

# First principles slab calculations of the regular Cu/MgO(001) interface

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## Abstract

Ab initio slab calculations are performed for the copper adhesion over magnesium ions on the perfect MgO(001) surface with 1/4 monolayer (ML), two types of 1/2 ML and 1 ML substrate coverages. Results of our calculations are compared with various experimental and theoretical data. Both small atomic polarization and charge redistribution give the dominant contributions to the *physisorption* bonding on a regular Cu/MgO(001) interface.

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## 1. Introduction

Two types of the densely-packed copper/magnesia interfaces have been mainly studied so far, both experimentally and theoretically: Cu/MgO(001) and Cu/MgO(111) [1–14]. The adsorption of copper moieties on the MgO(001) support was analyzed by means of the Auger electron spectroscopy [1]. Theoretical studies of the copper/magnesia interfaces were performed mainly at the ab initio level [2,8–14]. The neutral and ionized Cu atoms on a perfect and defective MgO(001) sub-

strate were considered for the first time in Ref. [8], using the Hartree–Fock (HF) method and the finite-cluster model. Further studies [2,9–14] were mainly performed using the density functional theory (DFT). Thus, the DFT method was used [9] in calculations of several finite-clusters of Cu atoms over the MgO(001) surface. In similar calculations [10], the authors applied a cluster model embedded in an array of point charges, in order to get a reasonable reproduction of surface Madelung field in the cluster region.

Taking into account noticeable mismatch ( $\approx 15\%$ ) between the MgO and Cu lattice constants, a couple of recent theoretical studies considered not a simple monolayer coverage of a substrate by a metal (as it is commonly used for the Ag/MgO(001) interface characterized by

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almost equal lattice constants for both components [15,16]) but copper *clusters* distributed on densely-packed magnesia substrates. An adsorption of small  $\text{Cu}_n$  clusters ( $n \leq 13$ ) onto the  $\text{MgO}(001)$  substrate simulated by two-layer slab was studied using Car–Parinello method [11]. It was found that the adsorbate–adsorbate interaction dominates over the substrate–adsorbate interaction. A study [11] shows that the small copper clusters ( $n = 1–5$ ) are readily adsorbed on the  $\text{MgO}$  surface with the adsorption energy *per* Cu atom ( $E_{\text{ads}}$ ) varied in the range of 0.4–0.9 eV, whereas  $E_{\text{ads}}$  for larger clusters is always smaller than 0.4 eV *per* adatom. The embedded cluster models of the  $\text{Me}/\text{MgO}(001)$  interfaces [12] were used in simulations on a *physisorption* of metal atoms on the regular magnesia substrate (including Cu adsorption) and a *strong binding* of metal atoms in the vicinity of anion oxygen vacancies with trapped two or one electrons (the so-called  $F_s^-$ - or  $F_s^+$ -centers, respectively). Both *ab initio* DFT and semi-empirical molecular-orbital MSINDO calculations [13] were applied to simulate various  $\text{Cu}_n$  clusters ( $n \leq 52$ )

on a  $(8 \times 8 \times 3)$   $\text{Mg}_{96}\text{O}_{96}$  cluster of the magnesia(001) substrate. Another, periodic mismatch alternative for the  $\text{Cu}/\text{MgO}(111)$  interface has been suggested, based on the experimental observations by means of the high-resolution transmission electron microscopy (HRTEM) and following HRTEM images' simulations [5]. The copper structure above the O-terminated magnesia substrate resembles a triangular network of  $1/6(1\ 1\ 0)$  partial dislocations along  $(1\ 1\ 0)$  directions. Comprehensive simulation of the  $\text{Cu}/\text{MgO}(222)$  interface has been also carried out [14].

Our paper is devoted to the *periodic slab calculations* of the regular  $\text{Cu}/\text{MgO}(001)$  interface. The Cu adhesion over Mg sites (Fig. 1) was chosen due to an obvious lack of information on the charge transfer and energetics of these sites. It is well-known fact that the most attractive sites for the metal adhesion on  $\text{MgO}(001)$  surface at low coverages are oxygen ions. But one should keep in mind that due to a large mismatch of the Cu and  $\text{MgO}$  lattice constants the adhesion over the  $\text{Mg}^{2+}$  ions also becomes possible. Another argument in

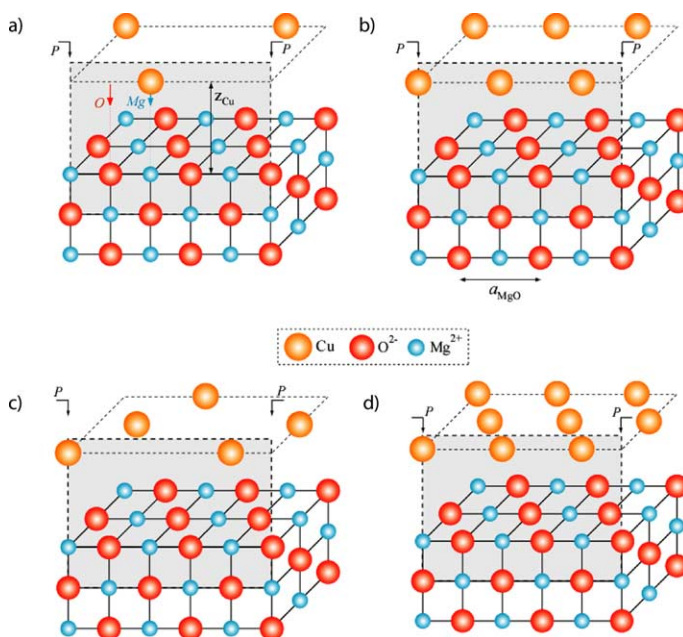


Fig. 1. Fragments of the regular  $\text{Cu}/\text{MgO}(001)$  interface with  $1/4$  ML (a),  $1/2$  net ML (b),  $1/2$  striped ML (c), and  $1$  ML (d) substrate coverages where Cu atoms are placed at the distance  $z_{\text{Cu}}$  above surface  $\text{Mg}^{2+}$  ions. The plane  $P$ – $P$  shown by dashed lines and gray background was used for construction of the difference electron density plots shown in Fig. 3. (For a colour version of the figure see the online paper.)

favor of this study is the probability to occupy the sites over Mg during Cu evaporation with a high rate. We focus on both the sub-monolayer and monolayer substrate Cu coverages and study the trends in the adhesion behavior and bonding as the amount of Cu above the oxide is varied. This study sheds more light on the physics underlying the properties of the Cu film on insulating substrate. For this purpose, we perform periodic DFT calculations as implemented into the CRYSTAL98 code [17].

## 2. Details of simulations

In the DFT-LCGTF method (each crystalline wave function is constructed as a linear combination of atom-centered Gaussian-type functions, GTF), the exchange and correlation potentials are included directly in the crystal Hamiltonian and then the Kohn–Sham equations are solved self-consistently. The choice of exchange and correlation functionals is an important issue for the interface calculations. The earlier-developed and widely used local density approximation (LDA) includes functionals that depend on the electron density only [18]. It is well suited for homogeneous media like bulk metals but its deficiency for heterogeneous systems like the interface between Cu and MgO(001) has to be taken into account. (Since LDA calculations usually underestimate the energy gap between the highest occupied and the lowest empty states and the width of the valence band for insulators (including MgO), a special *GW* correction based on the formalism of Green functions was used previously, to overcome this artifact [19,20].) The main focus of this paper is the *energetics* of the Cu adhesion on oxide surfaces. This is why we use here the non-local generalized gradient approximation (GGA) available in CRYSTAL code for both exchange and correlation functionals [17]. The GGA approach has shown very good results in previous CRYSTAL-DFT calculations on the metal reactivity [21,22] and metal adhesion energetics on the metal oxide interfaces [23]. The most adequate description of the regular Cu/MgO(001) interface was achieved by us when combining the Becke exchange func-

tional [24] with the Lee–Yang–Parr correlation functional [25].

Another crucial point in interface calculations was found to be a correct choice of the basis sets (BSs) used in Gaussian-type functions for copper, magnesium and oxygen. First, we carefully re-optimized the all-valence BS for Cu developed recently [22] using a small Hay–Wadt pseudopotential [26] for the reduced core of copper atom. It was done since all our attempts to use BS [22] for an adequate description of the Cu/MgO(001) interface (including recent HF-CC calculations [27]) were unsuccessful, even after a particular optimization of this BS. Sub-valence, valence and virtual shells for bulk Cu presented by 4111sp–41d GTFs were totally re-optimized by us using the recently developed code ParOptimize [28] interfaced with CRYSTAL98. It implements conjugated gradients optimization technique [29] with a numerical computation of derivatives. Fitting of the optimized basis set for the current interface calculations has been checked by computing both mechanical properties of copper crystal (lattice constant, bulk modulus, elastic constants and adhesion energy) as well as its band structure and other electronic properties. On the other hand, the all-valence BSs for MgO (8s–511sp and 8s–411sp for magnesium and oxygen, respectively) optimized earlier [30] for CRYSTAL calculations were found suitable for the current calculations and we only slightly re-optimized their external shells for both Mg and O. The same properties of bulk MgO as mentioned above for Cu also serve as a good test to estimate the fitting of the corresponding BSs. When trying to extend the basis sets for MgO by including polarization functions for 3d virtual states of both magnesium and oxygen, the basic properties of bulk magnesia have not been changed noticeably and thus we did not include them in our further calculations, in order to avoid unnecessary computational expenditures.

Both copper and magnesia bulk crystals possess a face-centered cubic (fcc) lattice structure. *Copper* is a typical transition metal with high conductivity provided by 4s<sup>1</sup>3d<sup>10</sup> valence electrons (according to our estimate, electronic population *per* one pair of Cu atoms in the framework of Mulliken analysis has been found to be  $p_{\text{Cu-Cu}} = 0.09$  e). Com-

parison of our DFT-LCGTF calculations with the previously published data show that our results are as good as other theoretical simulations, despite the fact that we use a reduced basis set when applying small Hay–Wadt pseudopotential for constructing the crystalline wave function for Cu. The band structure of bulk copper may be considered as another effective test of the validity of Cu BS. It has been calculated for the optimized value of the lattice constant  $a_{\text{Cu}}$  (3.68 Å). Quantitatively our results almost coincide with a band structure topology obtained in the first principles calculations on bulk Cu [22,31], except for some of the upper energy curves. The calculated width of the conduction band  $\Delta\varepsilon_{\text{CB}}$  is found to be  $\sim 9.40$  eV, which is in a good agreement with both theoretical result 9.35 eV [31] and experimental estimate  $8.59 \pm 0.41$  eV [32]. According to theoretical estimates for *bulk MgO* [30] that is a typical ionic crystal, the charge transfer lies in the range 1.9–2.0 e, whereas our calculations give 1.91 e for bulk magnesia and 1.85–1.9 e for non-polar MgO(001) substrate. The optimized values of  $a_{\text{MgO}}^{(0)}$  and  $B_{\text{MgO}}$  for magnesia and their comparison with earlier experimental and theoretical data show rather good agreement. Band structure of bulk magnesia was calculated for the optimized value of  $a_{\text{MgO}}^{(0)} = 4.24$  Å. We qualitatively reproduce direct energy gaps for  $\Gamma$ ,  $L$  and  $X$  points in the first Brillouine zone:  $\Delta\varepsilon_{\text{g}}^{(\Gamma)} = 6.9$  eV (theoretical and experimental values 8.2 [20] and 7.7 eV [33]),  $\Delta\varepsilon_{\text{g}}^{(L)} = 12.8$  eV (12.5 [20] and 10.8 eV [33]), as well as  $\Delta\varepsilon_{\text{g}}^{(X)} = 14.7$  eV (14.3 [20] and 13.3 eV [33]). Thus, our calculations on bulk Cu and MgO properties are quite satisfactory and we can use the BSs of copper and magnesia for qualitative study of the regular Cu/MgO(001) interface.

In spite of a space compatibility within the coherent Cu/Mg(001) interface, the mismatch of the lattice constants,  $a_{\text{Cu}}$  and  $a_{\text{MgO}}$  (3.6 Å vs. 4.2 Å [34]) results in a strained structure of a metal film. This is why such an interface is very likely completely incoherent or semi-coherent (with misfit dislocations) [35]. However, this is not relevant for the adsorption of *single* pseudo-isolated Cu atoms on substrate, therefore the regular models of 1/4 ML and 1/2 net ML coverages of the perfect MgO(001) surface (Fig. 1a and b) are well justifi-

fied for a simulation of the interaction between Cu atom and oxide substrate. The reason for the model of strained Cu coverages, 1/2 striped ML and 1 ML (Fig. 1c and d), is further comparative analysis of the interfacial properties when increasing concentration of metal atoms on oxide substrate, which is necessary to clarify the trend in the Cu/MgO bonding properties. Moreover, as follows from the symmetry considerations and from the Lifshitz criteria [36], both strained adsorbate configurations (striped 1/2 ML and 1 ML) are stable with respect to a formation of antiphase domains in Cu-“empty site” solid solution (analogously to our simulation of silver aggregation on the perfect MgO(001) substrate [16]) that may be considered as the Ising lattice above the MgO(001) surface.

In our theoretical simulations of the perfect MgO(001) substrate, we use three-layer slab which has a 2D periodicity. The choice of the MgO(001) slab was justified by a comparison of the results of calculations for three-, five- and seven-layer magnesia slabs with one- and two-sided metal coverages [37]. Since they were found to be qualitatively close, we have chosen the model which needs smaller computational resources and permits us to make more careful structural optimization. Since one-side copper coverage of magnesia slab, which we consider, was varied from 1/4 ML to a 1 ML, we have made a series of calculations for a  $2 \times 2$  extended surface unit cell of MgO(001). Fig. 1a–d show copper atom positions over surface  $\text{Mg}^{2+}$  ions. For all these structures we have carried out the 2D optimization of the total energy  $E_{\text{tot}}(a_{\text{MgO}}, z_{\text{Cu}})$  as a function of the substrate lattice constant  $a_{\text{MgO}}$  and the interfacial distance  $z_{\text{Cu}}$ . For the MgO substrate, we optimize the total energy  $E_{\text{tot}}(a_{\text{MgO}})$  as a function of the lattice constant. Similar to our recent simulations on the Ag/MgO(001) interface [15,16], we neglect here magnesia surface relaxation, which was earlier found to be rather small [38].

### 3. Results

In Table 1, we summarize the main properties of the Cu/MgO(001) interface obtained using

Table 1

Main properties of the Cu/MgO(001) interface with Cu atoms above  $\text{Mg}^{2+}$  ions (Fig. 1) as calculated using the DFT-LCGTF method and a comparison with previous results

Substrate coverage		Interface distance, $z_{\text{Cu}}$ (Å)	Adhesion energy <i>per</i> Cu atom, $E_{\text{adh}}^{\text{a}}$ (eV)	Charge transfer, $\Delta q_{\text{Cu}}^{\text{b}}$ (e)
0.25 ML	This paper	2.63	0.48	−0.03
	Li et al. [9]	2.5	0.5	~
	Zhukovskii et al. [27]	2.35	0.62	−0.01
0.5 ML	Net configuration	2.38 (2.68) <sup>c</sup>	0.42 (0.37) <sup>c</sup>	−0.016 (−0.013) <sup>c</sup>
	Striped configuration	2.78	0.26	−0.01
1 ML	This paper	2.98	0.13	−0.003
	Benedek et al. [14]	3.20	0.2	−0.06
	Zhukovskii et al. [27]	2.69	0.16	−0.005

<sup>a</sup> The adhesion energy is given *per* Cu adatom.

<sup>b</sup> A positive sign means an excess of the electron density as compared to a neutral atom.

<sup>c</sup> Values in parentheses correspond to second minimum on the energy curve (Fig. 2).

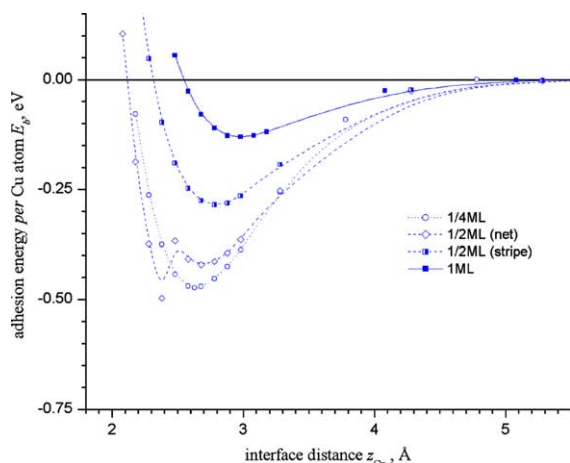


Fig. 2. The Cu/MgO(100) interface energy  $E_b(z_{\text{Cu}})$  *per* atom as a function of  $z_{\text{Cu}}$  for four different Cu configurations over surface  $\text{Mg}^{2+}$  ions on the MgO(001) substrate: 1/4 ML, 1/2 net ML, 1/2 striped ML, and 1 ML. The potential energy curves were drawn using the standard B-spline plotting option.

DFT-LCGTF method and their comparison with previous results. There is a marked qualitative difference in the adsorption nature at different copper coverages over surface  $\text{Mg}^{2+}$  ions (Fig. 2). A direct interaction energy between Cu adatoms and surface  $\text{Mg}^{2+}$  ions varies in the interval of 0.13–0.48 eV *per* adatom. Additionally, we have observed a noticeable bond population between nearest Cu atoms (0.075 e *per* atom) within the

metal plane at 1 ML coverage (Fig. 1d), which is not sensitive to a particular adsorption site. This monolayer reveals a conducting behavior, which could be important for microelectronic applications. The value of Cu–Cu bond population is smaller as compared with the Ag layer on MgO(001) surface (0.1 e [15]), which could be caused by a strain in 1 ML (since the lattice constants of silver and magnesia almost coincide). That is, our calculations confirm one general conclusion of previous studies on a comparatively small bonding (<0.7–1.4 eV) across the regular interface. The adhesion is physical in its origin and may be explained by a relatively weak polarization of copper adatoms (Fig. 3).

For a superlattice with a 1/4 ML coverage (Fig. 1a), the interatomic electron density concentration between Cu atoms is practically absent (Fig. 3a), and therefore its attraction or repulsion from the nearest substrate ions play no longer any role. For such a low Cu coverage over  $\text{Mg}^{2+}$  ions, there is a single nearest substrate neighbor ( $\text{Mg}^{2+}$  ion) and four next-nearest substrate ions of the opposite type ( $\text{O}^{2-}$  sites). We found that the adsorption of Cu atop  $\text{Mg}^{2+}$  ions for regular 1/2 net ML (Fig. 1b) results in an unusual *two* local minima on the energy curve vs.  $z_{\text{Cu}}$  (Fig. 2). This could be explained by a delicate interplay of the electrostatic attraction and repulsion of the polarized and slightly charged Cu adatoms with surface  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. This is also caused by the interplay

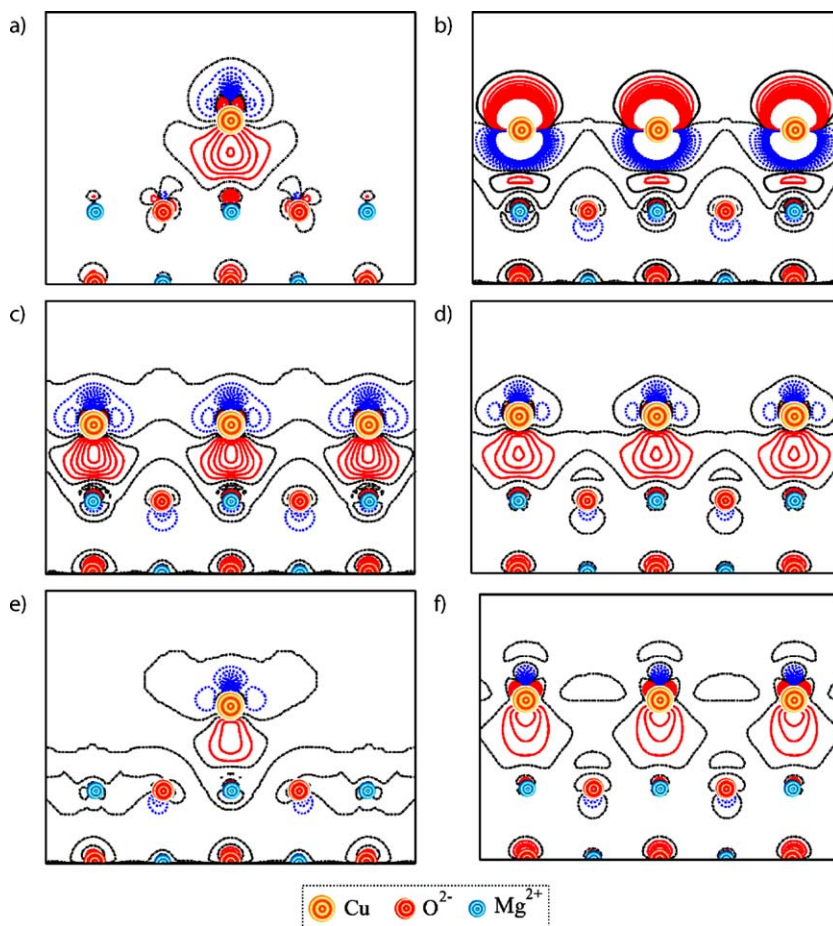


Fig. 3. The difference electron density maps  $\Delta\rho(\mathbf{r})$  (the total density minus a superposition of the densities for the isolated Cu and MgO slabs) in the cross-section perpendicular to the (001) interfacial plane (Fig. 1a–d): (a) 1/4 ML; (b–d) for 1/2 net ML, density plots are shown for three different distances over a  $\text{Mg}^{2+}$ , which correspond to two local minima on the energy curve shown in Fig. 2 (b,d) and saddle point between them (c); (e) 1/2 striped ML; (f) 1 ML. Isodensity curves are drawn from  $-0.05$  to  $+0.05$  e.a.u. $^{-3}$  with increments of  $0.001$  e.a.u. $^{-3}$ . The full, dashed, and chained curves show positive, negative and zero difference electron densities, respectively. (For a colour version of the figure see the online paper.)

of different spin states (the energy minimum at  $2.38$  Å closest to the surface corresponds to the triplet state whereas the more remote minimum at  $2.68$  Å as well as the most of other points on the energy curve shown in Fig. 2 belong to the singlet state). Existence of these two local minima on the adhesion curve reflects the complicated nature of the change of the polarization of interacting atoms. When Cu approaches the  $\text{MgO}(001)$  surface above  $\text{Mg}^{2+}$  this polarization change is not monotonic and is linked to the repolarization of

Cu atom. The detailed analysis of the electronic density maps (Fig. 3b–d) shows that the minimum closest to the surface is characterized by the substantial Cu electronic charge repulsion from the surface, the Cu atom becomes a highly polarized dipole. Contrary, at another minimum the Cu atom coming to the surface of MgO reveals the quadrupole interactions with the surface. Due to a mismatch between the lattice constants of Cu and MgO in the case of 1/2 striped ML (Fig. 1c) and 1 ML coverage, the relevant binding energy

per adatom are essentially smaller than those for 1/4 ML and 1/2 net ML (Fig. 2).

Our calculations show that all Cu configurations over surface  $\text{Mg}^{2+}$  ions are stable and have negative formation energy. The most stable is the interface with a 1/4 ML coverage. The striped configuration of 1/2 Cu ML is the energetically favorable as compared with a regular net configuration (this is true for a ratio of total energies  $E_{\text{tot}}$  but not for the adhesion energies  $E_{\text{adh}}$  whose ratio is opposite, i.e. less favorable, as shown in Fig. 2), although both configurations simulate the disposition of the same amount of Cu in a submonolayer. The equilibrium distance of 1/2 striped ML from the  $\text{MgO}(001)$  slab ( $z_{\text{Cu}} = 2.72 \text{ \AA}$ ) is somewhat larger than the remote minimum of 1/2 net ML ( $z_{\text{Cu}} = 2.68 \text{ \AA}$ ), due to different local environments of Cu atom in these two configurations (cf. Fig. 1b and c). Relative stability of 1/2 striped ML as compared with 1/2 net ML allows us to conclude about the tendency to form Cu clusters at sub-monolayer coverage. At the same time, the formation of Cu–Cu bonds at the distances corresponding to  $\text{MgO}$  substrate is unfavorable as compared with the length of these bonds in Cu bulk. This is why the Cu sub-monolayer seeks to increase its distance from the substrate and thus to reduce the  $E_{\text{adh}}$ . Fig. 2 illustrates the increase of the distance of the Cu layer from the underlying  $\text{MgO}$  slab with the (001) terminated surface as the atomic fraction of Cu increases. This may be considered as the result of a delicate balance of the charge re-distribution and the response of the system on the increase of the strain energy due to a mismatch in the initial stages of the Cu film growth—the increasing atomic fraction of Cu in a layer forces the metal layer to move away from the substrate.

#### 4. Summary

In this study we combined the periodic slab model and the first principles DFT-LCGTF method for the comprehensive description of the regular  $\text{Cu}/\text{MgO}(001)$  interface where Cu adatoms are placed over surface  $\text{Mg}^{2+}$  ions. The general conclusion of our simulations is that there

is no strong ionic bonding on the defectless interface between metal and metal oxide. Due to mismatch between the lattice constants of Cu and  $\text{MgO}$  crystals the absolute values of the adhesion energy per adatom for the 1/2 striped ML and 1 ML are essentially smaller than those for the 1/4 ML and 1/2 net ML where copper atoms may be considered as quasi-isolated. Our periodic DFT results are in a qualitative agreement with earlier experimental and theoretical studies on the  $\text{Me}/\text{MgO}$  interfaces, including our previous ab initio Hartree–Fock simulations on  $\text{Ag}/\text{MgO}(001)$  interface [15,16].

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