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# First principles simulations of 2D Cu superlattices on the MgO(0 0 1) surface

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## Abstract

First principles slab simulations of copper 2D superlattices of different densities on the perfect MgO(0 0 1) surface are performed using the DFT method as implemented into the CRYSTAL98 computer code. In order to clarify the nature of interfacial bonding, we consider regular 1/4, 1/2 and 1 monolayer (ML) coverages and compare results of our calculations with various experimental and theoretical data. Our general conclusion is that the physical adhesion associated with a Cu polarization and charge redistribution gives the predominant contribution to the bonding of the regular Cu 2D layer on the MgO(0 0 1) surface.

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**Keywords:** *Ab initio* calculations; Cu; MgO(0 0 1) surface; Copper adhesion; Superlattice

## 1. Introduction

Considerable part of numerous copper technological applications [1] is based on Cu epitaxial films grown on nonconducting substrates. These include integrated circuits and device structures, such as tunneling magnetoresistance devices (TMR) [2,3]. The Cu/MgO interface is also of great importance for such technological applications as catalysis, metal–matrix composites, recording media, etc. [4]. One of important problems is the understanding of the charge redistribution in the metallic thin film, which has a

great impact on its conductivity and also affects catalytic ability. Stability of metal films on oxide surfaces and their properties markedly depend on the adhesion nature, mechanical support, both heat and charge carrier transport across the interface, as well as its specific morphology.

Two types of the copper/magnesia interfaces are mainly studied experimentally and theoretically: Cu/MgO(0 0 1) and Cu/MgO(1 1 1) [5–18]. In the former case, oxide surface is non-polar, due to successive alternation of Mg<sup>2+</sup> and O<sup>2-</sup> ions on each magnesia (0 0 1) plane. The adsorption of copper on the MgO(0 0 1) support was analyzed using Auger electron spectroscopy (AES) [5] and spatially resolved electron energy loss spectroscopy (HREELS) [6]. On the other hand, the MgO(1 1 1) surface may be either

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$\text{Mg}^{2+}$ - or  $\text{O}^{2-}$ -terminated, thus the polar interface between copper and magnesia has a larger bonding energy than the non-polar one [7]. Due to mismatch of the lattice constants  $a_{\text{Cu}}$  and  $a_{\text{MgO}}$  (3.6 Å versus 4.2 Å), high-resolution transmission electron microscopy's (HRTEM) observations and further simulations of atomic images [8] predict a triangular network of 1/6 (121) partial dislocations along the [1 1 0] directions for the periodic copper structure above the O-terminated magnesia (1 1 1) substrate. Growth of MgO precipitates in a Cu matrix under the internal oxidation has been observed using the high-resolution atom-probe field ion microscopy (AFM) [9], HRTEM [10], and HREELS [11]. These studies reveal presence of the Cu/MgO(1 1 1) interfaces (with preferable  $\text{O}^{2-}$ -termination of magnesia substrate), and do not indicate presence of Cu/MgO(0 0 1). Microcalorimetric studies of Cu on MgO were performed, in order to measure directly both the energetic stability of adatoms on the substrate and the adhesion energy [12], which clarify the structural and chemisorption properties.

Theoretical studies of copper films on a magnesia substrate were mainly performed at the ab initio level [7,13–19]. Using Hartree–Fock (HF) method and a finite-size *cluster* model, Bacalis and Kunz [13] considered neutral and ionization states of Cu atom on the perfect and defective MgO(0 0 1) substrates. For the perfect MgO, the adsorption energy per copper atom positioned over  $\text{O}^{2-}$  ion was estimated to be rather small (0.38 eV). Further simulations [7,14–19] were mainly performed using Density Functional Theory (DFT). Li et al. [14] applied the DFT method for cluster calculations of Cu atom on the MgO(0 0 1) surface. In analogous simulations, Rösch et al. [15] applied a cluster model embedded into a large array of point charges. At the same time, Benedek et al. [7] performed the DFT calculations for the *periodic slab* models of the Cu/MgO(1 1 1) and Cu/MgO(0 0 1) interfaces and found strong sticking of copper atoms to the (1 1 1) surface of magnesia substrate, by a factor of 3 larger than that on the (0 0 1) surface.

Taking into account a noticeable mismatch between the lattice constants of MgO and Cu ( $\approx 15\%$ ), a couple of recent theoretical studies considered copper clusters on densely-packed magnesia substrates instead of the monolayer coverage of substrate by a metal (as it was done for the Ag on MgO(0 0 1) surface with almost

equal lattice constants for both components [20,21]). Using the Car–Parinello method, which combines DFT and a molecular dynamics techniques, Musolino et al. [16] have studied the adsorption of small  $\text{Cu}_n$  clusters ( $n = 13$ ) onto the MgO(1 0 0) substrate simulated by a two-layer slab. It was found that the competition between adsorbate–adsorbate and substrate–adsorbate interactions turns in favor of the former. The interaction between copper atoms inside the clusters determines the metal adsorption process. This is one of the reasons why three-dimensional (3D) structures are preferred in these simulations as compared to two-dimensional (2D): the energy gain due to bonding of copper atoms exceeds that due to 2D metal adsorption on oxygen surface ions. As it is shown [16], small copper clusters ( $n = 1–5$ ) are adsorbed on the MgO surface with the energies per Cu atom ( $E_{\text{ads}}$ ) ranging in the interval 0.4–0.9 eV, whereas for larger clusters,  $E_{\text{ads}}$  is always smaller than 0.4 eV per adatom. Matveev et al. [17] used the embedded cluster model of the Cu/MgO(0 0 1) interface for simulating both copper clustering on a regular magnesia substrate and a strong localization of metal atoms in the vicinity of anion oxygen vacancies with two and one trapped electrons (so-called  $F_s^-$  and  $F_s^+$ -centers, respectively) [17]. Jug and co-workers [18] used both first principles DFT and semi-empirical MSINDO calculations for simulating various  $\text{Cu}_n$  clusters ( $n \leq 52$ ) on a ( $8 \times 8 \times 3$ )  $\text{Mg}_{96}\text{O}_{96}$  cluster modeling the magnesia (0 0 1) substrate. It was found that the sticking probability of copper atoms to the MgO surface is reduced with an increase of substrate coverage since all adatoms cannot be adsorbed atop the oxygen ions. Instead, the Cu–Cu binding is invoked. At the first step, the growth of double layer takes place, on top of which formation of an *island* of metal atoms is expected. Comprehensive simulation of the Cu/MgO(222) interface has been carried out by Benedek et al. [19]. The periodic calculations were performed for both regular and semi-regular interfaces which mimic the lattice constant mismatch of the real system: a  $5 \times 5$  copper layer unit cell (UC) was placed on a  $4 \times 4$  magnesia UC. The terminating  $\text{O}^{2-}$ -layer as well as the surface Cu-layer exhibit warping albeit on a scale of less than 0.1 Å. It was also found that the surface atoms in relatively coherent regions move towards the interface and those in regions of poorer fit move outwards.

## 2. Method

Our present study is devoted to the periodic slab simulations of the regular 2D Cu superlattices on the MgO(0 0 1) substrate. We model both submonolayer and monolayer substrate coverages and also analyze isolated Cu slabs and MgO. For this aim, we perform the periodic DFT calculations as implemented in CRYSTAL98 code [22] with Gaussian-type basis set. An essential advantage of this code is its treatment of isolated 2D slabs, without the artificial slab periodicity in the  $z$  direction perpendicular to the surface, employed in most plane-wave surface calculations. Our previous studies of metals on oxide supports done in the framework of the periodic Hartree–Fock method with a posteriori electron correlation corrections (HF-CC) have combined the calculations of the electronic structure of regular 2D metallic layers deposited on the perfect and defective metal oxide surfaces [20] with thermodynamic theory of metal film growth on oxide substrate [21]. This approach allowed us to predict conditions for the metal atoms aggregation into clusters, and to estimate the metal density therein.

We use the DFT computational scheme combined with the non-local Generalized Gradient Approximation (GGA) for both correlation and exchange functionals. This approach gave very reasonable results in the DFT CRYSTAL simulations on the metal reactivity and the metal adhesion on oxide surfaces [20]. The most adequate description of the regular 2D Cu layer on the MgO(0 0 1) surface has been achieved by us when combining the non-local Becke exchange functional [23] with the correlation functional by Lee et al. [24].

Another crucial point of our simulations was the correct choice of the basis sets (BSs) for GTFs used for Cu, Mg and O. First, we carefully re-optimized all-valence BS for copper recently presented by Doll and Harrison for both DFT and HF calculations on the Cl/Cu(1 1 1) interface [25], using the small Hay–Wadt pseudopotential [26] for the Cu core. It was a necessary step due to failure of all our attempts to use the BS [25] for an adequate description of the Cu layers on the MgO(0 0 1) substrate, even after its partial optimization. At the same time, we have a quite positive experience with the small Hay–Wadt pseudopotential for silver atoms in modeling the Ag/MgO(0 0 1) system [20,21]. Sub-valence, valence and virtual shells

for bulk Cu presented by 4111sp-41d GTFs were totally re-optimized using a novel code ParOptimize [27] interfaced with the CRYSTAL98 package. It implements conjugated gradients optimization with a numerical computation of derivatives [28]. On the other hand, all-valence BSs for MgO optimized elsewhere for the CRYSTAL calculations [29] (8s-511sp and 8s-411sp for magnesium and oxygen, respectively) were found to be suitable for the current simulations and we only slightly re-optimized their external shells.

## 3. Model

Both Cu and MgO crystals possess a face-centered cubic (fcc) lattice structure, which belongs to the space symmetry group  $Fm3m$ . As mentioned above, there is a large (15%) mismatch of the Cu and MgO bulk lattice constants. This is why a real interface is very likely completely incoherent or semicoherent (with misfit dislocations) [30]. Nevertheless, this is not relevant for the adsorption of single pseudo-isolated Cu atoms on substrate, therefore regular “net” models of 1/4 ML and 1/2 ML coverages of the perfect MgO(0 0 1) surface (Fig. 1a and b) are justified for the simulation of the interaction between a single Cu atom and an oxide substrate. We simulated also two *strained* adsorbate configurations: striped 1/2 ML and 1 ML (Fig. 1c and d), necessary for further analysis of the trend in the Cu/MgO bonding properties as the metal atom concentration increases. The reason for a study of strained adsorbate configurations is a comparative analysis of the trend in interfacial properties as the function of an increasing concentration of metal atoms on oxide substrate, modeled in the framework of the periodic slab model.

In our theoretical simulations of the perfect MgO(0 0 1) substrate, we have applied three-layer slab which has a 2D periodicity in the  $x, y$  plane (Fig. 1). In order to simulate a one-side copper adsorption on a magnesia slab with a coverage varied from 1/4 ML to a 1 ML, we made a series of calculations for the  $2 \times 2$  extended surface unit cell. For all Cu coverages, we have carried out the total energy optimization according to the procedure [27,28] mentioned in the previous section. For the metal/oxide system, this means a 2D optimization of the total

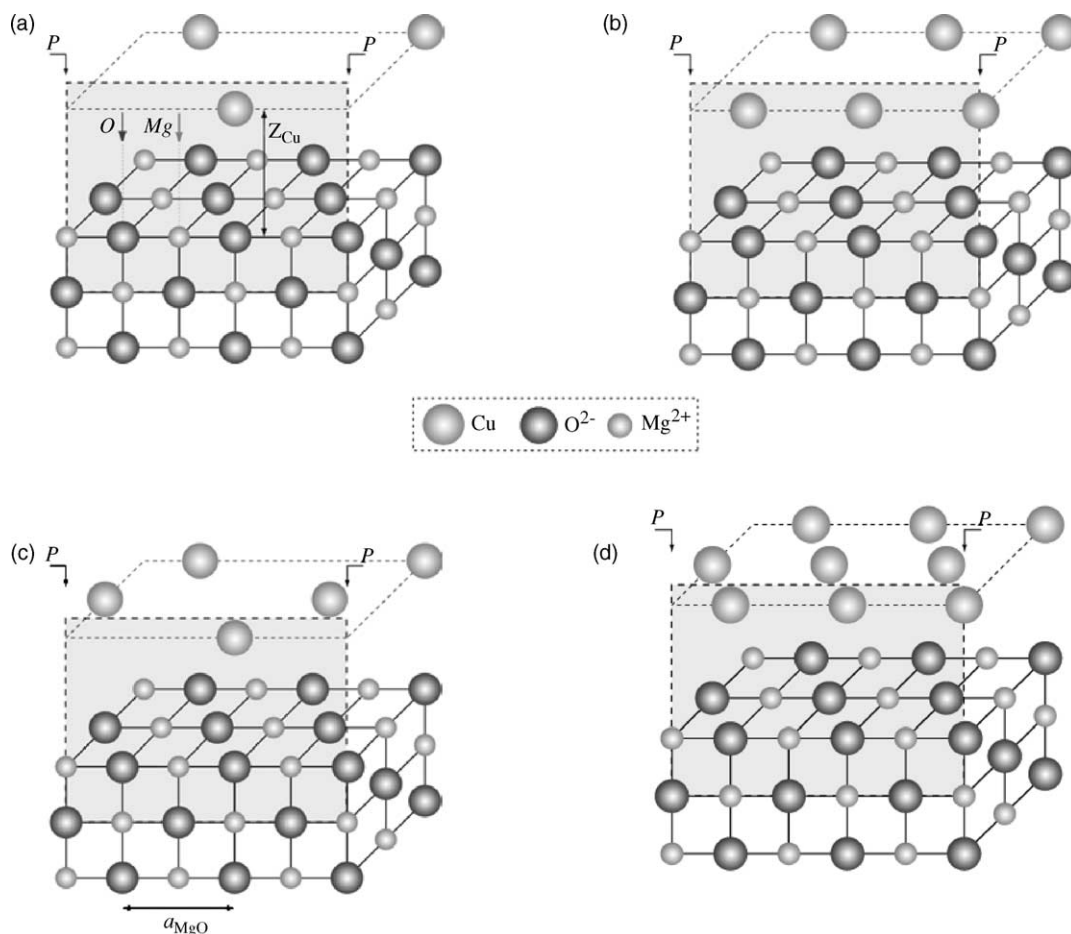


Fig. 1. Fragments of the regular 2D Cu superlattices on the MgO(0 0 1) support with 1/4 ML (a), regular “net” and striped 1/2 ML (b, c), and 1 ML (d) coverages where Cu atoms are placed in a plane at the distance  $z_{\text{Cu}}$  above surface  $\text{O}^{2-}$  ions. Another possible adsorption position above surface  $\text{Mg}^{2+}$  ions is not shown. All these configurations are cross-sectioned by the same plane  $P$ – $P$  limited by dashed lines and gray background that was used for construction of the difference electron density plots shown in Fig. 2.

energy as a function of the substrate lattice constant  $a_{\text{MgO}}$  and the Cu distance from the substrate ( $z_{\text{Cu}}$ ). For the MgO substrate, we optimize the total energy  $E_{\text{tot}}(a_{\text{MgO}})$  as a function of the lattice constant. We found that for all calculated Cu coverages the equilibrium value of the  $a_{\text{MgO}}$  remains the same, 4.16 Å, while the optimized  $z_{\text{Cu}}$  considerably changes.

#### 4. Main results

Our simulations confirm the general conclusion of previous theoretical studies of various metal/oxide

interfaces indicating the energy preference for the Cu atom adhesion over the surface  $\text{O}^{2-}$  ions. We observe a marked difference in the adhesion energies  $E_{\text{adh}}$  at low coverages, as Cu adatoms are placed either over surface  $\text{Mg}^{2+}$  or  $\text{O}^{2-}$  ions. For a low, 1/4 ML coverage over both sites, Cu atom has a single substrate neighbor (either  $\text{O}^{2-}$  or  $\text{Mg}^{2+}$  ion) and four next-nearest substrate ions of the opposite type (either  $\text{Mg}^{2+}$  or  $\text{O}^{2-}$ ). In this case, the energy of Cu adsorption over  $\text{Mg}^{2+}$  ions is 0.48 eV, by 30% smaller than that over  $\text{O}^{2-}$  ions (0.62 eV). This is accompanied by a substantial decrease of the equilibrium Cu distance from the surface (2.63 and 2.08 Å, respectively).

Results of our calculations performed for Cu configuration over  $\text{Mg}^{2+}$  ions are quantitatively close to the LDA plane wave calculations for cluster model of 1/4 ML [14] and 1 ML slab [7]. However, the same LDA studies give noticeably larger Cu adhesion energy over  $\text{O}^{2-}$  ions (1.4 eV [14] and 1.0 eV [7], respectively). The corresponding value defined using GGA cluster calculations (0.8 eV [17]) is much closer to our result.

As Cu coverage increases from 1/4 ML to 1/2 ML (a regular “net” distribution), the adhesion energy over  $\text{O}^{2-}$  ions increases up to 0.65 eV. This can be explained by an additional interaction between  $\text{Mg}^{2+}$  ions and an excess electron density concentrated in the interstitial positions between Cu atoms for 1/2 ML (see Fig. 2 and discussion below). We also found that the adsorption of Cu atop  $\text{Mg}^{2+}$  ions for a regular 1/2 ML results in an unusual two local minima on the potential  $E_{\text{adh}}$  curve versus  $z_{\text{Cu}}$ , which may be explained by the delicate interplay of the electrostatic attraction and repulsion of polarized and slightly charged Cu adatoms with surface  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions in this case. Two local minima on the energy curve for 1/2 Cu ML above the  $\text{Mg}^{2+}$  ions reflect the complicated nature of the Cu electronic structure: when adatom approaches the surface, its polarization changes non-monotonically and switches from the dipole to higher order (quadrupole) interactions. For the striped 1/2 ML and 1 ML configurations, the energies of Cu adhesion over  $\text{O}^{2-}$  ions are considerably smaller (0.37 and 0.33 eV, respectively). Very likely, this is due to the stress effect and/or specific features of the electron charge density redistribution in artificially extended metal “stripe” or monolayer. The relevant Cu distances from the MgO substrate (2.25 and 2.36 Å) considerably exceed those for the regular 1/2 ML and 1/4 ML.

The calculated Mulliken charges on Cu atoms for 1/4 ML and 1/2 ML coverages indicate either a negligible charge transfer towards adatoms over surface  $\text{O}^{2-}$  ions, or very small charge donation towards a substrate, in other 2D configurations. The difference electron charge distributions shown in Fig. 2 give the most convincing argument in favor of a decisive role of the electrostatic interaction between polarized Cu atoms and surface  $\text{O}^{2-}$  ions as the physisorption mechanism of copper thin film adhesion. The electron bond populations between metal atoms and substrate ions across the interface are practically zero. On the

other hand, there is charge redistribution *within* the metal layer. The electron density plot for 1/4 ML (Fig. 2a) indicates that at low coverages, single adatoms are markedly perturbed when are placed atop nearest  $\text{O}^{2-}$  ions and do not affect significantly the electronic shells of  $\text{Mg}^{2+}$  ions. The contribution of the subsurface substrate ions to the bonding of Cu adatoms is also negligible. Fig. 2c corresponds to the regular “net” 1/2 ML above  $\text{O}^{2-}$  ions and clearly demonstrates the appearance of an additional extra charge spread between the Cu atom positions as coverages grows up (cf. Fig. 2a and c). This coverage reveals the tendency to increase the conducting properties of the Cu submonolayer when its atomic fraction increases. The electronic density redistribution is well pronounced as the coverage increases (Fig. 2c and g), which results in the electrostatic attraction between the enhanced electron density concentrated around the hollow metal sites, and the  $\text{Mg}^{2+}$  ion below it. On the other hand, for the 1/2 ML and 1 ML adsorption over the  $\text{Mg}^{2+}$  ions, the repulsion arises between the interatomic electron density and the substrate  $\text{O}^{2-}$  ion below it (Fig. 2d and h).

Additionally, we have observed a noticeable bond population *between* nearest Cu atoms (0.075e per adatom) within the metal plane at the 1 ML coverage, which is not sensitive to the particular adsorption site. The value of Cu–Cu bond population is smaller as compared with the Ag layer on MgO(0 0 1) surface (0.1e [20]), which could be caused by a strain in Cu monolayer, whereas lattice constants of silver and magnesia almost coincide. That is, our calculations confirm one of conclusion from previous studies: a comparatively weak bonding across the regular interface between copper and magnesia substrate. The adhesion is physical in its origin and may be arise due to a comparatively weak polarization of Cu adatoms.

Moreover, our calculations show that the striped configuration of 1/2 ML Cu (Fig. 1c) is the energetically favorable as compared with a regular “net” configuration shown in Fig. 1b (this is true for a ratio of total energies  $E_{\text{tot}}$  not for the adhesion energies  $E_{\text{adh}}$  whose ratio is opposite, less favorable) although both configurations simulate the disposition of the same amount of Cu in sub-monolayer. The equilibrium Cu distance of a striped sub-monolayer from the MgO(0 0 1) slab ( $z_{\text{Cu}} = 2.25$  Å) is noticeably larger

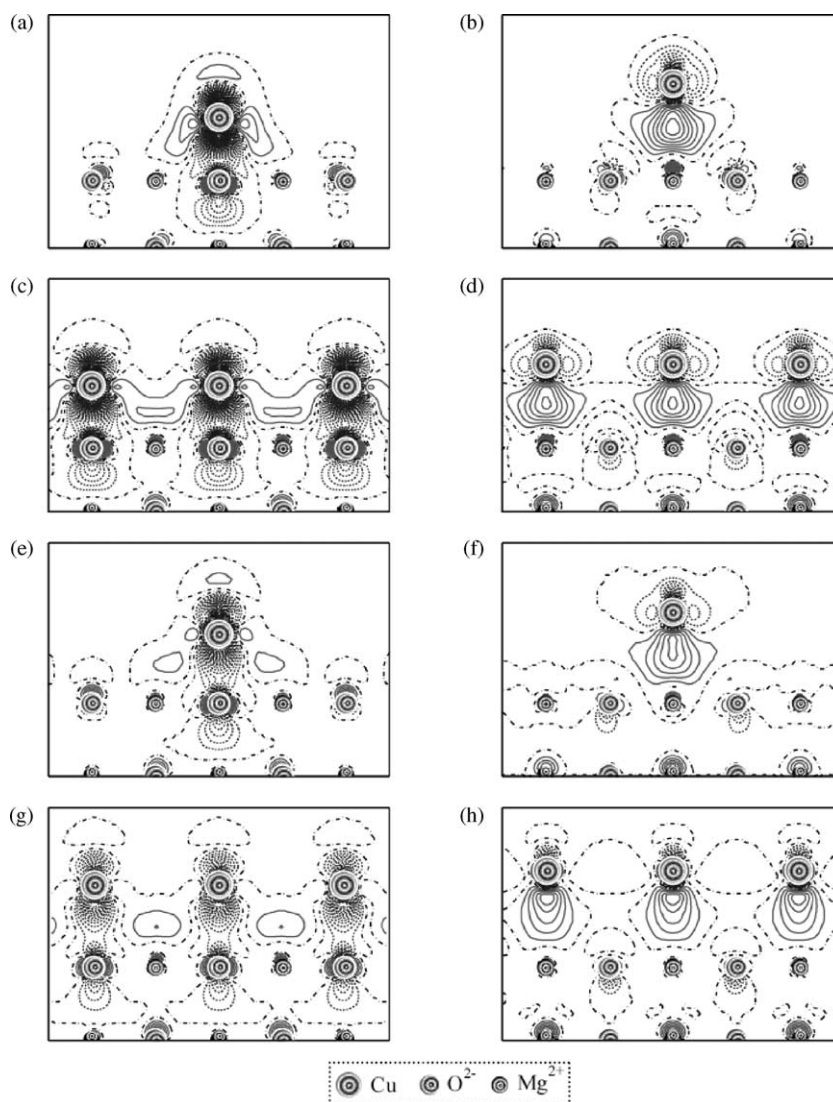


Fig. 2. Difference electron density maps  $\Delta\rho(r)$  (the total density minus a superposition of the densities for the isolated Cu and MgO slabs) in the cross-section perpendicular to the (0 0 1) interface plane (Fig. 1). Regular adsorption on the perfect magnesia surface for four different copper superlattices: (a) 1/4 Cu ML over a  $O^{2-}$  surface ion; (b) 1/4 Cu ML over a  $Mg^{2+}$  surface ion; (c) 1/2 regular “net” Cu ML over a  $O^{2-}$ ; (d) 1/2 regular “net” Cu ML over a  $Mg^{2+}$ , more remote configuration of adsorbed copper was chosen to draw this map; (e) 1/2 striped Cu ML over a  $O^{2-}$ ; (f) 1/2 striped Cu ML over a  $Mg^{2+}$ ; (g) Cu monolayer over a  $O^{2-}$ ; (h) Cu monolayer over a  $Mg^{2+}$ . Isodensity curves are drawn from  $-0.03$  to  $+0.03e$  a.u. $^{-3}$  with increments of  $0.001e$  a.u. $^{-3}$ . The full, dashed and chained curves show positive, negative and zero difference electron densities, respectively.

than that of “net” sub-monolayer ( $z_{Cu} = 2.11 \text{ \AA}$ ), due to the different local environment of Cu atoms in these configurations. In “net” configuration Cu atoms are distributed uniformly and each of them is surrounded by four nearest adatoms at the distance  $\sqrt{2}a_{MgO}$ . In contrast, in a striped configuration each Cu atom has

two neighboring adatoms at the distance  $a_{MgO}$  along direction of stripe and two next-neighboring adatoms at a distance  $2a_{MgO}$ . Relative stability of “stripe” as compared with “net” allows conclude that the tendency to form the clusters where Cu atom tends to surround itself with the nearest neighboring adatoms

is observed even at the sub-monolayer coverage. At the same time, formation of the Cu–Cu bonds at the distances corresponding to MgO substrate is unfavorable as compared with the length of these bonds in the Cu bulk and thus the sub-monolayer seeks to increase the distance from the substrate and to reduce the value of  $E_{\text{adh}}$ . Our simulations show the increase of the distance of the Cu layer from the MgO substrate as the Cu atomic fraction 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 mismatch on the initial stages of the Cu film growth—growing atomic fraction of Cu in a layer forces the layer to move away from the substrate.

Despite a number of experimental studies of the Cu/MgO(0 0 1) system, there is a lack of quantitative data which we could properly compare with our calculations. The most relevant experiments for the heat of Cu 0.03 ML adsorption on the MgO(0 0 1) substrate give the energy of  $\sim 2.5$  eV [12], much larger than our largest adhesion energy of 0.65 eV. It is possible, in these experiments Cu atoms were adsorbed in small concentrations predominantly on surface defects, where the binding energy is known to be much larger than on the regular MgO surface [17]. Our estimate of the Cu diffusion barrier energy, performed for 1/4 ML, gives the lowest value of  $\sim 0.4$  eV along the [1 1 0] direction, in good agreement with experimental value of 0.5 eV [6].

## 5. Conclusion

Our general conclusion is that there is no Cu chemisorption or strong ionic bonding on the defectless non-polar (0 0 1) magnesia surface. For all considered superlattices, the direct interaction between a polarized Cu adatom and surface  $\text{O}^{2-}$  ion is preferable over  $\text{Mg}^{2+}$ . We have shown that the peculiarities of the adhesion behavior for Cu on MgO(0 0 1) surface are linked to the fine features of the electronic charge density redistribution when the Cu coverage increases from sub-monolayer to a monolayer. The sensitive balance of the attraction and repulsion of polarized Cu atoms in the vicinity of the substrate affects the distance between the copper sub-monolayer plane and the magnesia slab. We found also the

increase of “in-plane metallic bonding” between Cu adatoms when their atomic fraction increases. This leads to a simultaneous decrease of polarization of Cu adatoms and (together with the strain-induced repulsion) results in a decrease of the physisorption-type bonding. As a consequence, when the fraction of Cu adatoms increases, the distance between the 2D lattice of Cu atoms and the underlying MgO slab also increases, while the adhesion energy decreases. Our calculations of the potential adhesion energy surface show that the process of the adatom approaching the oxide surface may be rather complicated. It may include several, in our case at least two local minima. That means that depending on the kinetic energy of the approaching atoms, they may be localized at different distances from the substrate surface, thus complicating the structure of growing thin film. A comparative analysis of the two different Cu superlattices corresponding with the same (1/2 ML) coverage allows us to predict the tendency to form copper clusters on the metal oxide surface. This trend is enhanced by the 15% mismatch of lattice constants.

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