PHYSICAL REVIEW B **78**, 235423 (2008)

Work function changes induced by deposition of ultrathin dielectric films on metals: A theoretical analysis

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(Received 7 October 2008; published 15 December 2008)

Ultrathin dielectric films deposited on a metal surface induce variations in the work function that can be relevant for the final properties of the metal/oxide interface. In this work we analyze with the help of density-functional theory calculations the effect of depositing three-layer films of insulating materials such as LiF, NaCl, MgO, CaS, and BaO on various (001) metal surfaces. We found that the change in work function $\Delta\Phi$ is due to three main contributions: an electrostatic "compression" effect which dominates for highly ionic films such as LiF, a charge-transfer effect which is largest for less ionic films such as BaO, and the surface relaxation induced by the formation of the interface bond which largely depends on the lattice mismatch between the dielectric film and the metal. Finally, we propose a universal correlation between the work function change and the energy difference between the position of the Fermi level of the metal surface and the top of the valence band of the dielectric film.

DOI: 10.1103/PhysRevB.78.235423 PACS number(s): 73.30.+y, 73.20.−r, 71.15.Mb, 73.90.+f

I. INTRODUCTION

Ultrathin films of insulating materials grown on metal substrates[1] constitute a new class of systems with tunable properties and several potential and actual applications: magnetic tunnel junctions,[2] dielectrics in miniaturized electronic devices, magnetic devices based on oxide nanostructures, plasma display panels,[3] modified supports for metal nanocatalysts,[4,5] etc. An important consequence of the deposition of a thin insulating film on a metal is the induced change in work function of the metal support which can be lowered or increased depending on the nature of the interface.[6] The model proposed by Schottky[7] states that when a metal and a dielectric are combined, there is no charge transfer across the interface and the Schottky barrier height is given by the difference between the work function of the metal Φ_m and the top of valence band of the dielectric E_{VB}. However, the Schottky model is not generally obeyed. In fact, the metal wave function decays into the dielectric in the energy range where the metal conduction band overlaps with the band gap of the insulator.[8] This gives rise to metal-induced gap states (MIGS) (Refs. 9–12) which can be simply due to the spatial penetration of the tails of the metal wave function into the dielectric or to the formation of a true chemical bond at the interface.[6] These latter MIGS can have donorlike or acceptorlike character.

The presence of other states at the interface induces a charge transfer (CT) across the interface creating a dipole μ, which shifts the position of the metal Fermi energy E_F [Fig. 1(a)]. In particular, a dipole which corresponds to negative charge above the metal results in a work function increase, while a reverse dipole contributes to lower the work function. As a result, the effective work function of the metal/dielectric system, $\Phi_{m/d}$, differs from the work function of the pure metal, Φ_m.

Examples of changes in work function by deposition of thin insulating layers have been reported in the literature. Based on the Anderson method it has been found that a monolayer (ML) of Al_2O_3 grown on Mo(110) lowers the work function by 0.7 eV (Ref. 13); Kelvin probe force microscopy or scanning tunneling microscopy (STM) studies of alkali chloride thin films on Au(111) and Ag(100) have shown work function reductions of 0.5–1.2 eV (Refs. 14 and 15); a more recent work based on field-emission resonance has found for NaCl islands of up to 3 ML a work function reduction of 1.3 eV.[16] Sometimes, the lattice mismatch between the dielectric film and the metal results in the modulation of the surface potential and the local work function, a phenomenon which can be used to induce self-assembling of deposited metals atoms.[17] Theoretical calculations have predicted a reduction in Φ for NaCl and MgO on various metals.[6,15,18–21]

The work function change $\Delta\Phi=\Phi_{m/d}-\Phi_m$ for a dielectric thin film on a metal is the central quantity in this study. $\Delta\Phi$ cannot be explained only with the CT model. Recently, it has been shown that MgO/metal interfaces give rise to substan-

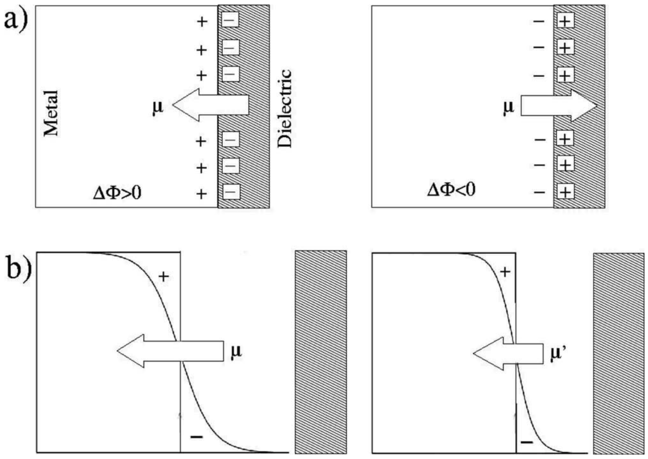

FIG. 1. Schematic representation of the two major contributions to the change in work function Φ induced by the deposition of an ultrathin dielectric layer on a metal support. (a) Charge transfer at the interface and (b) compressive electrostatic effect. Both terms lead to a change in surface dipole μ, and hence in metal work function.

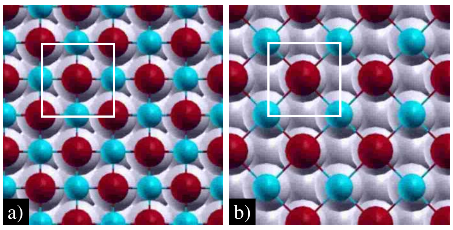

FIG. 2. (Color online) Top view of a dielectric layer deposited on a (100) surface of a metal with fcc structure and representation of the unit cells used in the calculations. (a) The dielectric film is in register with the metal support with the anions sitting directly on top of the metal atoms and the cations in the hollow sites; (b) the dielectric film is rotated by 45° and both anions and cations are on top of the metal atoms.

tial changes in work function despite a relatively small almost negligible CT.[18,20] The effect has been attributed to the substrate-induced polarization of the metal electrons, a basically electrostatic mechanism which has been proposed also for adsorbates on metal surfaces.[18,22–24] In particular, a recent work has emphasized the role of the exchange (or Pauli) repulsion in determining work function changes induced by rare gases on metals.[25] The "rigid wall" represented by the dielectric top layer pushes the electronic charge that spills over from the metal surface back into the metal, thus changing the surface dipole even in the absence of charge transfer between the metal and the insulating film [Fig. 1(b)]. While the CT mechanism dominates the work function changes for films with strong chemical interaction with the metal, the electrostatic or compression effect is important for films of highly ionic materials (e.g., NaCl). However, the two terms can act together or can have different signs, thus leading to an additive or a canceling global effect, respectively. Furthermore, the final change in work function can be rather different for different metals even in the presence of the same dielectric.

The scope of this paper is to quantify the relative importance of these two (and possibly other) contributions for a series of insulating films and supporting metals. The choice of the interfaces to model is restricted by the concrete possibility to prepare them experimentally. This implies that the mismatch between the lattice parameter of the dielectric and that of the metal support must be small, below 4–5 %. When this is not the case, the dielectric film does not wet the surface and forms islands or more complex patterns which result in imperfect interfaces.

We have considered a large set of insulators and metal surfaces and we have selected only those combinations which fulfill the requirement for epitaxial growth. These are five insulating systems, LiF, NaCl, MgO, CaS, and BaO, and six metal surfaces, Ag(100), Au(100), Pt(100), Pd(100), Mo(100), and Al(100). In some cases, the dielectric film must be rotated by 45° in order to obtain a good lattice mismatch (see below). This is the case of metals with small lattice constants placed in contact with insulators with large lattice constants (NaCl, CaS, and BaO). The unit cells are shown in Fig. 2. The charge transfer across the interface has been quantified, as well as the dependence of ΔΦ on parameters such the interface distance. A tentative to separate the two contributions is then discussed. Finally, in the conclusions we propose a universal correlation of the work function change with intrinsic properties of the metal support (the metal Fermi level) and of the dielectric film (the top of the valence band).

TABLE I. Properties of (100) metal surfaces: bulk lattice constant a_0 and work function Φ.

	a_0 (Å)		Φ (eV)	
	Calc.	Expt.[a]	Calc.	Expt.
Al (100)	4.05	4.05	4.32	4.20[b]
Pd (100)	3.96	3.89	5.16	5.55[c]
Pt (100)	3.99	3.92	5.71	5.84[d]
Mo (100)	3.15	3.15	3.90	4.53[e]
Ag (100)	4.16	4.09	4.23	4.22[f]
Au (100)	4.18	4.08	5.12	5.22[g]

[a] Reference 30.
[b] Reference 31.
[c] Reference 32.
[d] Reference 33.
[e] Reference 34.
[f] Reference 35.
[g] Reference 36.

II. COMPUTATIONAL METHOD

We performed density-functional theory (DFT) calculations at the level of the generalized gradient approximation [Perdew-Wang (PW) PW-91 exchange-correlation functional[26]]. The method is implemented in the VASP program[27,28] which uses a plane-wave basis set and a projector augmented wave (PAW) method[29] for the treatment of core electrons. Kinetic-energy cutoffs of 400, 400, 700, and 403 eV were used for O-, F-, Cl-, and S-containing systems, respectively. The atoms within the supercell are relaxed until the atomic forces are less than 0.01 eV/Å. The Al(100), Pd(100), Pt(100), Mo(100), Ag(100), and Au(100) metal substrates have been modeled by four metal layers, respectively. For all these systems the value of the experimental bulk lattice constant[30] is reproduced with errors of less than 2% (Table I). The computed work functions are reported in Table I and compared with the experimental values.[31–36]

The bulk lattice constants of the four insulators considered, NaCl, LiF, MgO, CaS, and BaO, are in close agreement with the measured ones[37] (errors of about 1%; Table II). The degree of ionic character χ in these materials has been evaluated from Bader charges and reported in Table II along with other properties such as the energy gap E_g. It should be mentioned that the Kohn-Sham energy gaps are largely underestimated with respect to the experimental gap.[38–43] In this respect, a word of caution is required about the accuracy of the results presented below. Since the DFT method is not suited for computing excited electronic states, some systematic errors may occur when the Kohn-Sham eigenvalues are used to estimate the relative positions of the metal work function Φ or the positions of the top of valence band and

TABLE II. Properties of insulating films: bulk lattice constants a_0, band gap E_g, top of the valence band E_{VB}, Bader charges q, and ionicity degree χ. The E_g value is computed for the bulk, while the E_{VB} value is determined for the (100) surface of the dielectric film.

	a_0 (Å)		E_g (eV)				
	Calc.	Expt.[a]	Calc.	Expt.	E_{VB} (eV)	q ($\pm e$)	χ (%)
LiF	4.10	4.03	8.6	13.6[b]	−7.74	0.88	88.3
NaCl	5.70	5.64	5.0	8.5[c]	−6.76	0.87	87.0
MgO	4.25	4.21	4.5	7.6[d]	−5.31	1.73	86.5
CaS	5.70	5.69	2.4	3.5,[e] 4.4[f]	−4.93	1.50	75.0
BaO	5.60	5.52	2.1	3.9[g]	−2.68	1.44	71.8

[a] Reference 37.
[b] Reference 38.
[c] Reference 39.
[d] Reference 40.
[e] Reference 41.
[f] Reference 42.
[g] Reference 43.

TABLE III. Dependence of the interface properties of NX/Ag(100) on the number of layers (NL) in the insulating film: work function Φ, work function change ΔΦ, adhesion energy per unit of surface E_{ad}/S, charge transfer for unit of surface CT/S, and interface distance d. d is defined as the minimum vertical distance between a metal atom and the anion on top of it.

	NL	Φ (eV)	ΔΦ (eV)	E_{ad}/S (meV/Å^2)	CT/S (e/Å^2)($\times 10^2$)	d (Å)
LiF/Ag(100)	1	3.52	−0.71	9.02	0.05	2.83
	2	3.49	−0.74	5.75	0.05	2.91
	3	3.52	−0.71	6.27	0.06	2.91
NaCl/Ag(100)	1	3.53	−0.70	7.23	0.22	3.06
	2	3.52	−0.71	5.19	0.13	3.08
	3	3.53	−0.70	5.90	0.12	3.09
MgO/Ag(100)	1	3.29	−0.94	31.53	1.35	2.66
	2	2.95	−1.28	23.19	0.63	2.67
	3	2.96	−1.27	23.84	0.65	2.67
CaS/Ag(100)	1	3.27	−0.96	33.46	1.21	2.67
	2	3.19	−1.04	22.47	1.07	2.71
	3	3.19	−1.04	24.06	1.10	2.71
BaO/Ag(100)	1	1.91	−2.31	33.18	0.79	2.41
	2	2.53	−1.70	13.24	0.47	3.13
	3	2.03	−2.20	16.92	0.89	2.59

bottom of conduction band of the insulator. The error is not necessarily the same for all these quantities, so the general concepts discussed here about the origin of work function changes should be valid and may apply to any metal/oxide interface. The specific absolute values of Φ and ΔΦ may be affected by some error.

The work function of metal and metal/oxide surfaces has been defined as the energy of the vacuum level (determined as the self-consistent potential in the vacuum) with respect to the Fermi level of the metal or of the metal/oxide interface. In a similar way, the energy of the top of the valence band, E_{VB}, is defined with respect to the vacuum level. Brillouin-zone integrations have been performed on a grid of $10\times10\times1$ (2×2 cell) Monkhorst-Pack points[44] for geometry optimizations and of $14\times14\times1$ points to generate the density-of-states (DOS) plots.

III. RESULTS

Before discussing the general features of the NX/M(100) interfaces, where NX is the insulator and M the metal, we consider the question of the dependence of the properties on the number of layers in the dielectric film (Table III). As a test case we discuss 1, 2, and 3 ML of NaCl on Ag(100). LiF, MgO, and CaS films exhibit a similar behavior. According to our calculations, Φ_m for Ag(100) is 4.23 eV (the experimental value is 4.22 eV).[35] By depositing an epitaxial NaCl film on Ag(100) the work function decreases significantly to about 3.5 eV (Table III).

The data clearly show that the properties of NaCl/Ag(100) do not depend on the number of layers in the dielectric film. The major drop in Φ is found after deposition of a single adsorbate layer, as recently reported experimentally for this system[16] but also for rare-gas adlayers on Cu(100).[45] This is because the NaCl structure is highly ionic already for a single layer, so that the characteristics of the interface bonding, of dominant electrostatic character, do not change by increasing the film thickness. The observed stability of the work function change as a function of the number of layers in the film is not necessarily a universal property but is certainly true for highly ionic materials.[46] In fact, some deviations are observed for the less ionic BaO films (Table III). In the following we restrict the discussion to dielectric films of 3 ML thickness (Table IV).

LiF is the most ionic compound among those considered here (Table II). This material, characterized by a large band gap of 13.6 eV,[38] has recently been employed in form of thin film on aluminum to increase the efficiency of organic electroluminescent devices.[47] The charge transfer is from the fluoride anions to the metal but is extremely low (Table IV), as expected for a highly ionic film. Only for the Al(100) surface the CT is in the opposite direction, but the value is so small that it is below the limits of accuracy of the calculations. The largest CT is found for Pt, which indicates this metal as one of the most reactive ones. Also the adhesion energy is very low for all systems and the interface distances go from a minimum of 2.80 Å for Pd to a maximum of 3.27 Å for Al.

The absence of chemical interaction at the interface is further confirmed by the analysis of the projected density of states (PDOS). As a representative example we take the LiF/Ag(100) interface (Fig. 3). The contribution of the LiF states at the Fermi level is negligible. Notice also the deep position of the LiF valence band with respect to the metal Fermi level, an effect which is responsible for the very small CT from the LiF valence-band states to the empty states of the metal. Similar DOSs (not shown) are obtained for the other LiF/metal interfaces. The weak interaction has the consequence that the structural relaxation at the interface is negli-

TABLE IV. Properties of NX/M(100) interfaces: work function Φ, work function change $\Delta\Phi$, adhesion energy per unit of surface E_{ad}/S, charge transfer for unit of surface CT/S, interface distance d, and surface rumpling SR. The surface rumpling SR is defined as follows: $\mathrm{SR}(\mathrm{M_{int}})=z(\mathrm{M_{cation}})-z(\mathrm{M_{anion}})$ where $\mathrm{M_{cation}}$ is the metal atom in direct contact with the cation and $\mathrm{M_{anion}}$ is the metal atom in direct contact with the anion; $\mathrm{SR}(\mathrm{D_{int}})=z(\mathrm{cation})-z(\mathrm{anion})$ for the dielectric layer at the interface (a positive value indicates that the anion relaxes outward); $\mathrm{SR}(\mathrm{D_{ext}})=z(\mathrm{cation})-z(\mathrm{anion})$ for the external layer of the dielectric film (a positive value indicates that the cation relaxes outward).

	Φ (eV)	$\Delta\Phi$ (eV)	E_{ad}/S (meV/Å^2)	CT/S (10^{-2} e/Å^2)	d (Å)	$\mathrm{SR}(\mathrm{M_{int}})$ (Å)	$\mathrm{SR}(\mathrm{D_{int}})$ (Å)	$\mathrm{SR}(\mathrm{D_{ext}})$ (Å)
LiF								
LiF(3 ML)/Al(100)	3.84	−0.47	5.73	−0.01	3.27		0.04	−0.06
LiF(3 ML)/Pd(100)	4.26	−0.90	8.38	0.08	2.80		0.01	−0.06
LiF(3 ML)/Pt(100)	4.96	−0.76	7.44	0.26	3.04		0.02	−0.06
LiF(3 ML)/Ag(100)	3.52	−0.71	6.27	0.06	2.91		0.02	−0.06
LiF(3 ML)/Au(100)	4.37	−0.75	7.47	0.12	2.98		0.02	−0.06
NaCl								
NaCl(3 ML)/Al(100)	3.83	−0.49	6.35	0.05	3.35	−0.15	0.04	−0.10
NaCl(3 ML)/Pd(100)	3.68	−1.47	17.20	0.47	2.67	−0.25	0.02	−0.12
NaCl(3 ML)/Pt(100)	3.85	−1.87	24.70	0.91	2.76	−0.21	−0.01	−0.11
NaCl(3 ML)/Ag(100)	3.53	−0.70	5.90	0.12	3.09	−0.14	0.04	−0.11
NaCl(3 ML)/Au(100)	4.22	−0.90	10.61	0.48	2.79	−0.15	−0.06	−0.11
MgO								
MgO(3 ML)/Al(100)	2.86	−1.46	17.35	0.13	2.73		−0.01	−0.05
MgO(3 ML)/Mo(100)	2.15	−1.74	133.81	0.25	2.14		−0.09	−0.06
MgO(3 ML)/Ag(100)	2.96	−1.27	23.84	0.65	2.67		−0.02	−0.05
MgO(3ML)/Au(100)	3.53	−1.60	26.48	1.46	2.73		−0.04	−0.05
CaS								
CaS(3 ML)/Pd(100)	3.54	−1.62	60.97	1.40	2.43	−0.36	0.01	−0.10
CaS(3 ML)/Pt(100)	3.38	−2.34	71.66	1.99	2.41	−0.40	0.00	−0.10
CaS(3 ML)/Ag(100)	3.19	−1.04	24.06	1.10	2.71	−0.36	−0.01	−0.11
CaS(3 ML)/Au(100)	3.46	−1.66	36.21	1.46	2.62	−0.35	−0.02	−0.11
BaO								
BaO(3 ML)/Pd(100)	1.99	−3.17	44.46	1.03	2.32	−0.53	0.03	0.15
BaO(3 ML)/Pt(100)	1.63	−4.08	49.01	1.38	2.28	−0.54	0.08	0.16
BaO(3 ML)/Ag(100)	2.03	−2.20	16.92	0.89	2.59	−0.57	−0.05	0.09
BaO(3 ML)/Au(100)	2.33	−2.80	29.40	1.45	2.59	−0.56	−0.05	0.09

gible for both the metal and the dielectric layers. Here we report the surface rumpling (SR) for the top metal layer in direct contact with the dielectric, $\mathrm{SR}(\mathrm{M_{int}})$, for the dielectric layer at the interface, $\mathrm{SR}(\mathrm{D_{int}})$, and for the top layer of the dielectric film, $\mathrm{SR}(\mathrm{D_{ext}})$ (Table IV). The rumpling is defined as the difference in height of metal atoms or of cations and anions of the dielectric. For the (2×2) supercells there is no metal rumpling since all metal atoms are in contact with the anions of the dielectric and assume the same height. For LiF/M(100) we notice that the rumplings are very small and more pronounced for the external than for the interface LiF layer. This is the obvious consequence of the weak interaction.

Despite the tiny CT at the interface, all LiF/M(100) systems exhibit a reduction in work function which goes from 0.5 to 0.9 eV (Table IV). This must be attributed primarily to the electrostatic compressive effect, which in turn is a function of the interface distance. In fact, the smallest change $\Delta\Phi=-0.47$ eV is computed for Al which has the longest interface separation, while the largest $\Delta\Phi=-0.90$ eV is obtained for Pd where the interface distance is shortest. The other metals exhibit intermediate $\Delta\Phi$ values of about −0.7 eV (Table IV).

NaCl is also a very ionic compound but a bit less than LiF (Table II). Because of the larger lattice constant, the NaCl films are rotated by 45° with respect to LiF. The CTs are still low but significantly larger than for LiF (Table IV). They also depend markedly on the metal substrate: almost zero for Al(100), extremely small for Ag(100), comparable for Au(100) and Pd(100), and largest for Pt(100). The fact that the interaction is slightly stronger than for LiF results in larger adhesion energies and, in general, in shorter interface distances. For instance, the NaCl/Pd(100) separation is 2.67 Å and also NaCl/Pt(100) and NaCl/Au(100) exhibit in-

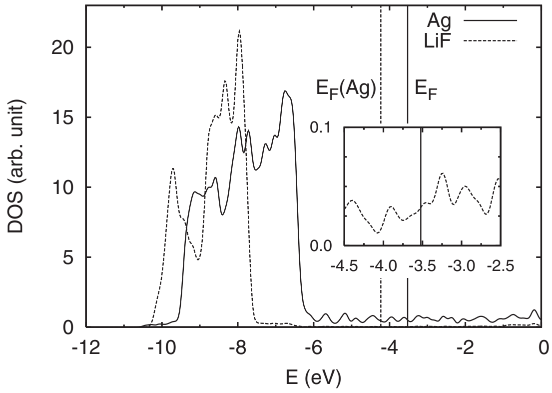

FIG. 3. Projected density of states of LiF(3 ML)/Ag(100) films. Dotted line: LiF; solid line: Ag. The vertical solid line indicates the position of the Fermi level (taken here as a measure of the surface work function) in the metal/dielectric system; the vertical dotted line indicates the position of the Fermi level in the pure metal substrate. The inset shows the LiF induced states at the Fermi level in a magnified picture.

terface distances below 2.80 Å. This shows that even an ionic solid such as NaCl interacts chemically with the metal support so that the change in work function cannot be ascribed solely to the electrostatic compressive term. In fact, we observe much larger work function changes than in the LiF case. For the group 10 metals, Pd and Pt, $\Delta\Phi$ is between −1.5 and −1.9 eV. For Pt the larger CT compensates the slightly longer NaCl-Pt interface distance compared to the NaCl-Pd one. The work function change for Ag and Au is similar, −0.70 and −0.90 eV, with a larger effect on gold due to both the shorter interface distance and the higher CT (Table IV). The $\Delta\Phi$ value computed here for NaCl(100) on Ag(100) is consistent with that reported by other theoretical studies[15] while it is underestimated with respect to the most recent experimental value $\Delta\Phi = -1.0/-1.3$ eV.[16]

The NaCl films are rotated by 45° with respect to the LiF ones, and in the $\sqrt{2}\times\sqrt{2}$ R45° supercell the metal atoms of the support are in contact with both the cations and the anions, giving rise to a non-negligible surface rumpling (Table IV). Depending on the system, the height of the metal atoms can differ from 0.14 to 0.25 Å. The rumpling of the NaCl interface layer is always quite small and always smaller than that of the top layer. These data on the surface relaxation show that NaCl interacts more strongly than LiF, but still the structural modifications can be considered small.

Ultrathin films of MgO deposited on metals are among the most studied systems due to their applications as dielectric barriers in tunnel magnetoresistance devices or as supports of nanoparticles for catalytic applications. MgO is a prototype of ionic oxides. Here Pd and Pt supports have not been considered because of the too large lattice mismatch. On the other hand, we included Mo(100) as a substrate since this has been widely used to growth thin MgO films[48] (Table IV). Al, Ag, and Au exhibit similar interface distances with MgO, about 2.7 Å, but Au shows a larger work function change (−1.60 eV) than Ag or Al (−1.27 and −1.46 Å, respectively), as a consequence of a larger CT (Table IV). However, the importance of the compressive effect is clearly shown by the MgO/Mo(100) results. Despite a very small CT, the adhesion energy is large and the interface distance is very short, 2.14 Å only. This results in a $\Delta\Phi$ of −1.74 eV, a value which is quite consistent with that reported experimentally for this interface.[49] The stronger bonding in MgO/Mo(100) is due to a pronounced hybridization of the metal with the oxygen states compared to the Ag case; this is shown for instance by the larger MgO contribution to the DOS at the Fermi level in the former case. Notice that the values in Table IV are slightly different from those reported in a previous theoretical study[6] [$\Delta\Phi = -1.18$ eV for MgO/Ag(100) and $\Delta\Phi = -2.14$ eV for MgO/Mo(100)] because of a different computational setup (no PAW was used in Ref. 6). The surface rumpling of the MgO films is small because of the good orientation of the dielectric layer (Table IV). This is important because it is clear that if the top metal and the bottom dielectric layers significantly modify their structure, additional contributions to the work function change arise, directly connected to the restructuring of the surface. In this case, the separation of the various contributions to $\Delta\Phi$ become even more complex.

CaS is definitely more covalent than the other ceramic films considered so far. The nature of the gap in CaS is controversial. Our calculations indicate an indirect Γ-X band gap of 2.4 eV (Table II); other studies suggest a direct Γ-Γ band gap (in this case higher gaps have been reported).[50] Also experimentally the situation is complex with reported values which range from 3.5 to 4.4 eV.[41,42] The top of the valence band is higher than the Fermi level of metals such as Au, Pd, and Pt and slightly below that of Ag. The higher covalent degree in CaS has the consequence that the CT to the metal support is in general larger than for halides and oxides. CaS gives rise to large atomic relaxations at the interface. The metal atoms have z coordinates which may differ by more than 0.3 Å. The final effect is a lowering of the work function to an extent comparable to that computed for MgO, but for CaS surface rumpling effects also contribute to the change in Φ.

The last dielectric considered is BaO. This material has significantly different properties from those of an ionic oxide such as MgO. BaO has a relatively small energy gap, 3.9 eV in the experiment[43] and 2.1 eV in the calculations, contrary to the other dielectrics. The top of the valence band is higher than the Fermi level of all the metals considered in this work. This means that BaO can behave as a much more efficient electron donor that the other insulating films (chemically, BaO is classified as a basic oxide). The much lower ionic character compared to MgO should result in larger chemical interactions at the interface. The surface of Al has not been considered because BaO interacts strongly with this metal, giving rise to pronounced distortions and to convergence problems. This probably indicates the tendency of Al to be oxidized at the expenses of Ba and to form mixed oxides at the interface.

The higher chemical reactivity of BaO results in stronger adhesion energies and hence in shorter interface distances. The adhesion energies in particular are about twice as large as those computed for NaCl on the same metal; as a consequence, also the interface separations are 0.2–0.3 Å shorter. The strongest adhesion is computed for Pd and Pt, which is

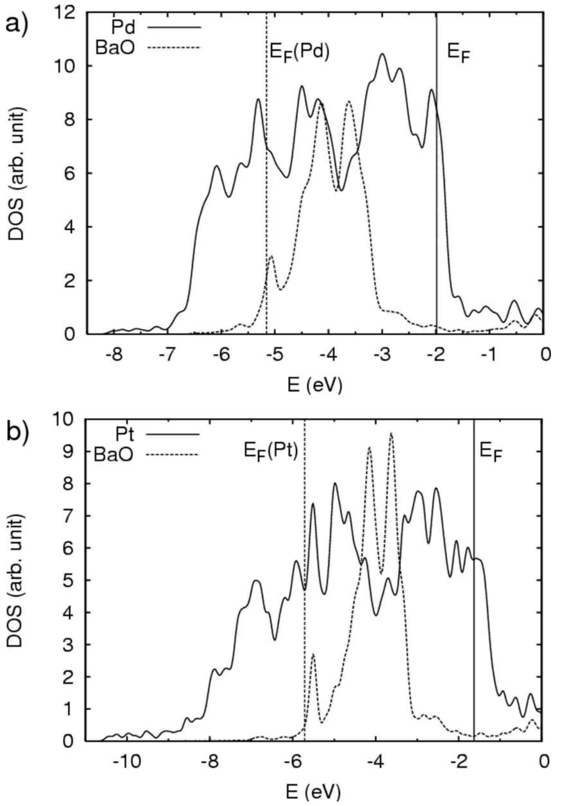

FIG. 4. Projected density of states of (a) BaO(3 ML)/Pd(100) and (b) BaO(3 ML)/Pt(100) films. Dotted line: BaO; solid line: Pd or Pt. The vertical solid line indicates the position of the Fermi level (taken here as a measure of the surface work function) in the metal/dielectric system; the vertical dotted line indicates the position of the Fermi level in the pure metal substrate.

sign of a special affinity of these metals for the oxygen atoms of the BaO film. These effects are expected to lower the work function of the metal supports and in fact BaO used to coat the filament of incandescent bulbs.[51] For all metals, Pd, Pt, Ag, and Au, BaO induces very large changes in the work function (Table IV). One goes from a reduction of 2.20 eV for Ag to 4.1 eV for Pt. The CTs from the oxide film to the metal are the largest found so far and indicate a strong mixing of the BaO and metal wave functions. This is clearly reflected in the PDOS which shows a substantial amount of BaO states at the Fermi level (Fig. 4). The very large $\Delta\Phi$ computed for Pt, −4.08 eV, is both the consequence of the short interface distance, 2.28 Å, and the large CT; on Pd(100), where the interface distance is similar, the smaller CT results in a smaller $\Delta\Phi$. The same effect is observed for Ag and Au. The interface distances are identical, but the larger CT for gold results in $\Delta\Phi$ which is larger in absolute value by 0.6 eV (Table IV).

As for NaCl and CaS, also BaO films are rotated by 45° so that both the Ba and the O atoms are on top of the metal atoms of the substrate. This, connected to the strong interaction of the metal with the O atoms of the film, induces large interface relaxations with rumplings of the supporting metal layer up to 0.57 Å. Of course, this results in a modification of the interface dipole which contributes to the final work function change.

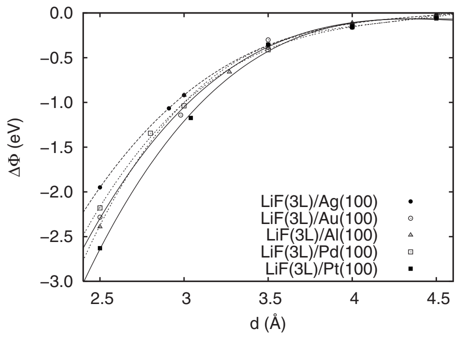

FIG. 5. Dependence of the change in work function $\Delta\Phi$ on the interface distance for LiF films deposited on Al(100), Pd(100), Pt(100), Ag(100), and Au(100).

IV. DISCUSSION AND CONCLUSIONS

The results presented in the previous paragraphs clearly show that the deposition of an ultrathin dielectric layer on a metal induces very large changes in the work function and that $\Delta\Phi$ can be expressed as the sum of three major terms as follows:

$$\Delta\Phi = \Delta\Phi^{\mathrm{CT}} + \Delta\Phi^{\mathrm{comp}} + \Delta\Phi^{\mathrm{SR}}, \tag{1}$$

where $\Delta\Phi^{\mathrm{CT}}$ represents the charge-transfer contribution, $\Delta\Phi^{\mathrm{comp}}$ is the electrostatic compressive effect, and $\Delta\Phi^{\mathrm{SR}}$ is the term due to the surface relaxation. We have seen that in some systems the surface relaxation is not large. This is true in particular for weakly interacting dielectrics (LiF and NaCl) or metals (Ag and Au); for these systems the approximation $\Delta\Phi^{\mathrm{SR}} \approx 0$ is justified and a separation of the $\Delta\Phi^{\mathrm{CT}}$ and $\Delta\Phi^{\mathrm{comp}}$ contributions can be attempted. For LiF films deposited on all metal supports we have recomputed $\Delta\Phi$ under the constraint that the positions of the atoms in the dielectric film and on the metal surface are fixed (no relaxation) and only the interface distance is optimized (Fig. 5). In this way, $\Delta\Phi^{\mathrm{SR}}=0$ by definition. Notice that this kind of calculations is not possible for more reactive substrates (e.g., Pd and Pt or CaS and BaO) because the calculations for rigid interfaces often do not converge and the assumption that $\Delta\Phi^{\mathrm{SR}} \approx 0$ is not justified. We have also seen that LiF behaves as an almost perfect ⟨⟨rigid wall⟩⟩, with little charge transfer; the LiF/M(100) interfaces, therefore, can be used to estimate the dependence of $\Delta\Phi^{\mathrm{comp}}$ on the interface distance by assuming that $\Delta\Phi^{\mathrm{CT}} \approx 0$; it follows that $\Delta\Phi \approx \Delta\Phi^{\mathrm{comp}}$. While this is not rigorously correct, for LiF it is very close to be true. The dependence of $\Delta\Phi^{\mathrm{comp}}$ on the interface distance for LiF/M(100) films is shown in Fig. 5.

The change in $\Delta\Phi$ is a smooth function of the interface distance *d*, but different metals show different curves because of the different spillover of charge from the top layer into the vacuum. Over the entire range of distances considered the $\Delta\Phi(d)$ curves have been fitted with a third degree polynomial which provides a rather accurate analytical expression of the dependence of $\Delta\Phi^{\mathrm{comp}}$ on the interface distance. If we now assume that $\Delta\Phi^{\mathrm{comp}}$ does not depend on the dielectric (i.e., every dielectric behaves as a ⟨⟨rigid wall⟩⟩) we can determine the $\Delta\Phi^{\mathrm{comp}}$ term at the equilibrium interface distance for every dielectric film on a given metal. Of

TABLE V. Properties of NX/Ag(100) and NX/Au(100) interfaces determined for fixed geometries. d=interface distance, $\Delta\Phi$=work function change, $\Delta\Phi^{\text{comp}}$=compressive contribution to $\Delta\Phi$, and $\Delta\Phi^{\text{CT}}$=charge transfer contribution to $\Delta\Phi$. $\text{CT}/(n_a/S)$=charge transfer normalized to the number of anions, n_a, per surface area S in contact with the metal atoms of the support.

	d (Å)	$\Delta\Phi$ (eV)	$\Delta\Phi^{\text{comp}}$ (eV)	$\Delta\Phi^{\text{CT}}$ (eV)	$\text{CT}/(n_a/S)$ (e Å^2)
NaCl(3 ML)/Ag(100)	3.18	−0.75	−0.67	−0.09	0.33
MgO(3 ML)/Ag(100)	2.67	−1.78	−1.54	−0.23	0.88
NaCl(3 ML)/Au(100)	3.12	−1.12	−0.85	−0.25	1.04
MgO(3 ML)/Au(100)	2.71	−2.31	−1.69	−0.61	1.48

course this is an approximation. The different size and polarizability of anions such as Cl^- or O^{2-} compared to F^- will certainly result in different compressive effects, but this should be a second-order effect with respect to the distance. The CT contribution can then be deduced from Eq. (1) as simple difference between $\Delta\Phi$ and $\Delta\Phi^{\text{comp}}(d_{\text{eq}})$. The results are shown in Table V for NaCl and MgO deposited on Ag(100) and Au(100). In this table we also report the CT normalized to the number of anions n_a per surface area S in contact with the metal atoms of the support, $\text{CT}/(n_a/S)$.

We notice that for these systems the compressive effect is more important than the CT one (Table V), confirming the importance of this purely electrostatic term. However, even for an ionic oxide such as MgO the CT term cannot be neglected. On a weakly interacting substrate such as Ag(100) it is the 13% of the global $\Delta\Phi$; on the more reactive Au support it represents 26% of the total $\Delta\Phi$. It is also interesting to note that the $\Delta\Phi^{\text{CT}}$ term derived with the assumptions and approximations described above shows a direct correlation with the amount of CT normalized to the number of anions per unit cell. Since these two quantities are obtained in an independent way, this confirms the validity of the decomposition.

Of course, it would be good to be able to predict the extent of work function change induced by a dielectric layer on a metal looking at intrinsic properties of the two separate components such as the degree of ionicity, the band gap of the dielectric, or the work function of the metal. The previous discussion has shown that $\Delta\Phi$ depends primarily on the compressive term, hence on the interface distance and on the charge transfer. The data of Table IV show unambiguously that a stronger adhesion corresponds to a shorter interface distance. A stronger adhesion is expected when the position of the filled levels of the insulator, as measured by the top of the valence band E_{VB}, is closer to the empty states of the metal, as indicated by the position of the Fermi level E_F. This favors not only the hybridization of the metal and dielectric electronic states but also the CT. For LiF, where E_{VB} is very deep (Fig. 3) very little CT is expected from these states; on the contrary, for BaO, where E_{VB} lies above E_F of all the metals considered (Fig. 4), the CT is expected to be particularly pronounced. Therefore, a key quantity which determines the adhesion strength, the interface distance, and the associated CT is $\Delta E = E_F^{\text{metal}} - E_{\text{VB}}^{\text{dielectric}}$, where E_F and E_{VB} are properties of the separated units before the interface is formed. Notice that for metal and a semiconductor forming an interface the difference between E_F and E_{VB} corresponds to the Schottky barrier height; here we are considering the two properties of the separated units, while a Schottky barrier is defined for the interface. In Fig. 6 we have plotted ΔE versus $\Delta\Phi$ for all systems considered. We observe a clear trend which indicates that the largest changes in work function are found for those compounds (BaO) where E_{VB} is above E_F (negative ΔE). In this case the chemical interaction at the interface is strong and dominated by CT terms, the interface distance is short, and two additive effects contribute to a strong lowering of the work function. On the other extreme we have wide gap insulators such as LiF, with E_{VB} much deeper than E_F. This gives rise to very weak interactions, no CT, and long interface distances. $\Delta\Phi$ is small and originates only from compressive effects.

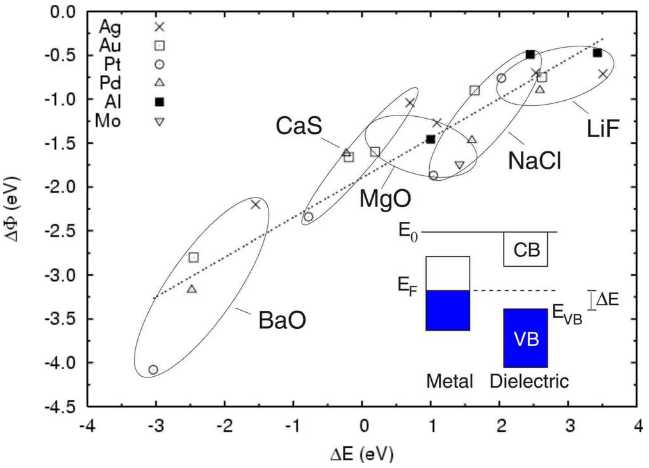

FIG. 6. (Color online) Relation between $\Delta\Phi$ and ΔE for a series of metal/dielectric interfaces. ΔE is defined as the difference between the metal Fermi level E_F and the top of the valence band in the dielectric E_{VB} (see inset).

ACKNOWLEDGMENTS

We thank Livia Giordano for the critical reading of the paper. The work was partly supported by the COST Action D41 “Inorganic oxides: surfaces and interfaces.” The computing time was provided by the Barcelona Supercomputing Center (BSC-CNS) and by the Milan supercomputing center (CILEA).

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