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Polarization and rumpling in oxide monolayers deposited on metallic substrates

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Relying on an *ab initio* approach to model MgO/metal interfaces, we unravel the specificity of polarization effects in the oxide monolayer limit. We show that rumpling of the supported oxide film is a structural response to the interfacial charge transfer. Surface characteristics of such complex supports can thus be directly tuned by an adequate choice of the metal and the oxide. This mechanism equally affects films of nonpolar and polar orientations. Contrary to thicker films, there is thus no electrostatic signature distinguishing the two types of orientation.

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I. INTRODUCTION

The last decade has witnessed important advances in the fabrication and characterization of crystalline ultrathin oxide films supported on metals. Various oxides, such as NiO, Al_2O_3, FeO, SiO_2, TiO_x, etc., have been synthesized on different metals substrates, and in particular, well-controlled crystalline MgO(100) (Refs. 1–6) and (111) (Refs. 7–10) films have been grown on Ag(100) and Ag(111) substrates. While initially these systems had been principally designed for spectroscopic measurements on insulators, without the limitations caused by charging effects typical for semi-infinite surfaces, it has rapidly become clear that ultrathin oxide films exhibit unique properties, different from those of their bulk counterpart surfaces. The rich variety of their unusual and tunable structures as well as their specific electronic properties may modify the substrate reactivity[11–13] and drive the nucleation site, the shape, and the reactivity of supported metal atoms and clusters.[14,15] The overall capacity to exchange electrons (work function) may be modulated by changing the underlying metal substrate, the deposited oxide, the film orientation, structure, and thickness. For example, it has been shown that changes in the work function induced by the oxide layer[16–20] influence the charging of metal adsorbates,[21–25] and, in some cases, lead to adsorbate self-organization.[26–28]

The role of polarization effects in the properties of such composite oxide/metal supports has recently been the object of attention and the three principal components of the total dipole moment have been identified:[17,24,29–31] (i) one due to the compression of the metal electronic density upon oxide deposition (D_{comp}), (ii) another due to the charge transfer between the oxide film and the metal substrate (D_{CT}), (iii) and finally that due to the intrinsic dipole moment of the rumpled oxide film (D_R) (rumpling r is defined as the separation between oxygen and cation atomic layers). In the most studied case of a few-layer-thick oxide films of nonpolar orientation, the third contribution may be neglected and, as recently shown for MgO(100) on transition-metal substrates,[30] D_{comp} and D_{CT} act in synergy yielding a total dipole moment which is essentially driven by the adhesion strength at the interface. However, in the well-(experimentally) represented limit of a single oxide monolayer, the situation seems much more complex, especially taking into account that oxide monolayers of polar orientations have also been stabilized. Indeed, the peculiar surface properties of FeO(111)/Pt(111) (Ref. 27) and TiO_x/Pt(111) (Refs. 32 and 33) were tentatively assigned to polarity-related strong enhancement of the D_R component.

In this context, the aim of the present paper is to reach a deeper understanding of the role of (orientation-dependent) polarization effects in the properties of supported oxide films, in the yet less-explored monolayer limit. At variance with thicker films, we find that the contribution of the film rumpling is not negligible and that the (moderate) total interfacial dipole results from a compensation of components which may be large. However, since the very nature of this compensation differs from that encountered at polar surfaces,[34] we will argue that the qualitative distinction between polar and nonpolar oxide films based on electrostatic considerations does not apply in the monolayer limit. Moreover, we will show that the structural flexibility of thinnest oxide films enables them to respond structurally to the interface formation and that electrostatic forces drive a strong coupling between the oxide structure (rumpling) and the interfacial charge transfer. This suggests that the structure of a deposited oxide monolayer may be tuned by a mere change in the metal substrate.

II. METHODOLOGY

In order to identify the factors which drive the structural and electronic characteristics of a (generic) ionic insulator film supported on a metal substrate, we simulate (111) and (100) epitaxial monolayers of MgO on surfaces of a variety of metals ranging from simple (Al, Mg), to transition (Mo, Pt), and noble (Ag). We adopt simple structural models and focus on the competing microscopic effects rather than exploring the ensemble of possible (meta)stable configurations for each system. The calculations rely on the density-functional theory at the PW-91 gradient-corrected level,[35] with ultrasoft pseudopotentials,[36] and a plane-wave basis set (kinetic-energy cutoff of 396 eV), as implemented in Vienna Ab-initio Simulation Package (VASP).[37] All MgO/metal systems are modeled by asymmetric MgO/metal slabs with one bare metal surface and one surface covered with the MgO

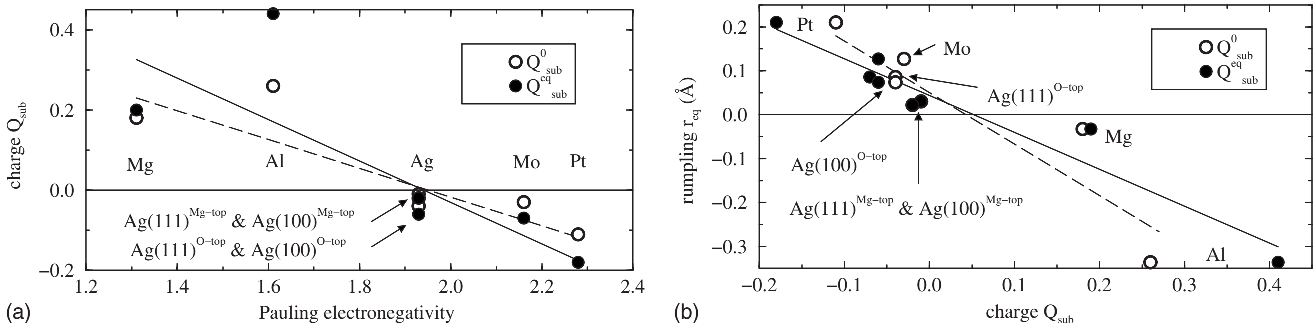

FIG. 1. Ground-state characteristics of MgO(111)/Me(111) (1×1) interfaces (MgO monolayer; Me=Al, Mg, Ag, Mo, and Pt; oxygens on-top metal atoms): Q^{eq}_{sub} is the charge born by the metal substrate (electrons per MgO unit), r_{eq} is the rumpling of the MgO film (Å). Results for the alternative interface registers (cations on-top of metal atoms) and for the (100) orientation are given in the case of the MgO/Ag interface. Results corresponding to flat MgO films $(r=0)$ are plotted with open circles. Lines are drawn to guide the eyes.

film, separated by a vacuum layer of about 10 Å. In such asymmetric configuration, the adsorption-induced change in the surface dipole moment is equal to the total dipole of the slab and is converged to within 3% with seven-layer-thick metal slabs. In VASP, the interaction between the total dipoles of repeated unit cells is eliminated thanks to the so-called dipole correction.

The choice for the structural model of the metal/oxide interface is motivated by the two following considerations. On one hand, regarding the MgO film atomic structure, we have recently predicted that polarity-related effects enhance the stability of graphitelike (h-BN) and zinc-blende structures over the rocksalt one.[38,39] However, in the limit of a single MgO monolayer, all these structures converge to the very same geometry. Indeed, at equilibrium, unsupported MgO monolayers of both square and hexagonal symmetries [referred to as MgO(100) and MgO(111), respectively] are perfectly flat, with (unsupported) equilibrium in-plane lattice parameters of, respectively, 2.83 Å (Ref. 16) and 3.26 Å.[38] On the other hand, the interaction with the metal substrate does in general modify both the in-plane lattice parameter and the rumpling of the oxide film. Such structural modifications are driven both by the constraint induced by the lattice mismatch and by electronic effects due to the metal-oxide interaction. While the first one is strongly system-dependent, the second one presents universal characteristics, which are at the heart of the present study. We thus focus on the strength of the metal-oxide bonding at the interface and the electron reservoir characteristics of the metal substrates and leave aside the lattice mismatch considerations. This can be achieved by working at the equilibrium lattice parameter of supported oxide films and by distorting the metal substrates accordingly. Equilibrium lattice parameters of supported oxide films are estimated from the minimum of the total-energy difference between MgO/metal and metal subsystems, as a function of lateral lattice parameter. This procedure eliminates the first-order contribution due to the metal distortion and minimizes essentially the energy of the oxide film augmented by the interaction energy at the metal/oxide interface. In practice, for each value of lateral lattice parameters, the energies of the separate subsystems are obtained by a full relaxation (residual forces smaller than 0.01 eV/Å) in a (1×1) (interface) unit cell. Equilibrium lattice parameters of the supported MgO films calculated in such a way are equal to 3.31 Å (Ag), 3.48 Å (Al), 3.40 Å (Mg), 3.43 Å (Mo), and 3.30 Å (Pt) for the (111) oriented films and 2.85 Å for MgO(100)/Ag(100). As expected, in the absence of a geometrical constraint, the principal effect of interaction at the interface is a systematic dilation of the oxide lattice parameter with respect to the free-standing films. We note that our estimation agrees with the experimental determination for of MgO films on both Ag(100) (Ref. 3) and Ag(111) (Ref. 7) substrates. Additionally, constrained calculations are performed for a series of fixed values of rumpling in MgO monolayers. In this case, the lateral lattice parameters are kept at their supported equilibrium values and the interfacial MgO-metal distance R_{int} and the interlayer spacings within the metal are fully relaxed. Atomic charges are estimated within a Bader method.[40,41]

III. RESULTS

Figures 1 and 2 summarize the principal equilibrium characteristics obtained for the MgO(111)/Al, Mg, Ag, Mo, and Pt interfaces: charge Q^{eq}_{sub} born by the metal, rumpling r_{eq} of the oxide layer, and interfacial potential jump D_{eq} due to the total interfacial dipole moment. While the ground state of all considered systems corresponds to oxygens on-top metal surface atoms (O-top), for the MgO/Ag system we also report the results obtained for the alternative register at the interface (cations on-top metal surface atoms: Mg-top) and for the (100) interface orientation. In the latter case, the present results agree with those of a previous study on MgO(100)/Ag(100).[17] Additionally, in order to highlight the effect due to the oxide rumpling, we plot both the equilibrium characteristics (r_{eq}, Q^{eq}_{sub}, and D_{eq}) and those obtained for flat $(r=0)$ MgO films (Q^0_{sub} and D_0).

Q^{eq}_{sub} quantifies the interfacial charge transfer between the oxide film and the substrate. In agreement with a previous study on constituted interfaces,[31] its strength and sign are principally driven by the metal electronegativity, as shown in Fig. 1(a). Deposition of an MgO film on a simple metal (Mg and Al) results in a positive charge of the substrate ($Q^0_{sub},Q^{eq}_{sub}>0$) while transition-metal substrates (Ag, Mo, and Pt) get negatively charged ($Q^0_{sub},Q^{eq}_{sub}<0$). We note that in the absence of rumpling, the interfacial charge transfer

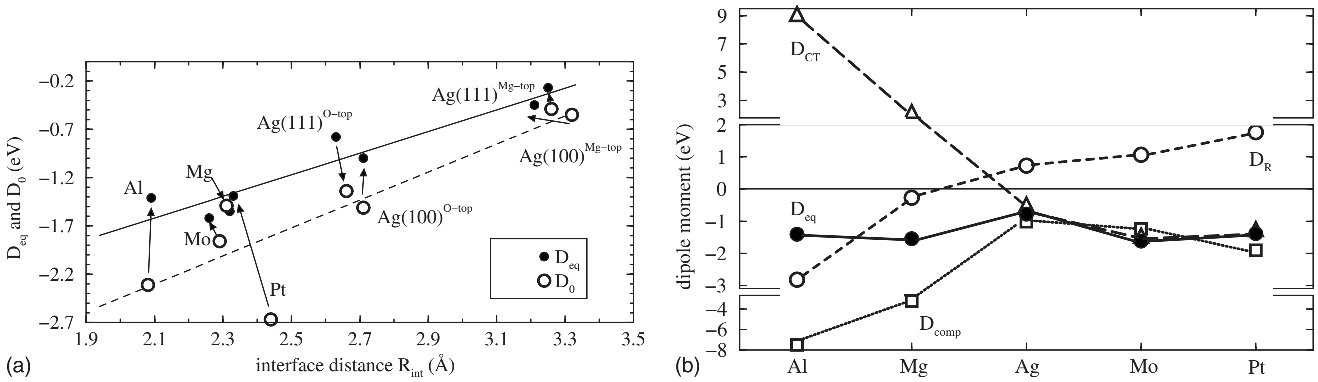

FIG. 2. Left panel: interfacial MgO/Me (Me=Al, Mg, Ag, Mo, and Pt) jump of electrostatic potential induced by the dipole moment D_{eq} (eV) as a function of the interfacial distance R_{int} for the same systems as in Fig. 1. Dipole moments D_0 corresponding to flat MgO films ($r=0$) are plotted with open circles. Right panel: decomposition of D_{eq} of MgO(111)/Me(111) into: electron compression D_{comp}, charge transfer D_{CT}, and rumpling D_R contributions (see text for details). Lines are drawn to guide the eyes.

Q^0_{sub} follows the same trend, but its absolute value is systematically smaller: $|Q^0_{sub}|<|Q^{eq}_{sub}|$. While perfectly flat when unsupported, the MgO monolayers get rumpled upon deposition. Simple metals (Al and Mg: $Q^{eq}_{sub}>0$) induce a negative rumpling (oxygens closer to the metal substrate); the trend is opposite on transition metals (Ag, Mo, and Pt: $Q^{eq}_{sub}<0$) (oxygens relax outward) [Fig. 1(b)]. The sign and the strength of r_{eq} correlate with the interfacial charge transfer (with both Q^{eq}_{sub} and Q^0_{sub}).

The total dipole moment is negative in all systems under consideration. Its strength $|D|$ decreases significantly for larger interface distances R_{int} [Fig. 2(a)]. While this is consistent with the behavior of the compression component only,[17,31] we note that larger R_{int} also correspond to weaker adhesion and thus to smaller interface charge transfers and smaller film rumplings. It is found that the rumpling significantly reduces the total dipole moment $|D_0|>|D_{eq}|$, the effect being particularly strong in the case of Pt substrate. Beyond this qualitative observation, we tentatively make a more quantitative decomposition of the total dipole D_{eq} in the following way [Fig. 2(b)]. Assuming that for $|r|<|r_{eq}|$, the interface distance R_{int} and the compression dipole D_{comp} do not noticeably vary with r and that D_{CT} is linear in Q_{sub} ($D_{CT} \approx R_{int}Q_{sub}$), it is possible to estimate $D_{comp}(r_{eq})$, $D_{CT}(r_{eq})$, and $D_R(r_{eq})$ from the calculated values of D_{eq}, $D_0=D_{comp}+D_{CT}(r=0)$, and $D_R(r_{eq})$ (this latter calculated for an unsupported film). While precise numbers should be taken with caution, the decomposition confirms that D_R gives a non-negligible contribution, of the order of 1–2 eV, whose sign is systematically opposite to that of the charge-transfer term D_{CT}. Along the series, the sign of Q_{sub} changes and, while charge-transfer and compression dipole moments are aligned in case of transition metals, they are antiparallel at simple metal interfaces. Their larger values in the latter case are consistent with a smaller interface distance R_{int} and a more diffuse electronic density.

In summary, the numerical results demonstrate that rumpling gives a non-negligible contribution D_R to the total dipole, and that it systematically opposes and partially compensates the charge-transfer term D_{CT}. The structure of the oxide film (r_{eq}) is thus strongly coupled to the interfacial charge transfer Q_{sub} ($r_{eq} \propto -Q_{sub}$) and, as a consequence, to the nature of the metal substrate. As exemplified by results on the MgO/Ag system, these trends do not depend on the interface register (O-top and Mg-top) and—more interestingly—nor on the orientation (polar/nonpolar) of the oxide film. This means that while a partial compensation of electrostatic dipoles takes place, there is no specific electrostatic signature distinguishing polar and nonpolar orientations, contrary to thicker films.[34,38,39]

IV. DISCUSSION

In order to unravel the origin of these effects, in Fig. 3 we show the results of a series of calculations for a self-standing and an Ag-supported MgO(111) monolayer, at fixed rumpling values $-0.6<r<+0.6$ Å. We first focus on the interfacial charge transfer Q_{sub}, which varies quasilinearly with r. Similarly to MgO(100)/Me(100) constituted interfaces,[31] Q_{sub} is principally determined by the difference between the metal Fermi energy E_F and the oxide point of zero charge

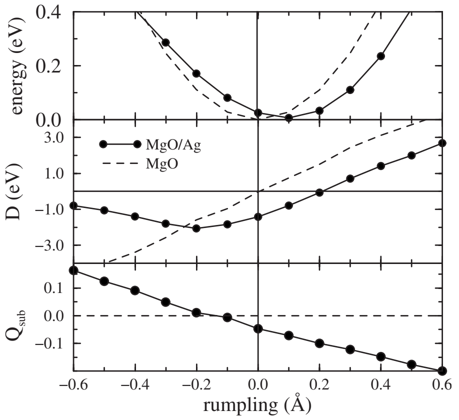

FIG. 3. Interface characteristics for a self-standing (dashed line) and an Ag(111)-supported (full circles) (1×1) MgO(111) monolayer, as a function of MgO rumpling r (Å). Top panel: MgO energy (eV); middle panel: total dipole moment $D(r)$ (eV); and lower panel: interface charge transfer $Q_{sub}(r)$ (per MgO formula unit).

$E_{\rm PZC}$ corrected by the total dipole D, and can be written as

$$Q_{\rm sub}(r) = \chi^{\infty}[E_F - E_{\rm PZC} - D(r)]. \tag{1}$$

The electronic susceptibility of the interface χ^{∞} is related to the optical dielectric function ϵ^{∞}. $Q_{\rm sub}$ may thus be seen as an electronic *response* of the interface to the band mismatch. Assuming that the charge-transfer and rumpling dipole moments may be approximated by the simple expressions $D_{\rm CT}=R_{\rm int}Q_{\rm sub}$ and $D_R=rQ$ ($\pm Q$ are the charges of Mg and O in the MgO layer, respectively), the solution of the implicit Eq. (1) for a fixed rumpling value r yields

$$Q_{\rm sub}(r) = \kappa\Delta E - \kappa r Q, \tag{2}$$

with $\Delta E = E_F - E_{\rm PZC} - D_{\rm comp}$ and $\kappa = \chi^{\infty}/(1+\chi^{\infty}R_{\rm int})$. Equation (2) shows that in the absence of rumpling, the interfacial charge transfer $Q^0_{\rm sub} = \kappa\Delta E$ depends principally on ΔE and, for a given oxide, is indeed driven by the metal electronegativity. In addition, Eq. (2) gives firm grounds to the quasilinear relationship between $Q_{\rm sub}$ and r [Fig. 3 (lower panel)]. It also supports the quasilinear behavior of $D(r)$ and $D_R(r)$, numerically found in the r range where the variations of $R_{\rm int}$ and $D_{\rm comp}$ are negligible [Fig. 3 (middle panel)].

The equilibrium rumpling of the supported oxide film may be seen as a consequence of the electrostatic field created by the interfacial charge transfer $\mathcal{E} = 4\pi Q_{\rm sub}(r)/S$ (S is the interface area per MgO unit). $\mathcal{E}$ exerts electrostatic forces which shift anions and cations in opposite directions and are counterbalanced by elastic forces. To first approximation, the latter is equal to $F_{\rm elastic} = -\beta r$ (β is an elastic constant), so that equilibrium is reached for a rumpling value equal to

$$r_{\rm eq} = -\frac{2\pi}{\beta S} Q Q_{\rm sub}(r_{eq}). \tag{3}$$

Since β and Q are positive quantities, Eq. (3) demonstrates that $r_{\rm eq} \propto -Q_{\rm sub}$, as found numerically (Fig. 1). Used with Eq. (2), it allows to derive a compact expression for the interfacial charge transfer at equilibrium,

$$Q_{\rm sub}(r_{\rm eq}) = \frac{\kappa\Delta E}{1 - 2\pi\kappa Q^2/\beta S} = \frac{Q^0_{\rm sub}}{1 - 2\pi\kappa Q^2/\beta S}. \tag{4}$$

Equation (4) gives a strong support to the quasilinear dependence of $Q_{\rm sub}(r_{\rm eq})$ upon ΔE (i.e., electronegativity) as found numerically. It also shows that rumpling reinforces the absolute value of charge transfer ($|Q^0_{\rm sub}| < |Q^{\rm eq}_{\rm sub}|$ in Fig. 1). Indeed, the charge-transfer dipole $D_{\rm CT}$ shifts the substrate and oxide bands, so as to effectively reduce ΔE and $Q^0_{\rm sub}$ [$\kappa < \chi^{\infty}$ in Eq. (2)]. The rumpling dipole, which opposes $D_{\rm CT}$ has the opposite effect: it increases $|Q^{\rm eq}_{\rm sub}|$ with respect to $|Q^0_{\rm sub}|$. Finally, Eq. (3) proves that due to simple electrostatics, rumpling may be indeed seen as a structural (polaronic-like) *response* of the oxide film to the band misalignment and thus to the interface charge transfer, as schematized in Fig. 4. The dipole moments associated to rumpling and charge transfer oppose and partially compensate each other, regardless of the polar/nonpolar film orientation.

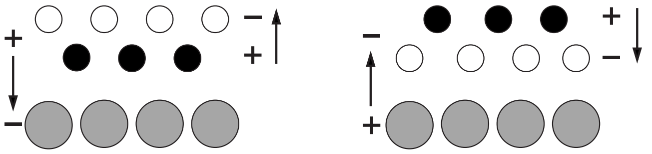

FIG. 4. Schematic representation of the charge-transfer and rumpling dipole moments (shown by arrows), for the two cases of positive and negative metal charging. Magnesium, oxygen, and metal atoms are represented as black, white and gray circles, respectively.

V. CONCLUSION

In summary, we have unraveled the complexity of interfacial polarization effects, specific to oxide monolayers deposited on metals. We have highlighted the important role played by the oxide rumpling not found in thicker films and seen here as a structural *response* to the interfacial charge transfer. Relying on analytical arguments, we have proved the general validity of this result, certainly not limited to MgO monolayers. We have shown that contrary to the macroscopic dipole compensation characteristic of polar surfaces, the compensation of electrostatic dipoles which takes place at metal-supported oxide monolayer is only partial and occurs along both polar and nonpolar orientations. This means that contrary to thicker films, there is no electrostatic signature distinguishing the two types of orientations. The existence of the strong coupling between electronic and structural degrees of freedom gives an additional guideline toward a practical tuning of such complex supports. Indeed, an adequate choice of the oxide/substrate electronic characteristics (point of zero charge of the oxide, metal electronegativity) may be used to tailor surface structural characteristics and thus to tune the electronic and reactivity properties of such supports.

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