



Electronic States and Schottky Barrier Height at Metal/MgO(100) Interfaces

JACEK GONIAKOWSKI*

*Centre de la Recherche sur les Mécanismes de la Croissance Cristalline—CNRS, Université de la Méditerranée,
Campus de Luminy, 13288 Marseille, France*
jacek@crmc2.univ-mrs.fr

CLAUDINE NOGUERA

*Groupe de Physique des Solides, UMR 7588 CNRS-Université Paris 6 et Paris 7, Tour 23, 2 place Jussieu,
75251 Paris cedex 05, France*

Abstract. Using an *ab initio* total energy approach, we study the electronic structure of metal/MgO(100) interfaces. By considering simple and transition metals, different adsorption sites and different interface separations, we analyze the influence of the character of metal and of the detailed interfacial atomic structure. We calculate the interface density of states, electron transfer, electric dipole, and the Schottky barrier height. We characterize three types of electronic states: states due to chemical bonding which appear at well defined energies, conventional metal-induced gap states associated to a smooth density of states in the MgO gap region, and metal band distortions due to polarization by the electrostatic field of the ionic substrate. We point out that, with respect to the extended Schottky limit, the interface formation yields an electric dipole mainly determined by the substrate characteristics. Indeed, the metal-dependent contributions (interfacial states and electron transfer) remain small with respect to the metal polarization induced by the substrate electrostatic field.

Keywords: metal-oxide interface, interface electronic states, Schottky barrier

1. Introduction

The microscopic mechanisms responsible for the structural, electronic and growth characteristics of metal deposits on insulating, ionic substrates have attracted a growing attention of both experimental and theoretical materials scientists. This is due to a large extent to the particular, but yet not fully understood, catalytic properties of oxide-supported metal clusters, and it has stimulated a significant theoretical effort to understand and efficiently model metal deposition on oxide surfaces. Although the electronic structure of such interfaces has also been studied, its microscopic description is still far from being settled [1–8]. In particular, although the results of the state-of-the-art *ab initio* calculations concerning the preferential adsorption geometry approach

closely the experimental evidence, the comparison concerning the electronic and energetic characteristics of the interface is much more challenging. On one hand, due to the complexity of the interface atomic structure, the comparison between experimental and theoretical results is rarely direct. On the other hand, due to non-vanishing contributions related to the Van der Waals and image charge interactions, the validity of existing theoretical techniques may be in some cases questioned.

In particular, the nature of metal-induced gap states (MIGS), which are a key ingredient underlying most of metal/semi-conductor models (for review see [9–11]), its relation to the interface orientation, to the epitaxy conditions, and to the detailed atomic structure of the contact region are still under study [12]. Also the influence of the chemical nature of the interacting species, and the role of orbital hybridization at the interface are

*To whom all correspondence should be addressed.

still not fully elucidated [11]. So is the relation between MIGS, the interface electron transfer, the interfacial dipole, and the resulting alignment of bands at the interface, which determines the Schottky barrier height (SBH) [14–16]. Whereas the main forces responsible for adhesion between a metal and an oxide are under debate, to our knowledge no systematic study on the nature of the interfacial states and on the SBH at metal-oxide contacts has been performed, especially from the theoretical point of view.

As a model ionic substrate, the MgO (100) surface is particularly suited for both experimental and computational reasons. In particular, its wide gap ensures no crossing between the Fermi level and the oxide bands for a wide range of different metals and its strong ionicity minimizes the effects due to the interfacial electron transfer. While these factors reduce the complexity of the SBH problem with respect to situations akin to covalent semiconductors, the strong electrostatic field of the MgO induces polarization of the metal at the interface, which is mostly absent in the latter systems. Finally, the crystalline structure rigidity and the resulting relatively simple atomic structure of the metal/MgO interface simplifies the interpretation of experimental results and the computational effort necessary to model this kind of systems.

In order to get a complete set of results and to be able to discuss systematic trends, we consider Me/MgO(100) interfaces for different metal (Me) characters: simple metals (Mg, Al), early and middle transition metals (Ti, Mn), and late transition metals from both the 3rd and the 4th series (Ni, Pd, Ag). Although some of these interfaces have already been considered in the literature [17–21], and some tendencies concerning the transition metals have already been established [22–24], to our knowledge no systematic information on the interface electronic structure, the charge transfer, the interface dipole, or the SBH has ever been given. On this basis, we discuss the nature of metal-induced states and the origin of the band alignment. We try to unravel the contributions arising from the structural characteristics of the interface, those associated to the metal character, or to the metal-oxide interaction. This gives a well defined basis for a microscopic understanding of the SBH which, after some corrections to the DFT-GGA values, can be related to the experimental measurements.

The paper is organized as follows. After a description of the computational methods and settings in Section 2, we present the results on the structural

and electronic interface characteristics for the series of metals, Section 3.1. We then focus on the role of the metal electronic structure in a detailed comparison of Pd/MgO(100) and Mg/MgO(100) interfaces, Section 3.2, on geometry-dependent features of the electronic structure for two different adsorption sites in the Pd/MgO(100) system, Section 3.3, and on the influence of the interfacial separation, Section 3.4. In Section 4, we discuss the alignment of the metal and oxide bands, the nature of the interface states, the origin of the SBH, and the corrections to perform in order to compensate the deficiencies of the DFT-GGA treatment. We finish by a comparison with experimental findings.

2. Computational Method and Settings

The present study makes use of the density functional-based, full potential linearized augmented plane waves (FP-LAPW) method [25], with the gradient-corrected form of the exchange-correlation potential by Perdew and Wang [26]. This approach has already been successfully used in surface and metal-oxide interface studies [27, 28]. In order to treat all considered metals on the same footing, we have neglected the spin-polarization effects in Ni and Mn. Within the FP-LAPW method, space is divided into non-overlapping spheres centered on the atomic sites. Sphere radii of 1.8 a.u. are used for oxygen, magnesium (in the MgO), titanium, nickel, and manganese atoms, 2.2 a.u. for aluminum, palladium, and silver, and 2.3 for magnesium atoms (in metal Mg). The basis set consists of plane-wave envelope functions which are augmented inside the atomic spheres by means of a numerical solution of the Schrödinger equation. Partial waves up to $l = 10$ are used inside the atomic spheres. So-called “local orbitals” are added in order to include the $O2s$, $Mg2sp$, $Al3p$, $Ti3sp$, $Mn3sp$, $Ni3p$, $Ag4sp$, and $Pd4sp$ as semi-core states. Plane waves of energies up to $k_{\max}^2 = 25$ Ry are systematically included in all calculations. Two-dimensional $\mathbf{k}$ point sampling of the Brillouin Zone (BZ) (with a Gaussian broadening of 2 mRy), is converged with 55 $\mathbf{k}$ points in the irreducible part of the BZ.

2.1. Metal-Oxide Systems

We consider pseudomorphic metal-oxide interfaces, where the metal deposit takes the fcc atomic structure

Table 1. Bulk metal structure: lattice parameter a_{fcc} (Å) (experimental value in brackets), lattice mismatch $\Delta a_{\text{Me}}^{\parallel}$ with respect to MgO ($a_{\text{MgO}} = 4.26$ Å) (in %), perpendicular lattice parameter of the distorted structure $a_{\text{Me}}^{\perp}$ (in Å) and tetragonal distortion $\Delta a_{\text{Me}}^{\perp}$ (in %) with respect to a_{fcc} .

	a_{fcc} (Å)	$\Delta a_{\text{Me}}^{\parallel}$ (%)	$a_{\text{Me}}^{\perp}$ (Å)	$\Delta a_{\text{Me}}^{\perp}$ (%)
Mg	4.54	−6	4.80	+6
Al	4.04 (4.05)	+5	3.81	−6
Ti	4.12	+4	3.91	−5
Mn	3.52	+21	2.56	−27
Ni	3.52 (3.52)	+21	2.49	−29
Ag	4.14 (4.09)	+3	3.99	−4
Pd	3.96 (3.89)	+8	3.49	−12

imposed by the MgO substrate. This does not modify the bulk atomic structure of Al, Ni, Ag, and Pd, but changes it for Mg (hcp), Ti (hcp), and Mn (complex cubic). We use a symmetric supercell containing five MgO(100) layers and seven metal(100) atomic layers. In all cases we impose a two-dimensional (1×1) unit cell, with the theoretical bulk MgO lattice constant $a_{\text{MgO}} = 4.26$ Å. With respect to the bulk fcc structure, this constraint ($a_{\text{Me}}^{\parallel} = a_{\text{MgO}}$) results in a tetragonal distortion of the metal lattice ($a_{\text{Me}}^{\perp} \neq a_{\text{Me}}^{\parallel}$), as shown in Table 1. As expected, the FP-LMTO GGA calculations reproduce well the experimental lattice parameters, the agreement being somewhat worse for heavy transition metals at the end of the 4d series. The tetragonal distortion acts strongly towards a conservation of the atomic volume. In the interface calculations, we freeze the structural degrees of freedom of the MgO and metal layers at their respective (distorted) bulk values, and we optimize the MgO-metal interlayer spacing d_{sep} only. We check that relaxation effects have a negligible influence on the calculated value of the SBH. For example, at the Al/MgO interface, where they happen to be the largest (2.5% reduction of the Al interlayer distance), the modification of the SBH does not exceed 1%.

2.2. Cleavage Energy

At the optimized value of d_{sep} , we estimate the energy necessary to cleave the interface (total energy $E_{\text{Me/MgO}}$) into a tetragonally distorted metal slab ($a_{\text{Me}}^{\parallel} = a_{\text{MgO}}$, $a_{\text{Me}}^{\perp}$; total energy E_{Me}), and a MgO slab

(total energy E_{MgO}):

$$E_{\text{sep}} = -\frac{1}{2}(E_{\text{Me/MgO}} - E_{\text{MgO}} - E_{\text{Me}}),$$

where the $\frac{1}{2}$ factor is due to the symmetry of the supercell used in the calculations. With this sign convention, E_{sep} is positive when an actual adhesion takes place. Use of the tetragonally distorted metal energy as a reference gives a direct access to the metal-MgO contribution, which is of main interest to our present study.

2.3. Analysis of the Electronic Density

Since the consideration of the electron distribution $n(\vec{r})$ based on the electronic populations inside the atomic spheres proves unreliable, in our previous study [27] we have proposed an alternative, Bader [29]—like method of partitioning $n(x, y, z)$. It consists in dividing the electronic cloud into “layers” delimited by the minima of the density profile $n(z) = \int n(x, y, z) dx dy$ along the [100] direction. In order to achieve a satisfactory convergence on atomic charges, we use a relatively dense grid (spacing 0.015 Å) in the numerical integration of $n(x, y, z)$.

Since the total dipole moment is equal to zero due to the supercell symmetry, the estimation of the *interfacial* dipole moment requires an additional hypothesis. Having checked that the central layers of the two materials are neutral, we include the contributions due to three metal layers and two MgO layers on each side of the interface. In the following, we will present results on the interfacial dipole moment: $D = \sum z_i Z_i - \int z n(z) dz$, where the discrete sum runs over the nuclear charges Z_i at the nuclei positions z_i in the i -th layer in the direction perpendicular to the interface. We will focus in particular on the *excess* interfacial dipole moment ΔD , calculated with respect to the two separated materials ($d_{\text{sep}} \rightarrow \infty$), which no longer includes the MgO(100) and Me(100) free surface dipole moments.

2.4. Calculation of the SBH

The value of the p -type SBH, defined as the energy difference between the Fermi level E_F and the oxide valence band maximum (VBM) far from the interface:

$$\phi_p = E_F - E_{\text{VBM}}^{\text{MgO}}$$

can be deduced directly from the calculated valence band structure of the metal-oxide system. However, whereas E_F is defined precisely, the estimation of $E_{\text{VBM}}^{\text{MgO}}$ in the MgO slab center may be subject to errors in the projection procedure of the local density of states (LDOS). Taking advantage of the all electron character of the FP-LAPW method, we rather adopt the procedure [13, 30, 31] which takes core levels as reference energies. In particular, ϕ_p can be written as a sum of two terms [32]: $\phi_p = \Delta E_b + \Delta V$, where ΔE_b and ΔV are the so-called *bulk* and *interface* contribution, respectively.

The *bulk* contribution is calculated by taking into account the energies of $1s$ core levels of oxygen E_{1s}^O (in bulk MgO) and metal E_{1s}^{Me} (in bulk metal): $\Delta E_b = (E_F - E_{1s}^{\text{Me}}) - (E_{\text{VBM}}^{\text{MgO}} - E_{1s}^O)$. It can be evaluated in separate (distorted) bulk calculations, and is not influenced by the properties of the interface. The *interface* contribution is calculated using the energies of the $1s$ core levels in the central layers of the MgO and metal slabs, in the metal/MgO system: $\Delta V = E_{1s}^{\text{Me}} - E_{1s}^O$. Beside an intrinsically atomic contribution it includes all effects due to the interface formation: electron transfers, polarization effects, etc.

In order to quantify the consequences of the structural bulk modifications: the change of bulk structure in the case of Ti, Mn, and Mg, and the tetragonal distortion for all metals, we calculate the corresponding variations of the metal $1s$ binding energy. We also estimate the difference between the distorted fcc bulk and the metal central layer in the interface calculation. Related modifications of SBHs happen to be less than 5%. Additionally, SBH variations of only a few hundredths of eV were found for a different choice of the reference core levels, both for metal ($1s$ versus $2s$ or $2p$ for the transition metals) and for MgO ($O1s$ versus $Mg1s$), leading to a total uncertainty of 0.05 eV in the final SBH. In general, the use of $1s$ core levels minimizes the uncertainty due to hybridization effects. Finally, the values of the SBH obtained from $\Delta E_b + \Delta V$ are in good agreement (within 0.1 eV) with those evaluated directly from the projected LDOS, $\phi_p = E_F - E_{\text{VBM}}^{\text{MgO}}$. The convergence on the SBH is better than 3% between $(\text{MgO})_3\text{Me}_5$ to $(\text{MgO})_5\text{Me}_7$ supercells.

3. Results

We start by a synthetic presentation of the main ground state structural, energetic and electronic characteristics of seven metal/MgO(100) interfaces. Then, rely-

ing on selected examples, we focus on electronic features which are dependent upon the metal-type (simple versus transition metal, exemplified by Mg and Pd, respectively), upon the epitaxial geometry (Pd adsorbed above oxygen or magnesium surface sites), and upon the interface separation d_{sep} .

3.1. Evolution Along the Series

Table 2 and Fig. 1 summarize the structural (d_{sep}), energetic (E_{sep}), and electronic (ϕ_p , Q , ΔD) ground state (metal on-top oxygen surface sites of MgO) characteristics obtained for the considered metal/MgO(100) interfaces. They also give the values of the metal Pauling's electronegativity χ , which is the usual parameter referred to when characterizing the junction.

Table 2. Calculated structural, energetic and electronic characteristics of Me/MgO interfaces: interface separation d_{sep} , cleavage energy E_{sep} per interface MgO unit, Schottky barrier height ϕ_p , interfacial charge transfer Q , and excess interfacial dipole moment ΔD per interface unit cell, and the Me Pauling's electronegativity χ . Q is positive if electrons are transferred from the metal to the oxide.

	Mg	Al	Ag	Ti	Mn	Ni	Pd
d_{sep} (Å)	2.38	2.21	2.65	2.19	2.05	2.03	2.38
E_{sep} (eV)	0.31	0.22	0.24	1.00	1.14	0.92	0.43
ϕ_p (eV)	3.32	3.28	2.25	4.06	3.70	3.17	2.35
Q (e)	0.18	0.07	-0.06	0.07	-0.03	-0.08	-0.10
ΔD (eÅ)	0.13	0.21	+0.08	0.10	0.18	0.13	0.12
χ	1.2	1.5	1.9	1.5	1.5	1.8	2.2

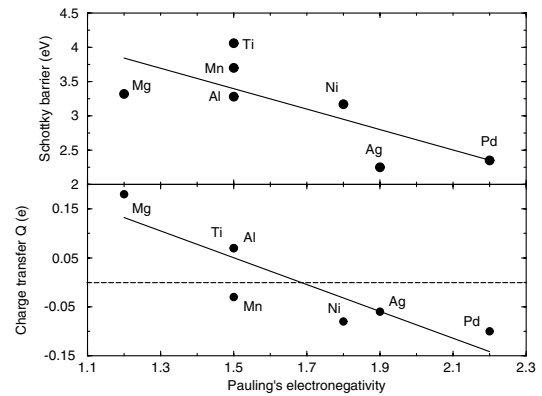


Figure 1. Schottky barrier heights ϕ_p (a), and interfacial charge transfer Q (b), as a function of the metal Pauling's electronegativity χ for Me/MgO interfaces in their ground state.

The cleavage energy E_{sep} for transition metals is systematically larger than for simple or noble metals, and it displays a distinct decrease along the second half of the series, accompanied by an increase of the Me-O distance d_{sep} . This trend fits well what has already been reported for transition metal *monolayers* deposited on the MgO(100) surface [23, 27]. In these works, the behavior of E_{sep} was mainly ascribed to changes in interfacial metal-oxygen hybridization and to a polarization of the metal layer by the electrostatic field of the substrate, which induced changes in metal cohesion. The *sp* character of the electronic states close to Fermi energy in Mg, Al, and Ag is associated with a considerably smaller cleavage energy. For these metals the contribution due to the formation of interfacial bonds is smaller (the correlation between E_{sep} and d_{sep} less explicit), and the part of image charge and van der Waals interactions is likely more important. This different nature of adhesion is emphasized by an opposite behavior of E_{sep} as a function of metal coverage at the Pd/MgO(100) and Ag/MgO(100) interfaces. Whereas for the former, E_{sep} decreases significantly between the limit of isolated atoms and that of a constituted interface [38, 28], for the latter a corresponding *increase* of separation energy has been reported [33].

As far as electronic characteristics are concerned, we notice that the different evolution of ΔD and Q along the series shows that charge transfer between MgO and metal is not the prime mechanism responsible for the formation of interfacial dipole. There is an important contribution from polarization effects, which turn out to be mainly localized in the interfacial metal and MgO layers. In the two limits of low and high electro-negativity (Mg, Al on one hand, and Ag, Pd on the other), ϕ_p and Q vary nearly linearly with χ : lower electronegativity results in a higher SBH and in a positive Q (electron transfer towards the oxide). A linear fit of ϕ_p as a function of χ gives an interface index $S = \partial\phi_p/\partial\chi = 1.5$, to be compared to the experimental estimation of 1.6 [34]. However, this simple pattern seems to break down for the three metals of equal electronegativity (Al, Ti, Mn) whose SBHs differ by as much as 0.8 eV, and whose electron transfers Q have not even the same sign.

3.2. Interfacial Electronic Structure for Simple and for Transition Metals

In order to get a deeper understanding into the interfacial electronic characteristics, we present the detailed

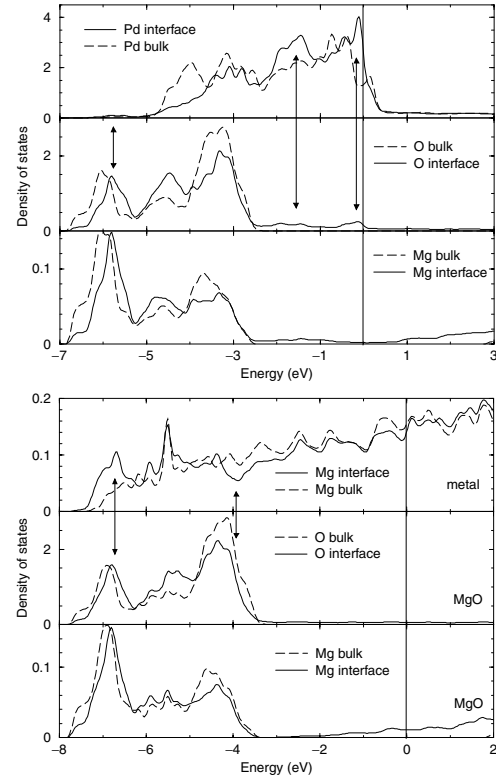


Figure 2. LDOS for Pd/MgO (top panel) and Mg/MgO (bottom panel) interfaces in their ground states. Projections on both interfacial (full lines) and bulk (dashed lines) atoms are plotted. All LDOS are convoluted by a 0.1 eV wide Gaussian function.

results for Mg/MgO(100) and Pd/MgO(100) in their ground state (oxygen adsorption sites), representative of a simple metal of low electronegativity and of a transition metal of high electronegativity, respectively. Although the equilibrium interface separations d_{sep} for the two metals are equal, Table 2, the cleavage energies are different, revealing a different character of the interfacial bonding. Figure 2 shows the LDOS at the two interfaces, enhancing interface-induced features, both in the metal and the MgO LDOS. The perturbation concerns mainly the interfacial layers and is rapidly screened as the distance from the interface increases. Its strength and character depend very strongly on the deposited metal.

In Pd/MgO, hybridization between oxygen and palladium orbitals is clearly visible. We detect interfacial Pd states below the bulk Pd band, and interfacial oxygen states in the MgO band gap. Among the latter, some

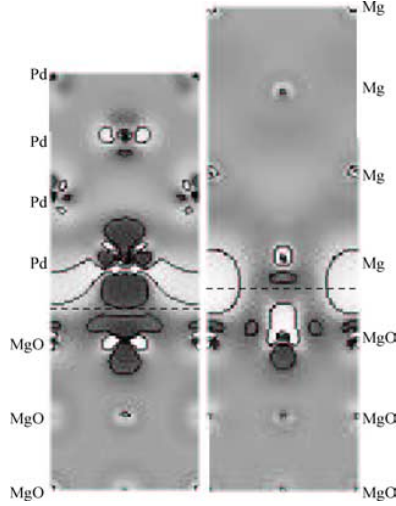


Figure 3. Differential electronic densities: $\Delta n = n_{\text{metal/MgO}} - n_{\text{metal}} - n_{\text{MgO}}$ for the Pd/MgO (left panel) and Mg/MgO (right panel) interfaces. Light and dark shadings correspond to positive and negative Δn , and indicate enhanced and reduced electronic populations, respectively. Dashed lines mark the minima of the integrated electron density profile $n(z)$ used in the charge decomposition.

contribute to a featureless LDOS in the whole MgO gap, while others are at well-defined energies—see arrows in Fig. 2. In the case of the Mg/MgO interface, the deformation of interfacial bands is less pronounced, and the Mg-induced states in the MgO band gap are practically structureless. These structureless features correspond to conventional MIGS.

A complementary information is given by the differential electronic density $\Delta n = n_{\text{metal/MgO}} - n_{\text{metal}} - n_{\text{MgO}}$ in Fig. 3. In addition to the effects of orbital hybridization mentioned above it evidences “image charge” effects, which correspond to a polarization of metal by the electrostatic field of MgO: electron depletion is found above surface oxygens and electron excess above surface magnesiums. We notice a much stronger localization of the polarized electrons at the Pd/MgO interface.

Figure 4 shows the dependence of the electronic profile $n_{\text{gap}}(z) = (E_F - V_{\text{BM}})^{-1} \int_{V_{\text{BM}}}^{E_F} n_{\text{metal/MgO}}(x, y, z, E) dE dx dy$ corresponding to occupied states in the energy range of the MgO band gap, as a function of their penetration inside the MgO substrate. Aside from oscillations on the MgO cores, $n_{\text{gap}}(z)$ displays an exponential behavior, characterized by a penetration length $l_p \sim 0.5 \text{ \AA}$, which is nearly independent of the metal (see the perfect superposition of slopes

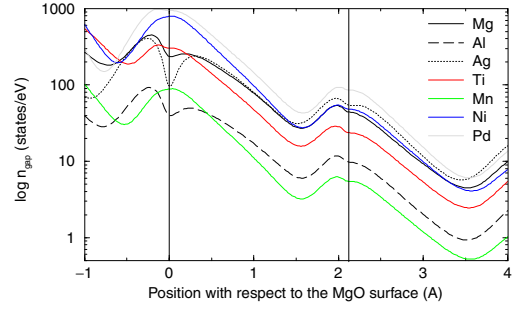


Figure 4. Penetration of the gap states electronic density n_{gap} inside the MgO substrate (see text). Distance to the interfacial MgO layer is given in $\text{\AA}$.

in the logarithmic plot, in the second interlayer region), in agreement with the MIGS theory developed in Ref. [14]. The value of n_{gap} at the interface, on the other hand is strongly metal-dependent, with values somewhat higher for the transition metals.

3.3. Geometry of the Interface: Dependence Upon the Adsorption Site

We remind, that although in our calculation the ground state configuration corresponds to metal atoms on-top oxygens, at actual interfaces, due to the lattice mismatch between MgO and the metal, a non-negligible percentage of interfacial metal atoms are positioned off their preferential adsorption sites [35]. A realistic interface should thus display energetic and electronic characteristics averaged over different adsorption sites. We have considered the pseudomorphic structure with metal atoms on-top surface magnesium, as a simple alternative geometry. It turns out that in this case, the calculated $E_{\text{sep}}(d_{\text{sep}})$ curve shows a well-defined minimum only for late transition metals (Ni, Ag, Pd). This result, already found for monolayer adsorption [23, 27], has been ascribed to the repulsion between metal and magnesium atomic cores. In the following, we focus on the Pd/MgO interface.

Figure 5 displays the LDOS calculated for Pd on top surface magnesium atoms, at its equilibrium interface separation $d_{\text{sep}} = 2.96 \text{ \AA}$, corresponding to $E_{\text{sep}} = 0.11 \text{ eV}$. Comparison between Figs. 2 and 5 shows that the relative positions of the Pd and MgO bands are strongly geometry dependent, yielding ϕ_p smaller for adsorption on-top magnesiums by 1.60 eV. In the case of monolayer deposition, the relative

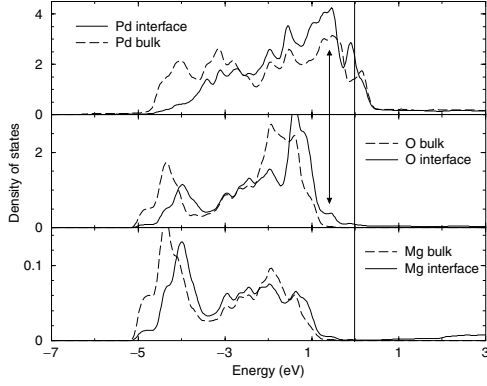


Figure 5. LDOS for the Pd/MgO interface with Pd on-top surface magnesium. Projections on both interfacial (full lines) and bulk (dashed lines) atoms are plotted. All LDOS are convoluted by a 0.1 eV wide Gaussian function.

positions of the metal and MgO bands showed a similar site-dependence for Pd [20] and other transition metals [23]. It was ascribed to the difference of MgO electrostatic potential on-top surface anions or cations. For constituted interfaces, the SBH correlates with the excess dipole moment ΔD . From simple electrostatic arguments applied to the present geometry, one expects indeed $\Delta D = 0.09$ eÅ to induce a change in the electrostatic potential barrier of 1.8 V.

For both interface geometries, the interaction at the metal-oxide interface results in the appearance of states in the bulk gap of MgO. However, due to the different values of d_{sep} and to the different spatial orientation of the atomic orbitals involved in the bond formation, their energy and their character are strongly geometry dependent. Also the interfacial electron transfer varies with the adsorption site. While keeping a constant sign, it is 0.06 electron smaller in the magnesium adsorption geometry.

3.4. Geometry of the Interface: Interface Separation

Another parameter which correlates with the bonding strength at an interface is the interface separation d_{sep} . We expect it to influence strongly the SBH values. For the series of metals, and for both adsorption geometries (on-top oxygens and on-top magnesiums), we have calculated the dependence of ϕ_p upon d_{sep} . At large separations ($d_{\text{sep}} \rightarrow \infty$), the system is equivalent to two non-interacting free surfaces. $\phi_p(\infty)$ is thus equal to the difference between the metal work func-

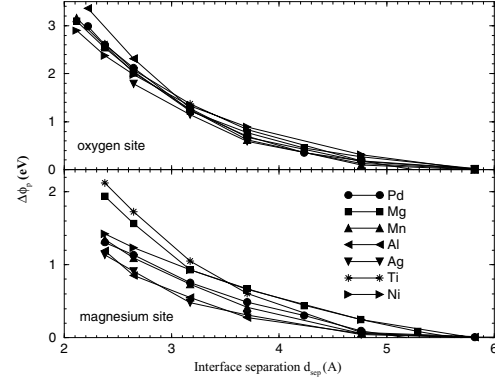


Figure 6. Dependence of $\Delta\phi_p = \phi_p(d_{\text{sep}}) - \phi_p(\infty)$ on the interface separation d_{sep} for the two interface geometries: metal on-top surface oxygen and metal on-top surface magnesium.

tion $\Phi_{\text{Me}}^{(100)}$ and the MgO ionization potential $IP_{\text{MgO}}^{(100)}$: $\phi_p(\infty) = IP_{\text{MgO}}^{(100)} - \Phi_{\text{Me}}^{(100)}$, and it is independent of the adsorption site. We find $\phi_p(\infty) = 1.0, 0.3, 0.6, 1.1, 0.7, 0.3$, and -0.2 eV along the series.

Figure 6 shows the evolution of $\Delta\phi_p = \phi_p(d_{\text{sep}}) - \phi_p(\infty)$, as a function of d_{sep} . Within the precision of our calculations the asymptotic value is reached already at $d_{\text{sep}} \sim 5.5$ Å. $\Delta\phi_p$ turns out to be systematically larger for the on-top oxygen geometry and its evolution as a function of d_{sep} depends little on the considered metal. This is particularly striking for the on-top oxygen geometry, where even at $d_{\text{sep}} \sim 3$ Å, the dispersion in SBH values is less than 10%. For the on-top magnesium geometry, the dispersion is larger, in absolute and relative values (SBH are smaller), and reduces to about 10% at $d_{\text{sep}} \sim 4.5$ Å.

4. Discussion

In this section we discuss the different factors which govern the electronic characteristics of the constituted Me/MgO interface, with some emphasis on the limitations imposed by the computational method, and on a comparison with experimental findings.

4.1. $d_{\text{sep}} \rightarrow \infty$ Limit

As mentioned in Section 3.4, when $d_{\text{sep}} \rightarrow \infty$, the alignment of metal and oxide bands depends only on the characteristics of the free MgO (100) and metal (100) surfaces: $\phi_p(\infty) = IP_{\text{MgO}}^{(100)} - \Phi_{\text{Me}}^{(100)}$. In this

non-interacting limit an extended Schottky model applies. It takes into account the dependence of the metal work function and of the oxide ionization potential on the surface orientation. Through the modification of $\Phi_{\text{Me}}^{(100)}$, $\phi_p(\infty)$ takes also into account the tetragonal distortion of the metal. Our calculations show that a moderate tetragonal distortion enhances $\Phi_{\text{Me}}^{(100)}$ for simple metals (by about 0.1–0.2 eV), and reduces it for transition metals (by about 0.1 eV). In the case of Ni and Mn where the distortion is especially strong, the modification of $\Phi_{\text{Me}}^{(100)}$ reaches 0.4–0.6 eV.

Since the DFT-GGA method is not suited to the calculation of excited electronic states, systematic errors are produced when using the Kohn-Sham eigenvalues for the estimation of $IP_{\text{MgO}}^{(100)}$ or $\Phi_{\text{Me}}^{(100)}$. They are not likely to compensate each other in ϕ_p , because they strongly depend upon the localization of the quasi-particle wave functions, which are different for the different materials. Indeed, when comparing calculated and experimental $\Phi_{\text{Me}}^{(100)}$ values, we find a tendency of GGA to underestimate it (by about 0.3–0.5 eV) for transition metals, and to slightly overestimate it (by about 0.0–0.1 eV) for simple metals. On the other hand, $IP_{\text{MgO}}^{(100)}$ is underestimated by about 1.0 eV (calculated value: 4.8 eV; experimental value: 5.8 eV [36]). We will use these corrections in Section 4.4, when comparing the SBH with experimental results.

In summary, the extended Schottky model applies in the limit of infinite separation, as a starting point for the analysis of the SBH. At this stage, the lattice mismatch between the two materials and the surface orientation are already accounted for, and the deficiencies of the DFT-GGA treatment can be easily corrected.

4.2. Interface States

At shorter separations, states characteristic of the interface are present in the LDOS. Various models of SBH rely on the existence of such states: at perfect defectless interfaces, the presence of exponential tails of the metal wave functions (MIGS) in the insulator was invoked [14, 37], and associated with a smooth DOS in the insulator band gap energy range. More recently, it was pointed out that states at well-defined energies (not only in the insulator band gap energy range) may also contribute to the interface features and to the SBH if an actual chemical bond across the interface is formed [11].

In the case of transition metals adsorbed on-top oxygens (see Pd/MgO, Fig. 2), we find that the interaction

between the $\text{O}2p_z$ and the $\text{Pd}3d_{z^2} + 4s$ orbitals induces new states at the bottom of the d -band in the Pd LDOS, and new states in the MgO band gap close to the Fermi level in the O LDOS. As already pointed out in Ref. [38], these are the bonding (B) and antibonding (AB) states of the O–Pd bond. The $\text{O}p_{x,y}$ – $\text{Pd}d_{xz,yz}$ contribution can also be seen in Fig. 2, lower in the gap. The bonding between surface oxygens and metal atoms can be traced in the plots of Δn , Fig. 3, where a clear depopulation of the $\text{O}p_z$ and $\text{Pd}d_{z^2}$ orbitals reflects the half-filled character of the AB component. When adsorption takes place on-top magnesiums, the overlap between Pd and O orbitals is smaller. It is only partially balanced by a smaller separation between the Pd and O bands on the energy scale and results in a considerably weaker bonding. In the case of the Mg/MgO interface, due to the delocalized character of the Mg sp valence band, the signature of the interfacial interaction on the LDOS is different. The orbital hybridization across the interface is small and induces little distortion of oxygen or magnesium LDOS. This is confirmed by the plot of differential electron density, Fig. 3, where only a small electron transfer along the (ionic) Mg–O bond can be detected. For all interfaces, the LDOS contains signatures of conventional MIGS in the MgO band gap, at energies where no bonding or antibonding metal-oxygen states are present. Such MIGS were predicted in models of jellium/semi-conductors (or insulators) interfaces [37]. They arise from the matching of wave functions at the interface, similarly to the exponential tails of metal wave functions in vacuum at free metal surfaces.

Additionally, in the interfacial metal LDOS, the valence band is distorted by a crystal-field-like coupling between the spatial symmetry of the MgO electrostatic field and the spatial orientation of the metal orbitals. This polarization effect, discussed already for transition metal monolayers deposited on MgO [20, 23], results in an electron redistribution among the different components of the metal band. By emptying the space above surface oxygens and by populating that above surface magnesiums it mimics the macroscopic “image charge” effect. In the case of Pd/MgO, the excess density regions remain relatively well localized at the metal surface (see their position with respect to the minimum of $n(z)$). Their extension and especially their shift towards the substrate is much larger in the case of Mg/MgO, where they clearly contribute to the electron transfer from Mg towards the MgO substrate.

In summary, three types of interfacial states are met at metal/MgO interfaces: states due to chemical bonding which appear at well defined energies (some of which are in the MgO gap and others below the metal band), conventional MIGS associated to smooth LDOS in the MgO gap region, and LDOS distortions in the metal band due to its polarization by the electrostatic field of the ionic substrate.

4.3. Charge Transfer, Dipole Moments

Although the charge transfer Q , Table 2, is relatively small for all metals due to the strong ionic character of MgO, its evolution as a function of Pauling's electronegativity χ is practically monotonic along the series, Fig. 1. Metals with small χ transfer electrons towards MgO, whereas metals with higher χ receive electrons from MgO. This is consistent both with the conventional MIGS models, in which Q is driven by the difference between the Fermi level and the Zero Charge Point (ZCP) of the insulator, and with models which associate the charge transfer with orbital hybridization across the interface.

A linear fit of the $Q(\chi)$ dependence gives a zero charge transfer across the interface at $\chi \sim 1.7$. This corresponds to a position of the Fermi level about 2.8 eV above the VBM of MgO and is close to the middle of the calculated bulk MgO band gap (4.8 eV). This finding is consistent with simple MIGS models which locate the ZCP roughly at mid-gap. However, our discussion on the nature of interfacial electronic states (Section 4.2) indicates clearly that other interfacial states contribute to the charge transfer Q . We stress that for the interfaces under study there is likely no conceptual reason why zero charge transfer should occur for E_F at exactly mid-gap.

Taking into account remarks made in Section 4.1, we wish to comment on the estimation of Q within a DFT-GGA approach. The underestimation of the MgO ionization potential results in a systematic underestimation of the energy separation between the metal and oxygen effective levels involved in the hybridization. The Me—O bond is thus predicted to be too covalent and the electron transfer across the interface is exaggerated. The underestimation of the transition metal work functions, on the other hand, yields an opposite effect but, being much smaller, does not revert the trend. We thus expect the actual electron transfer for the late transition metals to be smaller than the calculated one and an overall shift of the ac-

tual ZCP towards lower energies in the MgO band gap.

The interfacial excess dipole moment ΔD keeps a constant sign in the series, Table 2. It correlates neither with the metal electronegativity, nor with the charge transfer across the interface Q . As already pointed out when discussing the differential electronic densities, Section 4.3, it is rather related to the strength of the electron cloud polarization in the interfacial layers. This is a very important point to keep in mind, because most models of metal-oxide interface assume that the only contribution to the interfacial dipole comes from the charge transfer between the two materials and that there is a linear relationship between the two quantities. The presence of a strongly ionic material limits the electron transfer but yields important polarization effects, which is not the case when metals are in contact with elemental semi-conductors or very covalent compound semi-conductors. Finally, the interfacial dipole shifts the electrostatic potential at the interface. In the present case, its order of magnitude is 2–3 V (1 eÅ corresponds roughly to 20 V), and it is the principal contribution to $\Delta\phi_p$.

In summary, the interfacial charge transfer Q varies monotonically with the metal electronegativity. It interpolates at zero when the Fermi level is roughly located at mid-gap, although we do not think that there is any conceptual reason for it. The interfacial dipole moment is not proportional to Q . It contains a strong contribution from the substrate-induced polarization of the metal electrons. The related shift of electrostatic potential across the interface represents the principal contribution to $\Delta\phi_p$.

4.4. Schottky Barrier Height

The SBH values, Table 2, can be rationalized by splitting ϕ_p into two contributions: $\phi_p = \phi_p(\infty) + \Delta\phi_p$. The first one represents the infinite separation limit, Section 4.1, while the second comes from the actual interaction between the two materials. The $\phi_p(\infty)$ term is dependent separately upon the oxide and the metal through the quantities Φ_{Me} and $IP_{\text{MgO}}^{(100)}$, which contain the effect of surface (and thus interface) orientation. The behavior of $\Delta\phi_p$ as a function of d_{sep} for the whole set of metal/MgO interfaces under study and for the two adsorption geometries was represented in Fig. 6. For a given adsorption geometry $\Delta\phi_p$ is mainly determined by the separation d_{sep} between the two materials. Weak, metal-dependent features appear

at small distances only. Since within a good approximation $\Delta\phi_p(d_{\text{sep}})$ is metal-independent, the contributions from orbital hybridization across the interface and from charge transfer are small. The main contribution to $\Delta\phi_p(d_{\text{sep}})$ is the substrate-induced electric dipole.

The value of d_{sep} at equilibrium is an important parameter, which mainly depends on the interface interactions. For the MgO substrate (but also for TiO_2) some trends can be drawn from the variety of existing results. In particular, d_{sep} is minimal for transition metals in the middle of the series, becoming progressively larger at the beginning and especially at the end of the series. Compared to the transition metals, *sp* metals are associated to a larger d_{sep} (weaker adhesion). In the case of transition, closed *d*-shell metals (Ag), this can lead to a relatively large interface separation. In our study d_{sep} ranges from 2.06 Å (for Mn) to 2.76 Å (for Ag). This corresponds to a difference of 1.6 eV on the ϕ_p scale.

Before comparing our results to the Schottky barrier heights measured at realistic interfaces, we have to remind several points. First, we have systematically considered pseudomorphic metal/MgO(100) interfaces, whereas in practice a substantial number of metal atoms may depart from the perfect oxygen adsorption sites [35]. As a consequence, realistic d_{sep} are systematically larger than predicted in our study and the averaged (experimental) SBH is thus expected to be systematically smaller. This is particularly important in the case of strong lattice mismatch, e.g. at Mn and Ni/MgO(100) interfaces. In the following we will no longer discuss these two interfaces and we will correct other SBH values for the systematic DFT-GGA errors on the metal work functions and MgO ionization potential, as discussed in Section 4.1.

Once corrected, the calculated interface index S , defined as the derivative of the SBH with respect to the metal electronegativity: $S = \partial\phi_p/\partial\chi$ is equal to 1.9, to be compared to the experimental estimation of 1.6 [34]. Taking into account the precision of our evaluation (Sections 2.4 and 4.1), we conclude that this result corresponds to the highly-ionic limit of the metal-semiconductor interface index, in which the metal work function gives the major contribution $S \sim \partial\Phi_{\text{Me}}/\partial\chi \sim 1.7$. This result is not at all unexpected considering the wide gap and the strong ionic character of MgO. We stress however, that whereas the interface index S depends little on the interface-formation effects, the latter contribute substantially to ϕ_p through $\Delta\phi_p(d_{\text{sep}})$.

5. Conclusion

We have performed an *ab initio* total energy study of the electronic structure of metal/MgO(100) interfaces. By considering simple and transition metals, different adsorption sites and different interface separations, we have analyzed the major ingredients responsible for the LDOS characteristics, the interfacial electron transfer and dipole moment.

We have discriminated three types of interfacial states: states due to chemical bonding, conventional MIGS, and LDOS distortions in the metal band due to its polarization by the electrostatic field of the ionic substrate.

The interfacial charge transfer Q varies monotonically with the metal electronegativity. It vanishes when the Fermi level is roughly located at mid-gap, although we do not think that there is any conceptual reason for it.

We have shown that the interfacial excess dipole moment is not proportional to Q : its strength is rather governed by polarization effects, at variance with interfaces involving covalent semi-conductors. It yields an important contribution to the SBH at equilibrium separations, which adds itself to the free surface contribution $\Phi_{\text{Me}} - IP_{\text{MgO}}^{(100)}$, given by the extended Schottky model. The interface index, on the other hand, is close to the Schottky limit $S \sim \partial\Phi_{\text{Me}}/\partial\chi$, as expected for a metal in contact with an ionic, large gap insulator.

Acknowledgments

The most time consuming calculations were performed on the NEC-SX5 computer at IDRIS, under project No. 960732. We are grateful for a generous allocation of time on the machine.

References

1. V.E. Henrich and P.A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, 1994).
2. C. Noguera, *Physics and Chemistry at Oxide Surfaces* (Cambridge University Press, Cambridge, 1995).
3. F. Didier and J. Jupille, *Surf. Sci.* **314**, 378 (1994).
4. M.W. Finnis, *J. Phys.: Condens. Matter* **8**, 5811 (1996).
5. R.M. Lambert and G. Pacchioni (eds.), *Chemisorption and Reactivity on Supported Clusters and Thin Films* (Kluwer Academic Publishers, 1997).
6. C.R. Henry, *Surf. Sci. Rep.* **31**, 231 (1998).
7. G. Renaud, *Surf. Sci. Rep.* **32**, 1 (1998).

8. H.J. Freund, H. Kuhlenbeck, and V. Staemmler, Rep. Prog. Phys. **59**, 283 (1996).
9. W. Mönch, Rep. Prog. Phys. **53**, 221 (1990).
10. A. Franciosi and C.G. Van de Walle, Surf. Sci. Rep. **25**, 5 (1996).
11. R.T. Tung, Mat. Sci. and Eng. R **35**, 1 (2001); Phys. Rev. B **64**, 205310 (2001).
12. S. Picozzi, A. Continenza, G. Satta, S. Massidda, and A.J. Freeman, Phys. Rev. B **61** 16736 (2000).
13. G. Profeta, A. Blasetti, S. Picozzi, A. Continenza, and A.J. Freeman, Phys. Rev. B **64** 225312 (2001).
14. G. Bordier and C. Noguera, Phys. Rev. B **44**, 6361 (1991).
15. F. Bernardini and V. Fiorentini, Phys. Rev. B **57**, R9427 (1998).
16. S. Rubini, E. Pelucchi, M. Lazzarino, D. Kumar, A. Franciosi, C. Berthod, N. Binggeli, and A. Baldereschi, Phys. Rev. B **63**, 235307 (2001).
17. U. Schönberger, O.K. Andersen, and M. Methfessel, Acta Metall. Mater. **40**, S1 (1992).
18. R.-Q. Wu and A.J. Freeman, Phys. Rev. B **51**, 5408 (1995).
19. R. Benedek, M. Minkoff, and L.H. Yang, Phys. Rev. B **54**, 7697 (1996).
20. J. Goniakowski, Phys. Rev. B **57**, 1935 (1998).
21. Yu.F. Zhukovskii, E.A. Kotomin, P.W.M. Jacobs, A.M. Stoneham, and J.H. Harding, J. Phys.: Condens. Matter **12**, 55 (2000).
22. I.V. Yudanov, G. Pacchioni, K.M. Neyman, and N. Rösch, J. Phys. Chem. B **101**, 2786 (1997).
23. J. Goniakowski, Phys. Rev. B **59**, 11047 (1999).
24. J. Goniakowski and C. Noguera, Phys. Rev. B **66**, 085417 (2002).
25. P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology 1997 (Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, in Comput. Phys. Commun. **59**, 399 (1990)).
26. J.P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996).
27. J. Goniakowski and C. Noguera, Phys. Rev. B **60**, 16120 (1999).
28. L. Giordano, J. Goniakowski, and G. Pacchioni, Phys. Rev. B **64**, 075417 (2001).
29. R.F.W. Bader, Chem. Rev. **91**, 983 (1991).
30. S.H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987).
31. S. Massidda, B.I. Min, and A. J. Freeman, Phys. Rev. B **35**, 9871 (1987).
32. C. Berthod, N. Binggeli, and A. Baldereschi, Europhys. Lett. **36**, 67 (1996); C. Berthod, J. Bardi, N. Binggeli, and A. Baldereschi, J. Vac. Sci. Technol. B **14**, 3000 (1996).
33. D. Fuks, S. Dorfman, Yu F. Zhukovskii, E.A. Kotomin, and A.M. Stoneham, Surf. Sci. **499**, 24 (2002).
34. C. Assi, Doctor Thesis, (Rennes University, 2000).
35. W. Vervisch, C. Mottet, and J. Goniakowski, Phys. Rev. B **65**, 245411 (2002).
36. J.-P. Di Salvo and E. Gillet, Surf. Rev. and Lett. **5**, 363 (1998).
37. J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
38. J. Goniakowski, Phys. Rev. B **58**, 1189 (1998).