depends upon the MIGS density $n_0 \ell_p$. when $n_0 \ell_p$ is large, screening is efficient and the Fermi level is pinned at the position of the Zero Charge Point of the oxide, thanks to a strong band bending : this occurs when the oxide gap is small. A typical value of the transferred electron number is a few 10^{-2} electron per interfacial atom. In the other limit, encountered for highly ionic oxides, screening is inefficient, so that the Fermi level is imposed by the metal and differs from E_{ZCP} deep in the oxide, as can be seen from figure 2.

This study allows to calculate the Schottky barrier height Φ_B , i.e. the energy difference between E_F and the bottom of the oxide conduction band far from the interface. Φ_B has been measured for a large number of metal-semiconductor interfaces, and the index of interface behaviour $S = d\Phi_B/dX_m$ (X_m the metal electronegativity) has been determined. The dependence of S upon the oxide ionocovalent character is in good qualitative agreement with our findings in all the ionicity range of the insulator, which represents an improvement compared with previous approaches [25]. This study is also related to the question of the choice of the reference energy when discussing the core level shifts measured at a metal-insulator interface [27] : in most of the cases the vacuum level is taken as a common reference



a)



b)

Fig. 1. — MIGS local density of states n_0 at the interface (a) and MIGS penetration length l_p (b) at midgap vs the ratio of the gapwidth to the hopping integral of the insulator for both types of insulator structures and surfaces ; the anion atomic level is assumed to be 6 eV above the bottom of the metal conduction band, and the lattice parameter of the oxide is $a = 5 \text{ \AA}$.

for the metal and the oxide core levels : yet this neglects any effect of band bending, and should thus be valid only in the case of very ionic substrates.

Because it treats the metal as a continuum medium, the jellium model does not allow a separate characterization of the metal-oxygen and metal-cation interfacial bonds ; as a

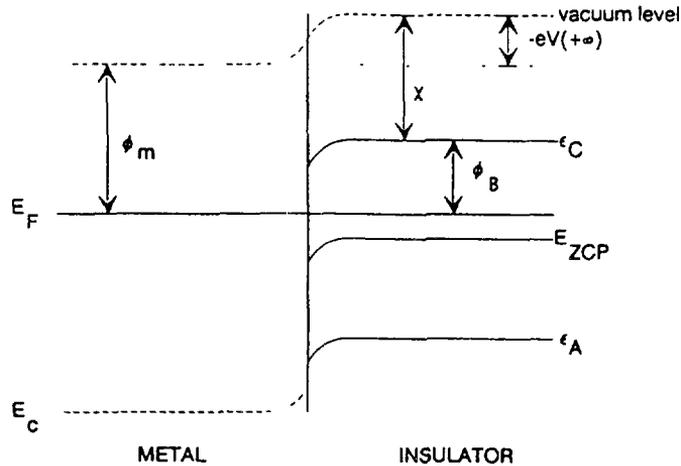


Fig. 2. — Local distortions of the metal and insulator band structures induced by the interfacial dipole potential. The Fermi level remains constant in all space. Φ_m , χ , Φ_B denote respectively the metal work function, the insulator affinity and the Schottky barrier height.

consequence, the comparison with numerical models of the interface is difficult. Yet, the charge transfer that we obtain at the end of the self-consistent resolution of the Poisson equation, is the result of the competition between the two interfacial bond types. When the metal Fermi level just coincides with E_{ZCP} , the two kinds of charge transfer exactly balance each other; when E_F is above E_{ZCP} , electrons are transferred from the metal to the oxide, suggesting that the metal-oxygen bond formation drives the charge transfer. In the opposite limit, electrons are transferred from the oxide to the metal overlayer, thanks to the formation of partially ionic metal-cation bonds.

2.4 DISCUSSION. — The model that we have elaborated is highly simplified, both considering the actual metal-oxide interfaces, and the actual surface electronic structures. First, it assumes that the oxide surface is perfect, with no structural or stoichiometry defects. Yet in many cases, there are steps or roughnesses at the surface, and very often also, depending upon the surface treatment, there may be oxygen vacancies. Many kinds of defects in insulators induce gap states, either filled or empty, which are available for charge transfer from or towards the metal. Secondly, at variance with our model, there may be some specific compound surfaces on which, even after hybridization with the metal states, surface states remain as virtual bound states in the gap. When this happens, the MIGS are no longer the only available gap states.

The determination of the position of the Fermi level and of the charge transfer at the interface, that we have made, is likely not to apply in the presence of defects or virtual surface states, because, even in the case where they mix with the metal continuum, these latter represent additional states, aside from the MIGS, available for electron transfer between the metal and the oxide. To our knowledge, there is no model specific of metal-insulator interfaces to account for this situation, but some may be found in the context of metal-semiconductor interfaces. At metal-semiconductor interfaces, in the case of covalent semiconductors, it is experimentally found that the Schottky barrier is independent on the metal characteristics, contrary to the first model given by Schottky [28]. There have been various explanations for this, relying upon the existence of gap states able to pin the Fermi level: aside from the MIGS model, one is due to Bardeen: it postulates the existence of surface states and has been

improved in the resonant dangling bond model [29] to fit to the (110) surfaces of the Zincblend structure where the surface states are of dangling bond-type and are hybridized with metal states at the interface. There is also the unified defect model [30] proposed by Spicer *et al.* In these models, the defect state energy or the dangling bond energy plays the role of a Zero Charge Point, and, due to the large density of interface states, they pin the Fermi level, as did the MIGS on covalent semiconductors. In such occurrences, great care should be taken in reconsidering the interfacial dipole formation and Fermi level position.

3. Adhesion energies.

3.1 EXPERIMENTAL AND THERMODYNAMIC APPROACHES. — A wealth of results concerning the adhesion of liquid metals on insulating substrates has been gathered along the years. We will mention here mainly those which are related to non-reactive adhesion.

First it should be noted that there is a close relationship between the adhesion energy W_{adh} and the wetting angle θ . The adhesion energy is the free energy required to disjoin a unit area of solid-liquid interface (SL), thus creating a solid-vapour (SV) and a liquid-vapour (LV) interface. Consequently, W_{adh} may be expressed thanks to the surface energies σ of these interfaces :

$$W_{adh} = \sigma_{SV} + \sigma_{LV} - \sigma_{SL} . \quad (2)$$

On the other hand, wetting is characterized by the value of the macroscopic contact angle θ , which is determined by the condition that the contact line between the three phases is at rest on an ideally homogeneous and smooth plane : this is the Young-Dupré equation, which relates θ to the surface energies σ of the three interfaces :

$$\cos \theta = \frac{(\sigma_{SV} - \sigma_{SL})}{\sigma_{LV}} . \quad (3)$$

These two relationships give :

$$W_{adh} = \sigma_{LV}(1 + \cos \theta) . \quad (4)$$

A measurement of a contact angle may thus yield a value of the adhesion energy provided that one knows the liquid surface tension. Equation (4) tells that an increase in W_{adh} leads to a spreading of the liquid (decrease of θ). In the case of liquids with low surface tensions (less than 0.1 J.m^{-2}) dispersion forces between the liquid and the solid, like van der Waals forces, yield a sufficient adhesion energy to reach complete wetting ($\theta = 0$, $W_{adh} > 2 \sigma_{LV}$). This is not the case for liquid metals for which the surface tension is one order of magnitude higher. In that case, the minimum binding energy per atom at the interface required for complete wetting is of the order of 1 eV, which corresponds to a strong chemical or electronic bonding.

In the context of metallic growth on a substrate, a similar thermodynamic criterion is used [5] to predict the growth mode. As recalled in figure 3, the layer by layer growth mode (or Franck van der Meer) corresponds to interfacial forces larger than the metal cohesion forces ; it is found when the total wetting condition $W_{adh} > 2 \sigma_M$ (σ_M the metal surface tension) is obeyed. In the other limit, three-dimensional growth (or Volmer Weber) occurs if $W_{adh} \ll \sigma_M$. The intermediate Stranski-Krastanov growth mode involves a more complicate criterion, since wetting of the substrate should occur for the first layer, and non wetting on the first metallic layer afterwards. Most of the metal-oxide interfaces which have been studied up to now display Volmer Weber or Stranski Krastanov growth modes.

There appear some systematic trends in the adhesion energy values of liquid metals on ceramics. First considering a given oxide, a systematic decrease of the adhesion energy when

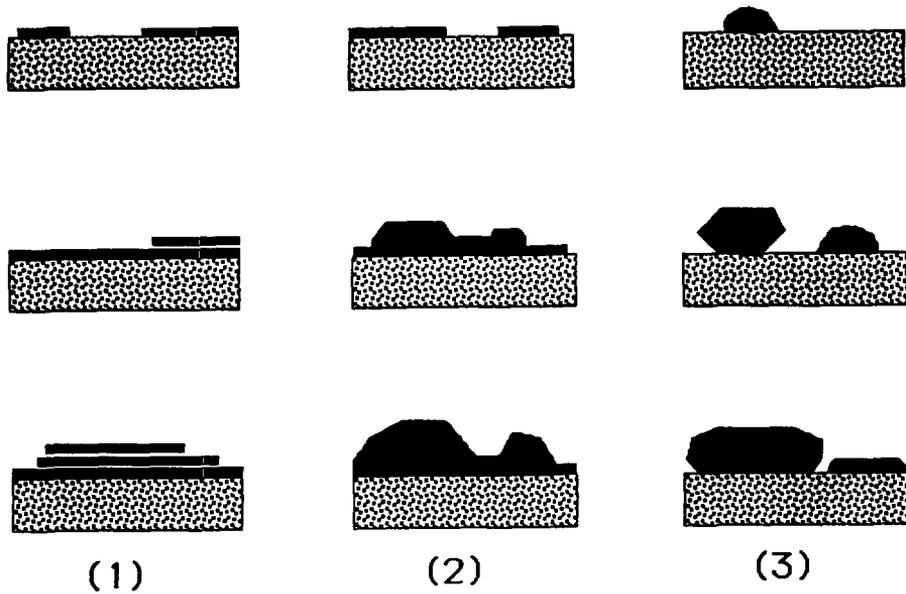


Fig. 3. — The three main classes of growth modes : (1) layer by layer mode (Frank van der Merwe), (2) intermediate Stranski-Krastanov mode (3) three-dimensional mode (Volmer-Weber).

going down a column of the periodic table for the metal is found [31] : e.g. for noble metals on alumina, W_{adh} is equal to 490, 325 and 265 mJ/m² respectively for Cu, Ag and Au ; similarly W_{adh} is equal to 950, 345 and 245 mJ/m² respectively for Al, Ga and In. This may be assigned to the increase of the atomic density of the metal, i.e. to a steric effect.

Second, considering a given liquid metal on various stoichiometric oxides, it is found that an increase in the insulating character of the oxide is generally associated with a decrease of the adhesion energy (increase of the wetting angle). Considering for example [39] Cu on MgO, Al₂O₃, UO₂, Ti₂O₃, TiO_{1.14} and TiO_{0.86}, θ is equal to 133°, 130°, 125°, 115°, 82° and 72°. In this series, the electronic gap is close to 8 eV for the two first oxides, 5 eV for UO₂ and vanishing for TiO, as x decreases [44]. Similarly, in a recent study [32] of the wetting of liquid gold on various phases of titanium oxides TiO₂, Ti₄O₇ and TiO, the wetting angles are found equal respectively to 122°, 121° and 88° : this is to be correlated with the expected decreasing gap widths in the series.

Yet care must be taken in trying to deduce a systematic trend of the adhesion energy *versus* the electric conductivity of the oxide. While it is true that larger gaps go together with lower conductivities, there may be conductivity processes connected with the existence of defects in the gap, for which the above correlation does not work : for example non-stoichiometric TiO_{2-x} samples exhibit increasing conductivity as x gets larger, while it has been shown [32] that the wetting angle of gold is nearly independent on the oxygen vacancy concentration up to $x = 7 \times 10^{-3}$.

The correlations that we have indicated above make use of separate properties of the metal on one side (the atomic density, the electron density) and of the oxide on the other (its gap, its dielectric constant). Yet, of course the adhesion energy, or the growth mode, depends upon the precise interfacial forces. This was the idea supporting the thermodynamical models of adhesion [33], later improved by Chatain [31] to include interfacial metal-cation interactions, which indeed proved to be very efficient to account reasonably for most existing adhesion

energy measurements. In its most elaborated form, this model correlates the adhesion energy to the partial enthalpies of mixing at infinite dilution of the oxygen and cation in the metal : $\Delta H^\infty(\text{O-Me})$ and $\Delta H^\infty(\text{X-Me})$. For an oxide of stoichiometry XO_n , W_{adh} reads :

$$W_{\text{adh}} = \frac{C}{V_{\text{Me}}^{2/3}} \left(\Delta H^\infty(\text{O-Me}) + \frac{1}{n} \Delta H^\infty(\text{X-Me}) \right) \quad (5)$$

where V_{Me} is the molar volume of the liquid metal and C a constant fitted to available experimental data. Assuming that entropic effects play a negligible role in the adhesion process (e.g., N. Eusthatopoulos, in this issue), the quantities $\Delta H^\infty(\text{A-B})$ can be written as a function of the coordination number Z around atom A, and the pair interaction energies ε_{AA} , ε_{BB} and ε_{AB} as : $\Delta H^\infty(\text{A-B}) = Z \{ \varepsilon_{\text{AB}} - (\varepsilon_{\text{AA}} + \varepsilon_{\text{BB}})/2 \}$. It is thus seen that, through the quantities $\Delta H^\infty(\text{O-Me})$ and $\Delta H^\infty(\text{X-Me})$, interfacial interactions between the metal atoms and respectively the surface oxygen atoms and surface cations are to some extent included in the model, although the counting of bonds at the interface is not a straightforward matter. Finally, through the factor $V_{\text{Me}}^{2/3}$, equation (5) takes care of steric interactions at the interface. This thermodynamic model is generally able to predict the intensity of wetting in non-reactive systems.

3.2 MICROSCOPIC CONTRIBUTIONS TO THE ADHESION ENERGY. — Aside from these thermodynamic approaches, several authors have estimated the adhesion energy at a more microscopic level, but generally, due to the approximations made, they have discarded one or several contributions to W_{adh} . We have noticed above that the adhesion energy is a combination of three surface tensions : σ_{SV} , σ_{LV} and σ_{SL} . Forgetting in a first step entropy factors, each of these surface tensions can be calculated, as usual, as the sum of electronic contributions (kinetic, electrostatic, exchange and correlation) and short range atom-atom repulsions. To our view point, aside a first attempt by Hicter *et al.* [34] no microscopic theory of the adhesion considers all these contributions, which unfortunately are likely to be of the same orders of magnitude, with positive or negative signs. In particular, the energy terms (kinetic and electrostatic) which origin lies in the change in the electronic wave functions at the interface, have not been fully considered in the past. Among the quantum mechanical modelizations of a metallic overlayer on an oxyde, quoted in the first part, only one [21] gives results for the interfacial energy of transition metal layers deposited on an alumina (0001) surface, and its decomposition into kinetic and short range, but it does not consider the electrostatic nor the exchange and correlation contributions. We shall try, in the following, to describe the physics associated with each of these terms with reference to the jellium model of a metal-vacuum interface [35].

3.2.1 Kinetic energy. — As a general statement, the kinetic energy is the energy gained by the quantum motion of the electrons which do not remain localized around the atoms but can jump from atoms to atoms. This energy depends upon the geometry of the system, and as a consequence contributes to the surface energy. At a metal-vacuum interface, the matching of the metallic electronic waves gives rise to an exponentially decreasing probability of finding the electrons in the vacuum region. This spill-over lowers their kinetic energy. The kinetic term thus gives a negative contribution to the surface energy (kinetic energy is gained when the surface is created), typically of the order of -1850 mJ/m^2 for a magnesium (jellium) surface (which surface energy is close to 600 mJ/m^2).

At a metal-insulator interface, band structure effects are more complicated : in the gap energy range, the metallic waves match to MIGS on the oxide side of the interface (in a way similar to the metal-vacuum interface), and there is a correlative decrease of the state numbers

in the valence band energy range. The kinetic energy term in the interface tension, to lowest approximation (no self-consistent electron-electron interaction included), can be written as a band filling term :

$$\langle T \rangle = \int_{-\infty}^{E_F} dE E N_s(E) \quad (6)$$

with $N_s(E)$ the interface density of states, including the MIGS and the valence band modifications. The order of magnitude for $\langle T \rangle$ should range from 10^{-1} to 1 Jm^{-2} , because the MIGS density $n_0 \ell_p$ is of the order of $10^{-2} \text{ state/eV/\AA}^2$ in an energy range of $\Delta/2$; consequently it should not be forgotten from the analysis. In the study of transition metal layers deposited on $\alpha\text{-Al}_2\text{O}_3(0001)$ [21], this energy amounts indeed to a few eV per oxygen atom, which is the same order of magnitude. As concerns the adhesion energy now, the kinetic energy contribution has to be compared with the corresponding contributions to the metal and the oxide surface energies. Its sign is thus uncertain; yet a large interfacial kinetic energy term favors adhesion.

3.2.2 Electrostatic energy. — Electrostatic interactions at a surface or an interface have various origins.

3.2.2.1 Surface dipole. — The existence of a surface dipole (such as at the metal-vacuum interface or at the metal-oxide interface when the metal Fermi level and Zero Charge Point of the oxide do not coincide) is associated with an electrostatic interaction. For example, at a metal-vacuum interface, there is a net negative charge outside the metal, exactly balanced by a net positive charge inside the metal. The electrostatic energy contributes positively to the surface energy. When ionic charge distribution is added to the jellium model, to account perturbatively for the presence of the positive ions, an additional positive electrostatic contribution to the surface energy occurs because the electrons which are outside the surface interact less effectively with the positive ions: orders of magnitude of these two terms are respectively 430 mJ/m^2 and 500 mJ/m^2 for magnesium, taken from the calculation of Lang and Kohn [35]; actually, the second term is overestimated due to the perturbative treatment.

At a metal-insulator interface, since we have self-consistently determined the charge density and the Fermi level within our simplified approach, we are able to write down an analytical expression of the dipole energy as a function of the metal and insulator Thomas-Fermi lengths, by integration of the interfacial potential :

$$\langle E_{el} \rangle = \frac{1}{2} \int_0^{\infty} dz \rho(z) V(z) \quad (7)$$

$$\langle E_{el} \rangle = \frac{\epsilon_1 \epsilon_0 (E_F - E_{ZCP})^2}{4 e^2} \frac{2 \ell_p (I_1^2 - I_0 I_2) + \epsilon_1 \ell_m I_1^2}{(\ell_1 I_0 + \epsilon_1 \ell_m I_1)^2} \quad (8)$$

In this expression, the Bessel functions are evaluated at $x = 2 \ell_p / \ell_1$. $\langle E_{el} \rangle$ is positive (as for the metal-vacuum surface); but it can vanish when the metal Fermi level gets equal to the insulator Zero Charge Point. The factor $(E_F - E_{ZCP})^2$ is maximal either for a low work function metal (alkaline metals) in contact with a large gap insulator, or for a high work function metal (noble metals: Au, Pt...) on a small gap insulator. The second factor in equation (8), which includes the screening lengths, vanishes in the ionic limit, due to the very low MIGS density, and the absence of band bending. In the covalent limit, it reaches an asymptotic value equal to $\epsilon_0 (E_F - E_{ZCP})^2 / 4 e^2 \ell_{\text{eff}}$, which is the energy of a capacitor, the electric potential of which is proportional to $(E_F - E_{ZCP})/e$ and for which the plate separation is the sum of the screening

lengths $\ell_{\text{eff}} = \ell_m + \ell_i/\epsilon_i$. Taking for $E_F - E_{\text{ZCP}}$ an average value of 1 eV, it is found that the dipole energy ranges from 10^{-2} to 10^{-1} J/m². Again, it is surely not a negligible contribution to the interfacial energy, but to our knowledge, it had never been considered previously. By analogy with the jellium model of the metal-vacuum interface, the occurrence of the interfacial dipole induces a second electrostatic (charge-charge) term, associated with the change in the interaction of the electrons with the cores of the atoms, either on the metal or on the insulator side of the interface. A large interfacial electrostatic energy is not favourable to the adhesion.

3.2.2.2 Polarization terms. — Another electrostatic contribution to the interface energy comes from the polarization of the metal under the electric field of the insulator ions (charge-induced dipole interaction). This image force term was described in details by Stoneham and coworkers [36, 37], for purely ionic oxides, and shown to have an order of magnitude close to a surface energy, i.e. of the order of W_{adh} . if one considers a rocksalt oxide cut along the (001) surface and assumes that the metal is a perfect electrostatic mirror at mid-distance between two (001) planes, the electrostatic images then correspond exactly to the missing oxide atoms, so that the associated energy is equal to the surface energy (when only electrostatic energies are considered). However, compared with experimental data on wetting angles, this term alone cannot account for the variations of the adhesion energies with the metal electronegativity, and the results of the model are too much dependent upon the orientation of the interface. Nevertheless, the question remains open since more recent experiments on model systems [1] stress the importance of geometrical factors (mismatch between the metal and the oxide structures, surface orientation...).

The image force approach predicts an increase of adhesion with an increased concentration of charged defects [38], which may be correlated with the fact that generally, adhesion is enhanced when the materials are irradiated with electrons or ions. Here again, more work is required because not all defects induce an increased adhesion as shown recently by experiments on non stoichiometric titania TiO_{2-x} , by gold, which prove that the wetting angle is independent on x [32].

3.2.3 Exchange and correlation energy. — The correlation terms in the energy include all processes which are beyond the mean-field approximation, for electron-electron interactions : their strength is related to the behaviour of the dielectric constant and to the characteristics of the screening effects in the material. The contribution to the interfacial energy comes from the difference between these polarization processes in the bulk of the separate materials and in the system with the interface.

At a metal-vacuum interface, the exchange and correlation contribution is mainly due to polarization processes created by the electrons outside the metal ; these latter are no longer completely screened as in the bulk, and their remaining interaction with their screening cloud contributes positively to the surface tension. Typically for a magnesium surface [34] this term is equal to 1 460 mJ/m².

At a metal-insulator interface, the correlation term comes from the mutual polarization of the two media, which gives rise to dispersion forces. This was the original idea of Naidich [39] who assumes that, apart from a small chemical term, the adhesion energy can be expressed as :

$$W_{\text{adh}} = \frac{3}{2} \frac{\alpha \alpha'}{R^6} \frac{(I - I')}{(I + I')} \quad (9)$$

This expression resembles the London formula for van der Waals energy between two atoms, with α and α' respectively the polarizabilities of the metal atoms and the O^{2-} ions (the oxide polarizability is assumed to be driven by the oxygen ion polarizability), R the metal-oxygen distance, and I and I' the ionization potentials. This expression for the atom-atom van der

Waals interaction is no doubt a contribution to the adhesion energy (although it assumes no electron sharing between the atoms). Yet, Eustathopoulos [40] argued that the variation of the predicted adhesion energy from one system to the other is definitely not large enough to reproduce the experimental data.

One possible reason is that it assumes that the polarizability of the two media simply reduces to the atomic polarizability. In other words, it neglects excitation processes of small energy in the metal (electron-hole pair excitations) and excitations across the electronic gap for the insulator (charge transfer excitations), which are known to be of major importance in condensed systems. Barrera and Duke [41] have proposed an improved approach : they have shown that, in complete analogy with the metal-metal interface [42, 43], the van der Waals energy at the metal-insulator interface may be calculated from the change in the plasmon zero-point energy upon the formation of the interface. Assuming uniform dielectric constants for the insulator :

$$\varepsilon_i(\omega) = 1 + \frac{\omega_{pi}^2}{\Delta^2 - \omega^2 - i\omega/\tau} \quad (10)$$

and for the metal

$$\varepsilon_m(\omega) = 1 - \frac{\omega_{pm}^2}{\omega^2 + i\omega/\tau} \quad (11)$$

they give a compact expression of the interface energy as a function of the metal and oxide characteristics : ω_{pm} , ω_{pi} and Δ . (ω_{pm} , ω_{pi} and τ are the metal and insulator plasmon energies and the insulator plasmon life time.) Stoneham [44], assuming that this term alone determines the value of the adhesion energy, and making some simplifying assumptions, has shown that it gives a correct order of magnitude for the adhesion energy and allows to discuss the adhesion energy variations as a function of the electron densities (included in ω_p) and as a function of the insulator gap Δ . An increased ionic character of the insulator is shown to decrease the adhesion energy, and a simple criterion for the occurrence of wetting is given, namely that the metal plasma frequency should be less than a critical value :

$$\omega_{pm} < 2 \sqrt{2} [\sqrt{\omega_{pi}^2 + 2 \Delta^2} - 2 \Delta]. \quad (12)$$

Stoneham concludes that this criterion does not classify systems correctly as wetting or non-wetting, at least in the simplest approximations. To our point of view, Barrera and Duke's approach is likely to be the best derivation of the van der Waals energy in the literature, in the context of metal-insulator interfaces, but its results should not be directly compared with experimental data, since it gives only one of the contributions to W_{adh} . The same could be said about the image force calculations.

3.2.4 Short range repulsion. — The exchange-correlation energy contains a part of the short range repulsion which takes place when two atoms are brought close to one another, because this repulsion is of exchange origine. Yet, if only valence electrons are included in the quantum mechanical treatment, one must generally add a repulsion term to account for inner shell exchange effects. This repulsion term is generally written under a Born-Mayer or a Lennard-Jones form. The short range repulsion is always a negative contribution to the surface energy, because repulsion is released when breaking bonds to create a surface. Its order of magnitude may range from a few tenths of eV to a few eV per broken bond.

4. Conclusion.

The theoretical study of metal-insulator interfaces is not advanced enough to give a clear and thorough analysis of the chemical bonding at the interface, nor to understand systematic trends in the adhesion energy. Many open questions remain, among which the following :

- At the first stages of metal atom deposition on an oxide, how does the relative strength of the metal-cation and metal-oxygen interactions determine the adsorption site and charge transfer ? What is the role of the relative electronegativity of the atoms and of the oxide surface orientation ?
- How does the insulator surface stoichiometry change the adsorption and growth processes ?
- When the cluster size increases, how do the metallic atomic levels gradually transform into MIGS and how does the Fermi level position vary ? Is there a percolation threshold at which the cluster induced MIGS laterally overlap, thus producing a uniform metallization of the insulator surface ?
- Is it possible to modelize the growth processes with quantum mechanical tools ? Up to now, for this purpose, only classical pair-interaction models have been introduced into Monte-Carlo codes.
- A thorough analysis of the various contributions to the interfacial energy is lacking even for model systems (e.g. an ordered metallic monolayer on top of an oxide surface). A deeper connection between thermodynamic and microscopic approaches is desirable.

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