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Metal film growth on regular and defective MgO(001) surface: A comparative ab initio simulation and thermodynamic study

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Abstract

In order to understand the difference in metallic film growth modes on *perfect* and *defective* oxide substrates, we have combined ab initio B3LYP periodic calculations on the slab models of the corresponding Me/MgO(001) interfaces (Me = Ag, Cu) with thermodynamic theory of solid solutions. For a defectless magnesia surface, we confirm the experimentally observed submonolayer growth of 3D metallic islands (Ag possesses a higher trend than Cu). Formation of F_s centers (neutral O vacancies) on the substrate markedly enhances metal atom adsorption as compared to physisorption over regular sites on a defect-free substrate. For the first time, we predict that the presence of these surface defects (beginning with concentrations of 5% for Cu and 22% for Ag) can stimulate the growth of uniform 2D metallic sublayers.

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Technologically important interfaces between the simple metal oxides (e.g., MgO) and deposited transition metals continue to attract great attention due to numerous applications in micro- and nanoelectronics, as well as in optical devices and catalysis [1–3]. It is well known that during epitaxial growth of thin films of several transition metals, 3D *metallic islands* start to grow on the magnesia substrate, already at submonolayer coverages [3,4]. In spite of numerous first principles simulations on *homogeneous* adlayers of various metals with varying density of regularly distributed atoms over the defect-free metal oxide substrates, the number of theoretical studies which consider morphology of metallic film growth on such substrates, including formation of 3D islands, is rather limited. For example, our recent studies [5–7], which combine first principles calculations

on the regular Me/MgO(001) interfaces with statistical thermodynamic treatment based on interatomic potentials extracted from the first principles calculations, have given a successful description of the metallic film *growth mode* on a defect-free magnesia surface.

Meanwhile, the role of *surface point defects* in this process is still unclear, despite significant experimental and theoretical efforts [8–11]. Obviously, control of the nature and density of point defects on the oxide surface could open the way towards tailoring wetting, adhesion and dispersion of metal particles and films for specific applications [12]. This requires a better understanding how point defects (as well as surface hydroxylation [13]) affect the nucleation and growth of metal overlayers. The *kinetic* approach, which has been applied recently [14,15], considers the surface point defects as nucleation sites for metallic island growth on a substrate. However, careful ab initio calculations [12] have shown that this is not so trivial; the propensity for the F_s centers (neutral oxygen vacancies) to

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nucleate metal islands has been found to be strongly element-dependent: to the right in a period, where d-shell filling is substantial, vacancies typically inhibit nucleation, whereas the opposite holds for far-left elements. In this Letter, we compare the electronic structure and growth mode for Ag and Cu adsorbates (both belong to the nominal $d^{10}s^1$ electronic configuration) on the MgO(001) surface, either perfect or containing surface F_s centers.

Ab initio study of both regular and defective Ag/MgO(001) and Cu/MgO(001) non-polar interfaces has been performed using magnesia slab models including three and five substrate layers (for one- and two-sided adsorption, respectively) [5–7]. The surface F_s centers have been simulated by a removing one of four outermost O^{2-} ions in the 2×2 surface supercell, retaining in the vacancy the wave function of the missing ion. We have modeled the two adsorption patterns containing several regular coverages of substrate by metal adatoms (from 0.25 ML, to 1 ML) positioned over regular outermost O^{2-} ions or

(and) F_s centers on a MgO(001) substrate (Fig. 1a and b, respectively). Other possible adsorption sites (mainly outermost Mg^{2+} ions) have been found energetically less favorable (Table 1). The local relaxation of the substrate structure around point defects has been first calculated for pure slabs and then reoptimized for the defective Me/MgO(001) interfaces using procedures implemented in the CRYSTAL-03 code [16]. To perform DFT calculations in the framework of the non-local generalized gradient approximation (GGA) we have used the hybrid B3LYP exchange-correlation functional [17], which realizes a partial incorporation of the exact, nonlocal Hartree–Fock (HF) exchange operator into the Becke exchange functional (with varying mixing ratio) and mixes both local and non-local correlation functionals. Computational schemes of the CRYSTAL-03 code [16] use localized Gaussian-type atom-centered functions (GTFs), with a basis set (BS) for each type of atom. We have optimized the Ag and Cu BSs [18] using a small core Hay–Wadt pseudopotential

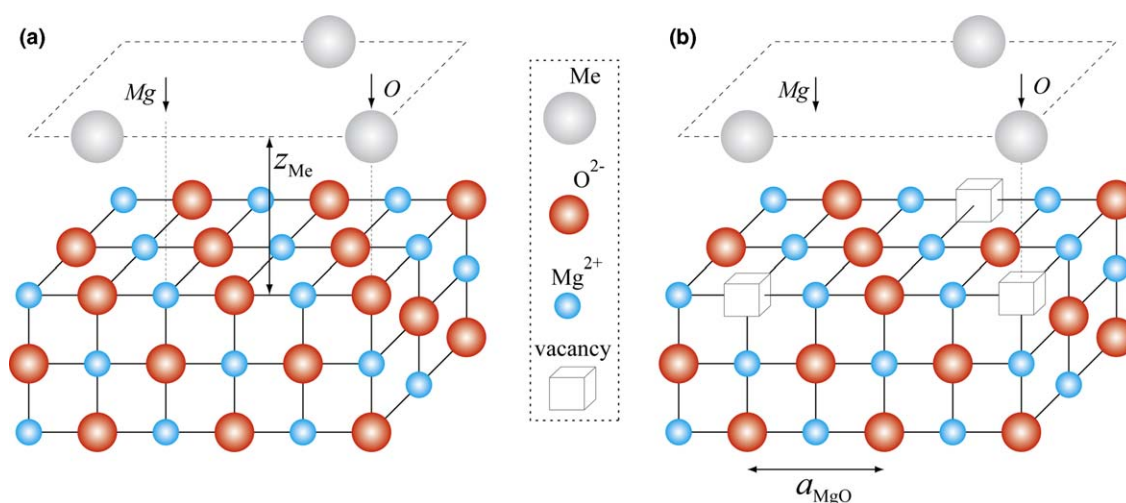


Fig. 1. Slab models of the Me/MgO(001) interface: (a) regular and (b) defective (containing metal adatoms and F_s centers distributed with a 2×2 periodicity).

Table 1
Comparison of the adsorption properties for both regular and defective interfaces

Adatom over surface site	Metal adatom	Adsorbate coverage (ML)	Distance to substrate $Z_{Me}^{(0)}$ (Å)	Adsorption energy per adatom, (eV)	Charge transfer Δq_{Me}^a , (e)
O^{2-} ion	Ag	0.25	2.50	0.40	0.031
		1	2.97	0.17	0.007
	Cu	0.25	2.08	0.62	0.047
		1	2.36	0.33	−0.007
Mg^{2+} ion	Ag	0.25	2.83	0.38	0.009
	Cu	0.25	2.63	0.48	−0.027
F_s center	Ag	0.25	1.81	2.12	0.32
		1	1.83/2.87 ^b	0.80 ^c	0.30/0.011 ^b
	Cu	0.25	1.62	2.36	0.41
		1	1.64/2.32 ^b	1.05 ^c	0.39/0.005 ^b

^a A positive sign means excess of the electron density as compared to a neutral atom.

^b Optimized values for adatom positions above F_s center and O^{2-} ion.

^c Averaged value of energy for monolayer adsorption per adatom.

[19]. The all-electron BSs for Mg and O optimized elsewhere [20] have been found suitable to perform calculations on both regular and defective Me/MgO(001) interfaces and we have reoptimized only the external shells of Mg^{2+} and O^{2-} ions [18]. When comparing results of our most recent B3LYP calculations on the Me/MgO(001) interfaces [7,18] with those performed by us earlier using the HF-CC method (with a posteriori correlation corrections) [5,6,11], one observes now more realistic results, especially those obtained for the case of the defective interface [18].

The Mulliken charges on metal adatoms show negligible interfacial charge transfer (Table 1) on the defect-free magnesia substrate. The difference electron density re-distributions in adlayers of Ag and Cu positioned over O^{2-} ions, which are presented in Refs. [6,7,18], show that Cu atoms are more strongly polarized by the substrate than Ag atoms. This results in the difference between their adsorption energies presented in Table 1. For copper and silver adsorption over the substrate containing neutral F_s centers, we found noticeable electron charge transfer ($<0.5e$) from defect site to Me adatom above it (Table 1 and Fig. 2), thus forming a pair of oppositely charged defects, $\text{Me}^{\alpha-} / F_s^{\beta+}$ ($\alpha = 0.41e$ vs. $0.32e$ and $\beta = 0.42e$ vs. $0.34e$ for Cu and Ag, respectively [18]). As a result, again Cu atoms are more strongly bound over the F_s centers than Ag atoms (2.36 eV vs. 2.12 eV *per adatom*) and the length of a $\text{Cu}^{\alpha-} - F_s^{\beta+}$ bond is shorter by 0.19 Å (Table 1). However, the Mulliken

population of the $\text{Me}^{\alpha-} - F_s^{\beta+}$ bond is larger for Ag ($0.33e$ vs. $0.25e$ for Cu [18]). Comparison of Fig. 2a and b illustrates these differences. Analysis of the charge redistribution across the (001)-terminated MgO slab containing three or five layers with neutral F_s -centers on the surface shows that these point defects perturb significantly the electron density inside the first two coordination semispheres around them in the outermost interlayer of slab. However, this perturbation decreased markedly deeper into the semi-bulk, even in the presence of adatoms. This justifies our further calculations in the framework of three- or five-layer slab models.

To study the influence of F_s centers on the formation of a thin metal film (either Ag or Cu) on the MgO(001) substrate, we have applied a thermodynamic approach [5–7] where the growing metallic film is treated as a 2D solid solution of metal atoms (Me) and empty lattice sites (E). Briefly, thermodynamics of such Me–E solid solution may be formulated with the help of the *effective mixing site interaction potential*:

$$\tilde{V}(\mathbf{r}, \mathbf{r}') = V_{\text{Me-Me}}(\mathbf{r}, \mathbf{r}') + V_{\text{E-E}}(\mathbf{r}, \mathbf{r}') - 2V_{\text{Me-E}}(\mathbf{r}, \mathbf{r}'), \quad (1)$$

where $V_{\text{Me-Me}}(\mathbf{r}, \mathbf{r}')$, $V_{\text{E-E}}(\mathbf{r}, \mathbf{r}')$ and $V_{\text{Me-E}}(\mathbf{r}, \mathbf{r}')$ are the *effective interatomic potentials* between metal atoms, between quasi-particles and between metal atoms and quasi-particles, respectively, extracted from ab initio calculations; \mathbf{r} and \mathbf{r}' are the positions of the sites in 2D lattice. The problem of the *ordering and/or decomposition* tendencies in

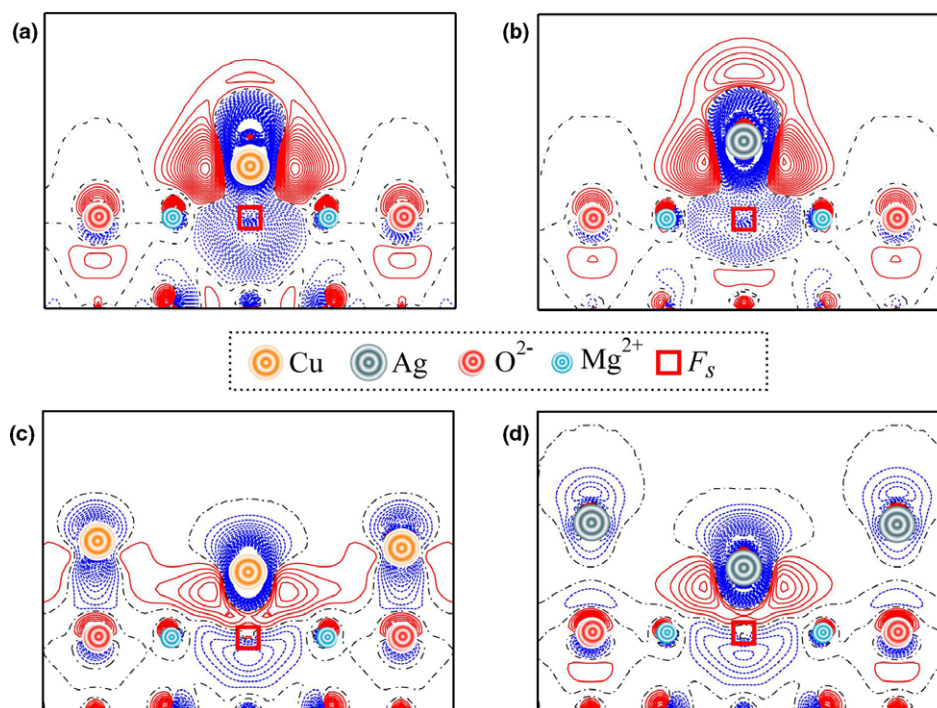


Fig. 2. 2D difference electronic density plots $\Delta\rho(\mathbf{r})$ (total electron density minus a superposition of densities of well-separated metal adsorbate and substrate) in the cross-section perpendicular to the interface plane are shown for two different atomic fractions of Cu (a) and (c) and Ag (b) and (d) in the Me/MgO(001) interface containing F_s centers: 0.25 ML (a) and (b) and 1 ML (c) and (d). Isodensity curves are drawn from $-0.05e$ a.u. $^{-3}$ to $+0.05e$ a.u. $^{-3}$ with increments of $0.001e$ a.u. $^{-3}$. The full (red), dashed (blue) and chained (black) isolines show positive, negative and zero densities, respectively. (For interpretation of the references in colour in this figure caption, the reader is referred to the web version of this article.)

a binary Me–E system on the 2D Ising lattice may be considered in the framework of the Concentration Wave (CW) approach [21]. The distribution of atoms A in a binary solid solution is described in this approach by a *single occupation probability function* $n(\mathbf{r})$. This function gives the probability to find the atom A (Me) at the site \mathbf{r} of the crystal lattice and determines a distribution of solute atoms in an ordering phase. The configurational part of the *free energy of formation of a 2D solid solution per atom* is given by

$$F = \frac{1}{2N} \sum_{\substack{\mathbf{r}, \mathbf{r}' \\ \mathbf{r} \neq \mathbf{r}'}} \tilde{V}(\mathbf{r}, \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') + kT \sum_{\mathbf{r}} \{n(\mathbf{r}) \cdot \ln n(\mathbf{r}) + [1 - n(\mathbf{r})] \cdot \ln[1 - n(\mathbf{r})]\}. \quad (2)$$

Here T is temperature, and k is the Boltzmann constant. The summation is performed over the sites of the 2D Ising lattice.

To simulate the coating of substrate by metal atoms, we have chosen the same *2D regular reference structures* for the occupation probability functions, as recently described for Cu/MgO(001) [7]:

$$0.5 \text{ “net” ML : } n_1(\mathbf{r}) = c_A^{(1)} + 0.5\eta \cdot e^{2\pi i x}, \quad (3)$$

$$0.5 \text{ “stripe” ML : } n_2(\mathbf{r}) = c_A^{(2)} + 0.5\eta \cdot e^{\pi i(x+y)}, \quad (4)$$

$$0.25 \text{ and } 0.75 \text{ ML : } n_3(\mathbf{r}) = c_A^{(3)} + \gamma\eta_1 \cdot e^{2\pi i x} + \gamma\eta_2 [e^{2\pi i(y+z)} + e^{2\pi i(y-z)}], \quad (5)$$

where x and y are the coordinates of the lattice sites of the Ising lattice (in lattice parameter units), η_k the long-range order (LRO) parameters of the CW, $c_A^{(1)} = c_A^{(2)} = 0.5$, $c_A^{(3)} = 0.25$ or $c_A^{(3)} = 0.75$ for $\gamma = 0.25$ and $\gamma = -0.25$, respectively. Direct substitution of coordinates of the Ising lattice sites shows that for these structures in the ordered states and stoichiometric compositions the occupation probabilities $n(\mathbf{r})$ are equal to unity in the sites occupied by metal atoms and are equal to zero in the empty sites. The condition $n(\mathbf{r}) = c_A = \text{const.}$ corresponds to a *disordered 2D solid solution* when all LRO parameters are equal to zero. The *internal formation energies* for the regular phases (U_1 , U_2 and U_3) were defined earlier [5], via Fourier transforms of the potential $\tilde{V}(\mathbf{r}, \mathbf{r}')$ described in Eq. (1) and the LRO parameters η , η_1 , and η_2 , which are equal to unity for the ordered phases and are zero for absolutely disordered state. According to our ab initio calculations, for absolutely ordered structures for both Cu–E and Ag–E solid solutions, U_1, U_2 and U_3 are positive; i.e., *the ordered phases cannot exist*. On the other hand, the internal energy of formation of ordering superstructure per atom can be presented, using the CW approach [21], in the form:

$$U = \frac{1}{2} \tilde{V}(\mathbf{0}) \cdot c_A^2 + \frac{1}{2} \sum_{s, j_s} \gamma_s^2(j_s) \eta_s^2 \tilde{V}(\mathbf{k}_{j_s}), \quad (6)$$

where the index $\{j_s\}$ enumerates the wave vectors in the Brillouin zone, that belong to the star s , η_s the LRO param-

eters, $\gamma_s(j_s)$ the coefficients determining the symmetry of the superstructure with respect to rotation and reflection symmetry operations, $\tilde{V}(\mathbf{k}_{j_s})$ the Fourier transform of the potential $\tilde{V}(\mathbf{r}, \mathbf{r}')$, with $\tilde{V}(\mathbf{0})$ the same for the vector \mathbf{k}_{j_s} equal to zero. Solving the set of Eq. (6) with preliminary calculated U_1 , U_2 and U_3 for the ordered structures defined by Eq. (5), we obtain $\tilde{V}(\mathbf{0})$, $\tilde{V}(\mathbf{k}_1)$, $\tilde{V}(\mathbf{k}_2)$.

As all ordered structures are unfavorable with respect to the heterophase mixture of components, we conclude that only *disordered 2D Me–E solid solution* may be formed at finite temperatures. For this case, *the free energy of formation* for such solution can be transformed from Eq. (2):

$$F(c) = -\frac{1}{2} \tilde{V}(\mathbf{0}) \cdot c(1 - c) + kT [c \ln c + (1 - c) \ln(1 - c)], \quad (7)$$

where index A of concentration c presented in Eqs. (3)–(6) is omitted according to the corresponding condition for disordered solutions mentioned above.

Thus, for Cu/Ag–E solid solution on (001) MgO the single key energy parameter, which defines the *scenario* of metal film growth on the substrate, is $\tilde{V}(\mathbf{0})\{c\}$ entering in Eqs. (6) and (7): as $\tilde{V}(\mathbf{0}) > 0$ one observes metal atom solubility (random distribution over substrate); as soon as $\tilde{V}(\mathbf{0}) < 0$, metal aggregation occurs. It worth to mention, that in our study we go beyond the regular solid solution approximation and account for the dependence of $\tilde{V}(\mathbf{0})$ on the atomic fraction of adatoms. The dependence of $\tilde{V}(\mathbf{0})$ on c arises due to the changes in the bonding between adatoms in the film and MgO, and to a weak dependence of the equilibrium interfacial distance z_{Me} on c . The dependence of $\tilde{V}(\mathbf{0})$ on z_{Me} has been obtained when solving the set of Eq. (6). Keeping in mind that each z_{Me} corresponds to the specific c_A defined in Eq. (5), this dependence may be translated into the dependence of $\tilde{V}(\mathbf{0})$ on c . For more details we refer the reader to Ref. [7]. For Ag–E and Cu–E solid solutions, $\tilde{V}(\mathbf{0})\{c\} = -0.7908 - 0.2104 \cdot c$ and $\tilde{V}(\mathbf{0})\{c\} = -0.6858 - 0.0823 \cdot c$ (eV), respectively. Thus, the tendency of aggregation for Cu is lower than for Ag (in spite of the larger metal adsorbate lattice mismatch of $\sim 15\%$ [18] with the substrate in the former case).

The *phase diagrams* calculated from Eq. (7) and shown in Fig. 3 represent the limited metal solubility. The *solubility curve* shown by the *solid line* is determined by the necessary minimum condition $dF(c)/dc = 0$. The dashed *spinodal curve* is given by equation $d^2F(c)/dc^2 = 0$. These phase diagrams demonstrate our predictions for the metal film growth mode on the MgO(001) substrate. For relatively small metal amounts in submonolayer film two scenarios may be realized: (i) in the region of solubility between the solvus and spinodal the well-separated and compact Me-rich 2D clusters are expected; (ii) under the temperature and concentration conditions of decomposition, when a system falls below the spinodal, a loose, worm-like morphology of the film can arise. For details on the morphology of the solid solutions under spinodal decomposition readers are referred to a review [22] and

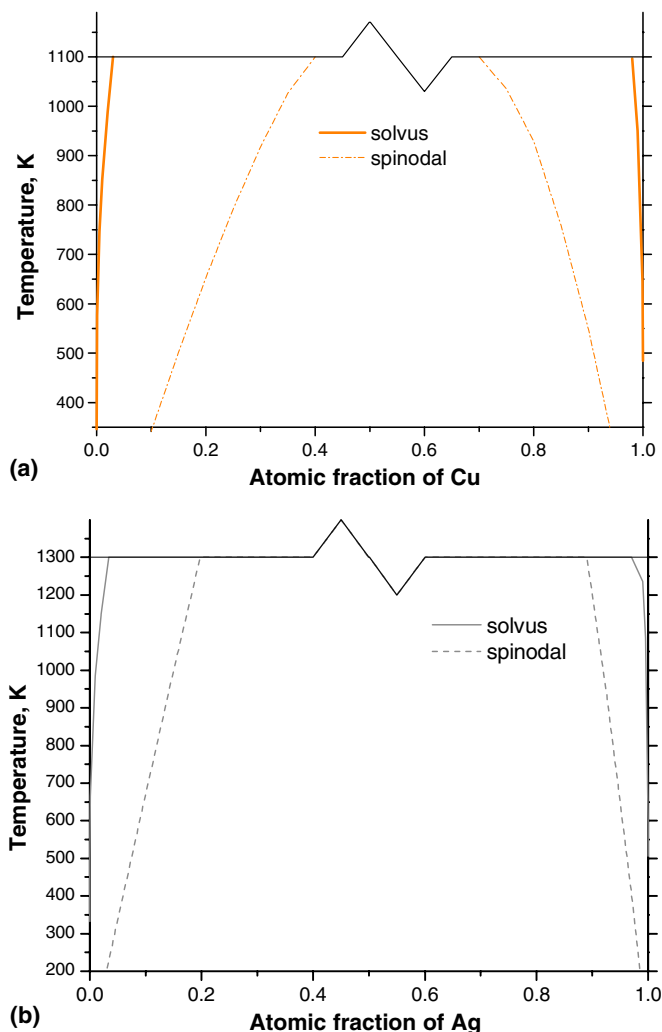


Fig. 3. Calculated phase diagrams for Cu–E (a) and Ag–E (b) solid solutions over a defectless MgO(001) surface.

[23] where our recent Monte-Carlo simulations on the structure of 2D Ag–E solid solution on MgO are reported. At temperatures above the solubility curve metal atoms are randomly distributed on the surface.

On the defective substrate containing periodically distributed F_s centers (Fig. 1b), occupying 25% of O sites, the decrease of vertical displacements of metal adatoms above the point defects were found to be about $\sim 25\%$ of the z_{Me} over the outermost O^{2-} ion, i.e. 22% for Cu and 28% for Ag (Table 1). Thus, we can consider Me–E solid solutions as quasi-2D. As for the defect-free MgO substrate, it has been found that all possible regular Me/MgO structures are unfavorable as compared to disordered structures. Our calculations show that as compared to the case of defect-free MgO substrate, the value of $\tilde{V}(0)$ defined by Eq. (6) for a defective interface depends now on the F_s center concentration. Thus, $\tilde{V}(0) = 1.09$ eV for a Cu on the MgO(001) substrate with the surface fraction of F_s defects $c_F = 0.125$. The corresponding value for Ag is $\tilde{V}(0) = -0.35$ eV. This means that for the given defect fraction,

the Cu–E system forms disordered solid solution on a 2D Ising lattice ($\tilde{V}(0) > 0$), while Ag–E still shows a tendency for the decomposition ($\tilde{V}(0) < 0$); i.e., Ag-rich clusters again can be formed between solvus and spinodal at low Ag coverage. This result clearly demonstrates the dependence on the surface fraction of F_s defects, $\tilde{V}(0)$ may become positive, changing the tendency in Me–E solid solution from the spinodal decomposition to solubility. Considering, let us say, the case of 0.1 ML Me coverage which corresponds to the spinodal decomposition in both Me–E systems above a defectless MgO(001) substrate in a wide temperature range, to very low temperatures (see Fig. 3), it is easy to estimate the dependence of $\tilde{V}(0)$ on c_F . For both systems in this case $\tilde{V}(0)$ is well approximated by equation

$$\tilde{V}(0)\{c_F\} = -a + b \cdot c_F, \quad (8)$$

where the values of both a and b parameters are positive. For the Cu–E system, the obtained values are $a = 0.687$ eV and $b = 14.16$ eV, whereas for Ag–E, $a = 0.812$ eV and $b = 3.69$ eV. According to Eq. (8), the change of the growth mode from dense islands towards homogeneous disordered films ($\tilde{V}(0)$ changes sign from negative to positive) occurs at $c_F \sim 5\%$ for Cu, while for Ag, this happens at substantially larger defect concentrations, $c_F \sim 22\%$ (see Fig. 4). The reason for this was discussed above [12]: although the metal adatom is strongly bound to the O vacancy, in fact it mimics the cation, and the surrounding adatoms are slightly affected by the presence of the defect. The difference electron charge redistributions for a 1 ML coverage of defective substrate by Cu and Ag (Fig. 2c and d, respectively) clearly show that instead of the metallic bonding between atom adsorbed above the oxygen vacancy and those positioned over the neighboring

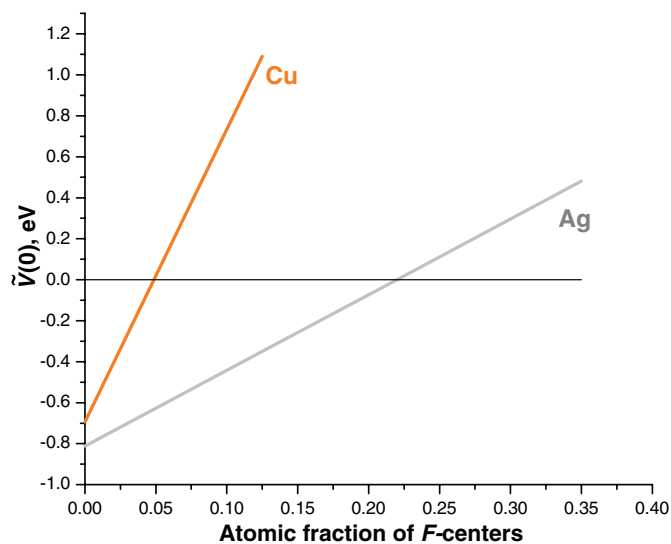


Fig. 4. The dependence of the energy parameter $\tilde{V}(0)$ for Cu and Ag on the concentration of periodically distributed F_s centers on the MgO(001) surface.

surface oxygen ions the additional polarization appears between the latter adatoms and defective substrate, which leads to a larger stability of 2D adlayer as compared to the defectless interface. (Again, for Cu, this effect is found to be more pronounced than for Ag). Thus, our calculations support conclusions made in Ref. [12] using analysis of results obtained in a series of first principles calculations and disagree with kinetic descriptions of defective interfaces [14,15], which neglect local electronic structure effects. Finally, the results of our study of thermodynamic features of phase transitions in 2D Cu/Ag–E solid solutions formed on (001) MgO surface are qualitatively similar to the results reported in Ref. [24] (in that study thermodynamics of the monoatomic layers formed on the substrate is discussed in the framework of the parametric lattice gas model and mean-field approximation), and to results of Ref. [25], where an approach similar to [24] is applied to study the phase transformations in an in submonolayer formed on the Si surface. The main advantage of our study is an extraction of thermodynamic parameters from ab initio calculations.

Summing up, our ab initio calculations combined with a thermodynamic study definitely show that the changes of bonding tendencies between the metal adatoms in the vicinity of the defect-free versus defected substrate influence the thermodynamic conditions and the morphology of the forming monolayer. F_s centers on the MgO(001) surface strongly enhance metal adhesion to the oxide substrate. Copper is bound more strongly than silver on both regular and defective MgO(001) surfaces, whereas Ag possesses both larger covalence over the surface F_s center as well as higher ability to form dense clusters on perfect MgO(001) surface than Cu. The surface F_s centers weaken tendency toward metal aggregation and lead to formation of disordered 2D metallic films. The former is more preferable at low defect concentration, but increasing concentration makes the latter unavoidable. The calculated critical defect concentration for Cu is noticeably smaller than for Ag (5% vs. 22%). Experimental confirmation of our predictions would be of great interest: this may be achieved by controlled irradiation of MgO surface aimed at forming different amounts of F_s defects, followed by further Cu or Ag deposition. Our results are physically consistent with the calculated tendencies for the decomposition in Cu–E or Ag–E on the defect-free substrate: the higher is the tendency for the spinodal decomposition in the absence of F_s centers, the larger should be the fraction of these point defects to change this tendency to the total solubility.

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