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Effect of electron correlation corrections on phase competition in Ag film on MgO substrate

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Abstract

The effect of electron correlation corrections in the novel theory predicting the growth mode of a thin metallic film on an insulating substrate has been studied. We discuss the influence of the substrate slab thickness on the energies of formation for several two-dimensional phases, which, in principle, may form in Ag layer on (0 0 1) MgO substrate. We analyze also the sensitivity of the key energy parameter—Fourier transform of the mixing potential $\widetilde{V}(0)$ to the choice of correlation functionals. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The pattern (i.e., the microstructure and morphology) of metal films deposited on oxides proves to depend strongly on growth conditions, especially for thin layers [1–3]. The growth mode usually falls into one of three categories: layer-by-layer; formation of a three-dimensional (3D) metal island; growth to a layer and then to islands [4].

Despite much theoretical work on the adhesion of noble and transition metals on regular MgO substrates, using widely varying models and computational methods, there is still a lack of full understanding of interface formation and of interface properties on an atomic scale. Partly this is because there are sensitive balances between contributions to the energy of metal on an oxide substrate. Both of the traditional ab initio formalisms of Hartree-Fock (HF) and density functional theory (DFT) have been used to calculate the electronic structure explicitly. Finite-cluster

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models of the Me/MgO interfaces were studied both by HF [7,8] and DFT [9,10] methods. Periodic slab models of the same systems have mainly used variants of DFT [11–16], based on local spin density (LSD) and generalized gradient approximations (GGA) approaches.

In this paper, we use the results of ab initio HF–CC calculations on the electronic structure of a regular Ag/MgO(0 0 1) interface as a basis for a study of an influence of electron correlation corrections on energy parameters that define the morphology of thin Ag films on (0 0 1) MgO surface. We demonstrate also the influence of the thickness of the slab on energies of competing phases in an Ag layer. Although our general methodology was recently briefly formulated in Ref. [5], this paper complements the latter study with the essential physical background. Thus, we supplement our pilot study [5] with the analysis of the role of different electron correlation corrections (LSD- and GGA-type) in the thermodynamics of interfacial system and we analyze the sensibility of thermodynamic predictions to the details of ab initio modeling.

2. Ab initio simulation for the ordered Ag/MgO-(0 0 1) interface

2.1. Theoretical background

In our theoretical simulation of the perfect MgO substrate, we have considered finite-thickness slabs with two-dimensional (2D) periodicity. Since the Ag coverage of the MgO(0 0 1) surface was varied from 1/4 metal layer (1:4 coverage) to a monolayer (1:1 coverage), we have made a series of calculations for the 2×2 extended surface unit cells of magnesia slabs. These allow us to model *four* kinds of Ag structures on the Ag/MgO(0 0 1) interface, as shown in Fig. 1. In our previous studies, we have found and explained why silver atoms adhere preferentially to the O-site on the MgO(0 0 1) surface ([17] and references therein). Indeed, such a metal/oxide interface configuration agrees well with experiment. Thus, we consider Ag over O-sites on MgO as appropriate for all four structures, which are: silver monolayer (Fig. 1a), two regular configurations of 1:2 Ag coverage (Fig. 1b and c), and 1:4 coverage (Fig. 1d). Our choice of the structures presented by Fig. 1b–d is dictated by symmetry consideration (see Ref. [5]). In constructing effective site interaction potentials for thermodynamic simulations of Ag film growth on an MgO(0 0 1) substrate, for all of these structures we have carried out total energy optimization. For the metal/oxide system, this is a 2D optimization of the total energy $E_{\mathrm{tot}}(a_{\mathrm{MgO}}, d_{\mathrm{Ag-O}})$ as a function of the substrate lattice constant a_{MgO} and the interface distance $d_{\mathrm{Ag-O}}$. For the MgO substrate, we optimize the total energy $E_{\mathrm{tot}}(a_{\mathrm{MgO}})$ as a function of lattice constant.

We used a periodic slab model containing either three or five MgO(0 0 1) layers with one- and two-side silver adhesion, respectively. As in earlier studies on the three-layer substrate [17], we neglect surface relaxation of magnesia slab, which is known to be small [18]. For both models containing one and two Ag adlayers, the corresponding adhesion energy per atom (E_{adh}) is defined according to the universal binding energy relation [13,17].

In our ab initio calculations we use the HF–CC formalism as implemented in the CRYSTAL98 code [19], with a wide choice of various a posteriori electron correlation corrections to the total energy. Although a standard HF approach usually overestimate bond length and underestimate the binding energy per chemical bond, the correlation corrections certainly do improve quality of HF calculations on the total energy [20]. In the present paper, we have analyzed not only Perdew–Wang (PWGGA) correlation corrections [21], as earlier, but also other kinds of correlation functionals, both GGA-type [22] and LSD-type [23,24]. The basis sets (BS) for Mg, O, and Ag, and some other computational details are the same as in our previous papers in which we calculated the atomic and electronic structure of defective and perfect monolayers, and three-layer Ag/MgO(0 0 1) interfaces [6,17]. We use the same BS, but we have estimated more carefully the BS superposition errors (BSSE) for different configurations of Ag/MgO(0 0 1) interfaces according to CRYSTAL98 computational scheme [19].

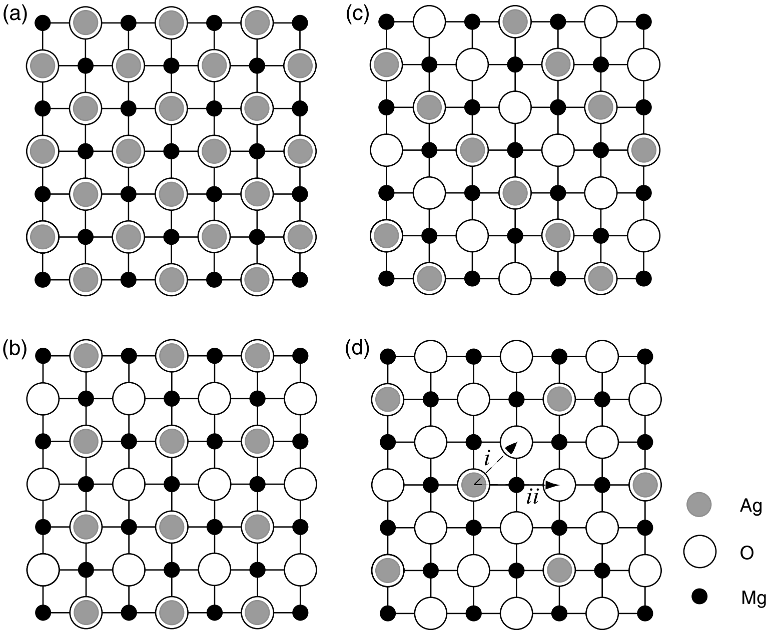

Fig. 1. Top view of the MgO(1 0 0) surface with different superstructures of Ag atoms placed atop it. (a), (b), (c) and (d) images correspond to Ag coverages of 1:1 (a regular monolayer), 1:2 (a square distribution), 1:2 (a striped distribution),and 1:4 (quasi-isolated metal atoms), respectively. Directions marked as *i* and *ii* denote two trajectories of possible surface diffusion of Ag atoms.

2.2. Results and discussion

The results of the latest ab initio calculations, going beyond our recent simulations of the regular Ag/MgO(0 0 1) interface [17] are collected in Table 1. These new data are essential for further treatment of thermodynamic parameters.

The value of the lattice constant for the pure MgO(0 0 1) substrate optimized for a 2 × 2 supercell has been found to be smaller than in our previous calculations for the bulk unit cell. We find this value in the range 4.09–4.15 Å for various correlation functionals and adhesion models, to be compared with the previous result 4.21 Å [17] and with the experimental bulk value 4.205 Å [18]. One component of the difference comes from the surface stress which like the surface tension of a liquid, tends to reduce the interatomic spacing. This effect can be seen from the systematic differences of about 0.02 Å between three-layer and five-layer systems. The interface distances between silver atoms and substrate have been optimized using the $E_{\mathrm{tot}}(a_{\mathrm{MgO}}, d_{\mathrm{Ag-O}})$ function for all four structures shown in Fig. 1. As the Ag coverage increases from 1:4 to 1:1, the equilibrium $d_{\mathrm{Ag-O}}$ distance decreases negligibly, by less than 3% (Table 1) and is accompanied by the adhesion energy increase by 0.03–0.04 eV. For all used correlation functionals, the Ag adhesion energy lies between 0.18 and 0.26 eV per adatom, showing that we have physisorption. The adhesion energy is even smaller (a less stable interface) for the case of the striped 1:2 Ag coverage shown in Fig. 1c, where $d_{\mathrm{Ag-O}}$ is larger than for other configurations (Table 1). Using the LSD-type correlation functionals, the equilibrium values of both a_{MgO} and $d_{\mathrm{Ag-O}}$ are found to be slightly larger, but the corresponding values of E_{adh} smaller than those for the GGA-type functionals. These trends are typical for HF–CC and DFT methods implemented in CRYSTAL98 code [19].

The BSSE corrections [25] were found to be quite small (0.01–0.02 eV per adatom); they are included in results presented in Table 1. The lateral interactions between adjacent Ag atoms are rather small for 1:4 and even 1:2 square coverages shown

Table 1
Main results of the HF–CC simulation on the Ag/MgO(0 0 1) interface

Optimized parameters of calculations	Different a posteriori electron correlation corrections and substrate models							
	Perdew–Wang GGA		Lee–Yang–Parr GGA		Perdew–Zunger LSD		Vosko–Wilk–Nusair LSD	
	Three-layer[a]	Five-layer[a]	Three-layer[a]	Five-layer[a]	Three-layer[a]	Five-layer[a]	Three-layer[a]	Five-layer[a]
Pure MgO(0 0 1) surface								
a_{MgO} (Å)	4.09	4.11	4.10	4.12	4.13	4.14	4.12	4.14
1:4 Ag coverage of MgO(0 0 1) surface (Fig. 1d)								
a_{MgO} (Å)	4.09	4.10	4.09	4.11	4.13	4.13	4.13	4.14
d_{AgO} (Å)	2.58	2.59	2.59	2.60	2.63	2.64	2.64	2.65
E_{adh} (eV)	0.23	0.22	0.22	0.21	0.20	0.19	0.19	0.18
1:2 Ag coverage of MgO(0 0 1) surface (a square distribution, Fig. 1b)								
a_{MgO} (Å)	4.08	4.10	4.09	4.10	4.12	4.13	4.12	4.13
$d_{Ag\text{–}O}$ (Å)	2.58	2.58	2.59	2.59	2.62	2.63	2.63	2.64
E_{adh} (eV)	0.23	0.22	0.22	0.21	0.20	0.20	0.20	0.19
1:2 Ag coverage of MgO(0 0 1) surface (a striped distribution, Fig. 1c)								
a_{MgO} (Å)	4.08	4.09	4.09	4.10	4.12	4.12	4.12	4.13
$d_{Ag\text{–}O}$ (Å)	2.69	2.69	2.68	2.69	2.74	2.76	2.73	2.75
E_{adh} (eV)	0.12	0.11	0.12	0.11	0.10	0.10	0.10	0.09
1:1 Ag coverage of MgO(0 0 1) surface (Fig. 1a)								
a_{MgO} (Å)	4.07	4.08	4.08	4.08	4.12	4.13	4.12	4.13
$d_{Ag\text{–}O}$ (Å)	2.55	2.56	2.56	2.56	2.60	2.61	2.61	2.61
E_{adh} (eV)	0.26	0.25	0.25	0.25	0.22	0.21	0.21	0.20

[a] Three and five-layer magnesia slabs are used in the models of one- and two-side silver adhesion, respectively.

in Fig. 1b and d, respectively. This is why their stable configurations have practically the same values of E_{adh}. However, these lateral interactions are more significant for the striped configuration (Fig. 1c), which is clearly energetically unfavorable, and so has larger interfacial distances (Table 1). In the case of the two-side adhesion model, the corresponding values of E_{adh} are slightly smaller, but the equilibrium interface distances are nearly the same as for the one-side case. This confirms that interaction between Ag atoms positioned on the two opposite sides of the slab is negligibly small and that three-layer substrate slab is thick enough for further modeling using one-side adhesion model.

3. Influence of correlation corrections on the energy parameters for Ag layer on (0 0 1) MgO

The energies of formation of 2D phases U_1, U_2, and U_3 corresponding to Fig. 1b–d respectively are given in Table 2. The dispersion in the calculated energies does not exceed 25% for any of these quite different correlation corrections, and this consistency is enough for our qualitative conclusions about mechanisms of thin film growth mode. As follows from Table 2 the thickness of the underlying magnesia slab also does not affect significantly the values of the energies of formation of 2D phases considered in our study. The main result remains unchanged: all three energies U_1, U_2, and U_3 are always positive (for all investigated models of correlation corrections). This means that the states represented by the phases considered (Fig. 1b–d) have a higher energy than the reference state, and thus the *decomposition* of Ag-E solid solution should occur. At the same time, the obtained data allow us to calculate the energy parameter $\widetilde{V}(0)$ needed to describe this decomposition. For details of methodology we refer to Ref. [5]. We get $\widetilde{V}(0) \approx -2.791$ eV for PWGGA correlation functional and three-layer magnesia slab. For the five-layer slab with the same correlation corrections. We get $\widetilde{V}(0) \approx -2.604$ eV that as compared with aforementioned result obviously demonstrates that three-layer slab is enough for thermodynamic predictions—the variation of the energy parameter is about 7%. This result proves also that the polarization effects are small in the case of Ag/MgO system. Table 3 illustrates the sensitivity of $\widetilde{V}(0)$ to the choice of correlation functionals used in the calculations with three-layer MgO slab. It is well seen that $\widetilde{V}(0)$ does not vary by more than 10% when different correlation corrections are used.

Table 3
The sensitivity of the Fourier transform of the mixing potential $\widetilde{V}(0)$ (eV) to the choice of the correlation corrections (the same as in Table 1). Data for the three-layer slab different a posteriori electron correlation corrections

Perdew–Wang GGA	Lee–Yang–Parr GGA	Perdew–Zunger LSD	Vosko–Wilk–Nusair LSD
−2.791	−2.828	−2.830	−2.944

4. Conclusions

To clarify the effect of the correlation corrections on the relative energies for some ordered phases, which define the phase competition in 2D solid solution that is formed in the Ag monolayer on (0 0 1) MgO surface we performed HF–CC

Table 2
The internal formation energies (eV) for three superstructures shown in Fig. 1b–d. The correlation functionals are the same as in Table 1

U (eV)	Different a posteriori electron correlation corrections and substrate models							
	Perdew–Wang GGA		Lee–Yang–Parr GGA		Perdew–Zunger LSD		Vosko–Wilk–Nusair LSD	
	Three-layer	Five-layer	Three-layer	Five-layer	Three-layer	Five-layer	Three-layer	Five-layer
U_1	0.552	0.518	0.566	0.474	0.433	0.408	0.426	0.409
U_2	1.031	1.058	1.029	0.973	0.865	0.906	0.865	0.904
U_3	0.828	0.821	0.843	0.782	0.716	0.718	0.716	0.718

calculations with different electron correlation functionals (LSD- and GGA-type) and compared the obtained results. We have shown that variation of the formation energies for considered phases does not exceed 25%, which does not affect the qualitative conclusions. We discussed also the sensitivity of the key energy parameter—Fourier transform of the mixing potential $\widetilde{V}(0)$ to the choice of correlation functionals. The effect of correlation corrections on the value $\widetilde{V}(0)$ is less than 10%. The sign of $\widetilde{V}(0)$ also remains the same confirming our conclusion about the spinodal decomposition mechanism of the formation of silver monolayer.

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