

Density-functional study of Cu atoms, monolayers, films, and coadsorbates on polar ZnO surfaces

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The structure and electronic properties of single Cu atoms, copper monolayers, and thin copper films on the polar oxygen and zinc terminated surfaces of ZnO are studied using periodic density-functional calculations. We find that the binding energy of Cu atoms sensitively depends on how charge neutrality of the polar surfaces is achieved. Bonding is very strong if the surfaces are stabilized by an electronic mechanism which leads to partially filled surface bands. As soon as the surface bands are filled (either by partial Cu coverage, by coadsorbates, or by the formation of defects), the binding energy decreases significantly. In this case, values very similar to those found for nonpolar surfaces and for copper on finite ZnO clusters are obtained. Possible implications of these observations concerning the growth mode of copper on polar ZnO surfaces and their importance in catalysis are discussed.

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I. INTRODUCTION

The ternary composite system Cu/ZnO/Al₂O₃ is an important commercial catalyst for the methanol synthesis, the water-gas shift reaction, and the methanol-steam reforming process.^{1,2} Although ZnO (doped with Cr₂O₃) by itself is a good high-temperature catalyst for hydrogenation and dehydrogenation reactions, only the combination with Cu makes it an effective and selective catalyst for low-temperature applications on an industrial scale. The particular role of copper, including its electronic and atomistic structure on ZnO surfaces, is not clearly understood. There exist many controversial models to explain how copper enhances the activity of such ZnO-based catalysts.^{3,4} Different “active species” are proposed in the literature, such as the existence of Cu⁺ impurities at the ZnO surfaces, but the most commonly accepted picture is that Cu forms small metallic clusters which are dispersed on defect-rich and heterogeneous ZnO surfaces.

The initial growth of vapor-deposited copper on different ZnO surfaces at ultrahigh vacuum (UHV) conditions has been studied experimentally by various techniques such as x-ray photoelectron spectroscopy (XPS),⁴⁻⁷ low-energy ion-scattering spectroscopy (LEIS),⁴⁻⁷ surface x-ray diffraction (SXRD),⁸ and scanning tunneling microscopy (STM).^{9,10} Campbell *et al.*⁴⁻⁷ reported a Cu growth mode between a Volmer-Weber and Stranski-Krastonov behavior on the two polar surface terminations of ZnO. They found that initially the deposited Cu atoms form two-dimensional islands (i.e., clusters with a thickness of one atom) until a critical coverage is reached, at which further Cu atoms begin to add on top of the islands to form three-dimensional clusters, whereas the metal-free regions between the clusters fill only very slowly.^{5,6} This behavior was attributed to *purely kinetic* limitations at low temperatures since a thickening of the islands was observed upon annealing the surfaces. The critical coverages at which three-dimensional growth of the clusters begins, depends slightly on temperature and was estimated to be about 1/2 monolayer for the O-terminated (000 $\bar{1}$)-O

surface⁵ and 1/3 of a monolayer for the Zn-terminated (0001)-Zn polar face of ZnO.⁶ However, for the Zn-terminated polar surface these results were questioned by a recent STM study.⁹ On well prepared surfaces immediately a three-dimensional growth of Cu was observed. Also for the clean adsorbate-free nonpolar (10 $\bar{1}$ 0) surface exclusively three-dimensional islands were found with STM at all coverages.¹⁰

The main focus of theoretical investigations of the bonding of metal films and clusters on oxide surfaces has been on the MgO (001) surface¹¹⁻¹⁶ and to a lesser extent on the surfaces of more complex oxides such as TiO₂,¹⁷ Al₂O₃,^{18,19} and MgAl₂O₄.²⁰ Almost all studies were restricted to nonpolar surface terminations. Polar surfaces, on the other hand, such as the two basal planes of ZnO, may show a completely different behavior compared to nonpolar surfaces. The reason is that polar surfaces are characterized by an “excess” of one atomic species²¹ which leads to an interesting interplay between their electronic and atomic structure: In order to be charge neutral the polar surfaces either have to adopt an electronic structure with partially occupied surface bands (sometimes referred to as “metallization” of polar surfaces), or they have to reconstruct (preferentially by the loss of suitable surface atoms) in order to avoid partial band filling, or charged species have to be adsorbed.²²⁻²⁴ Depending on which mechanism is realized in a particular system, very different properties of the interaction with metal films and coadsorbates may occur.

Theoretical studies of the interaction of copper with ZnO surfaces are very scarce. In an early semiempirical quantum-chemical study³ the electronic structure and atomic charges were calculated for various ZnO clusters with adsorbed and substituted Cu atoms, but no information on binding energies and relaxed atomic structures was obtained. In addition, clusters without embedding were used which cannot catch the peculiarities of the polar surfaces described above. A proper embedding was taken into account only in two recent cluster studies: a density-functional calculation of small Cu clusters on a particular atomic model of the polar Zn-terminated

surface²⁵ and a quantum-chemical *ab initio* investigation of the adsorption of single Cu atoms on cluster models for both polar surfaces.²⁶

In the present study we have calculated the adhesion energy and structure of single Cu atoms, copper monolayers, and thin copper films on the two polar surface terminations of ZnO. The surfaces are described by periodically repeated slabs so that the different stabilization mechanisms for the polar surfaces, in particular, the existence of partially occupied surface bands, can be handled without any restrictions. Additionally, atomic relaxations are fully taken into account. The main focus of this study will be on how the charge neutralization process of the polar surfaces and the filling of the surface bands influences the adsorption properties of copper spanning the range from single atoms to full monolayers.

II. COMPUTATIONAL METHOD

Self-consistent total-energy calculations based on density-functional theory (DFT) (Ref. 27) were carried out to determine the adsorption energies and structures of Cu atoms and monolayers on the polar ZnO surfaces. The exchange-correlation energy and potential were treated within the generalized-gradient approximation (GGA) using the functional of Perdew, Burke, and Ernzerhof (PBE).²⁸ For systems with an odd number of electrons all calculations were checked with the spin-polarized version of the PBE functional. However, in all cases the spin-polarization was either quenched by the formation of a “metallic” state or the unpaired electron was well localized at single Cu atoms so that taking energy differences between polarized and unpolarized calculations gave basically identical results. All calculations were done with the Stuttgart “mixed-basis” DFT code.²⁹ Normconserving pseudopotentials³⁰ were employed together with a mixed-basis set consisting of plane waves and non-overlapping localized orbitals for the O-2*p*, Zn-3*d*, and Cu-3*d* electrons. Since we include localized basis functions, a plane-wave cutoff energy of 20 Ry is sufficient to get well converged results (see Ref. 31).

The polar surfaces are represented by periodically repeated slabs. In the ZnO wurtzite structure no mirror symmetry parallel to the polar surfaces is present. This implies that all slabs are inevitably Zn terminated on one side and O terminated on the other. For the study of Cu monolayers (1×1) surface unit cells and very thick slabs consisting of eight Zn-O double layers were used to reduce the residual internal electric field.³¹ All atomic configurations were fully relaxed by minimizing the atomic forces. The calculations for single Cu atoms were performed on (2×2) surface unit cells (corresponding to a Cu surface coverage of 1/4 monolayer), and the slab thickness was reduced to four ZnO double layers. The interlayer spacings were taken to be the extrapolated values for an infinitely thick slab as reported in Ref. 31, and no further relaxation of the slabs was taken into account. The residual internal electric field³¹ in these thin slabs was quenched by saturating the broken surface bonds on the Cu-free side of the slabs with hydrogenlike atoms. An artificial atom with a nuclear charge of 1/2 and 3/2 for a O- and a Zn-terminated surface, respectively, was added for

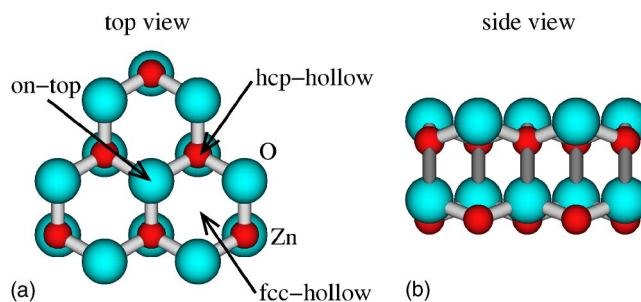


FIG. 1. Schematic diagram of the high-symmetry adsorption sites on the polar ZnO surfaces, shown here for the oxygen surface termination only.

each surface atom to guarantee that the surface bands of the Cu-free side are always fully occupied and that ideal charge neutralization for this side of the slab is enforced. In a (2×2) surface unit cell arrangement the Cu atoms are more than 6.5 Å apart. The interaction energy between the Cu atoms is calculated to be less than 0.02 eV so that this setup is sufficient to describe isolated Cu atoms.

Three different high-symmetry adsorption sites are present at the polar ZnO surfaces (see Fig. 1): an “on-top” position which would be the regular lattice site for the next atomic layer, a “hcp-hollow site” above atoms in the second surface layer and a “fcc-hollow site” with no atoms beneath. All three adsorption sites are considered in the present study. Copper atoms are only adsorbed on one of the two slab terminations. The electrostatic potential is calculated as for a genuinely isolated slab^{32,33} so no artificial electrostatic interactions between the periodically repeated images of the slabs are present. Monkhorst-Pack *k*-point meshes³⁴ with a density of at least ($6 \times 6 \times 4$) points in the Brillouin zone of the primitive ZnO unit cell are chosen. For more details on convergence parameters, the construction of appropriate supercells as well as the calculated bulk and clean surface structures of ZnO we refer to Ref. 31, where the same computational settings as in the present study were used.

III. RESULTS AND DISCUSSION

A. Validation of the method: Finite cluster model

Before we start our investigation of copper on the polar ZnO surfaces, we address the question of how well our DFT method and in particular the PBE functional are able to describe the interaction of Cu with ZnO surfaces. For Cu on MgO(001) significant differences between various wavefunction-based quantum-chemical methods and DFT calculations using different GGA functionals were observed.¹⁶ As a general trend it was found that DFT slightly overestimates the adhesion energy of Cu on MgO clusters compared to best coupled-cluster calculations, with noticeable variations between the GGA functionals.

To test the reliability of our DFT results we have calculated the binding energy and equilibrium distance of Cu atoms on a small, isolated Zn₄O₄ cluster which we can compare with recently published results of an accurate multireference coupled-cluster-type calculation.^{26,35,36} Spe-

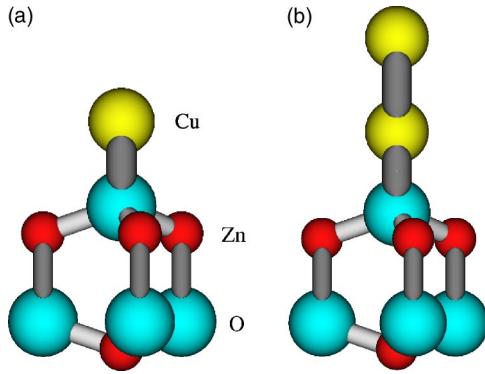


FIG. 2. Adsorption geometries of (a) single Cu atoms and (b) Cu dimers on top of a finite Zn_4O_4 cluster.

cifically, the multiconfiguration coupled electron-pair approximation (MC-CEPA)³⁷ was used which includes all single and double excitations of a configuration-interaction ansatz plus all higher excitations that are necessary to make the calculation size consistent. A wurtzitelike cluster structure was chosen in order to mimic the stacking sequence of polar slabs (see Fig. 2). The Cu atom is adsorbed to the top O and bottom Zn atom of the cluster which are threefold coordinated as at a ZnO surface.

The Zn_4O_4 cluster itself is a closed-shell system, but with the additional Cu atom it becomes open shell. Therefore, in the first calculation for a single Cu atom on top of the threefold O atom of the cluster we used the spin-polarized version of the PBE functional to obtain the total energy of the adsorbate system as well as for the energy of the single Cu reference atom. The binding energy and the equilibrium distance are given in Table I. No significant differences in the adsorption properties are found if the spin polarization is completely neglected and both, the calculations for the adsorbate system and the separate Zn_4O_4 cluster and the isolated Cu atom are done with the nonpolarized PBE functional. Also using a Cu dimer instead of a single Cu atom gave a very similar result. Since the inclusion of spin polarization doubles the computational cost, we only used a Cu dimer for the study of the interaction of Cu with the threefold coordinated Zn atom of the finite cluster.

Compared to MC-CEPA results we find a satisfying agreement for the binding energies and equilibrium distances. As

TABLE I. Equilibrium distances d_0 and binding energies E_{ad} of Cu atoms and Cu_2 dimers on the Zn_4O_4 cluster for different adsorption sites as indicated; “sp” refers to spin-polarized/open-shell and “np” to nonpolarized DFT calculations. The MC-CEPA values are taken from Ref. 26.

Adsorption geometry		PBE		MC-CEPA	
		d_0 [Å]	E_{ad} [eV]	d_0 [Å]	E_{ad} [eV]
O-Cu	sp	1.91	0.98	1.98	0.73
	np	1.91	0.96		
O- Cu_2	np	1.92	0.92	2.91	0.12
Zn-Cu	sp				
Zn- Cu_2	np	2.48	0.26		

TABLE II. Equilibrium distances d_0 and binding energies E_{ad} of single Cu atoms for different adsorption sites on the ideal O- and the Zn-terminated polar ZnO surfaces with partially filled surface bands. Slabs with a (2×2) surface unit cell and a thickness of four Zn-O double layers were used for the calculation.

Adsorption site	(000 $\bar{1}$)-O		(0001)-Zn	
	d_0 [Å]	E_{ad} [eV]	d_0 [Å]	E_{ad} [eV]
on top	1.84	2.51	2.41	1.72
hcp hollow	1.90	1.80	1.97	1.86
fcc hollow	1.22	2.86	1.88	2.05

in the case of Cu on MgO, the DFT calculation (here with the PBE functional) slightly overestimates the bond strength. However, the adsorption energy is “equally” too large by 0.15 to 0.25 eV, so that the relative stability of the O and the Zn adsorption site is quite well described. Overall we find that Cu preferentially binds to oxygen atoms with an adhesion energy of almost 1 eV. The same behavior was also found for MgO,¹⁶ but with a lower binding energy of 0.4 eV (coupled-cluster) and 0.6 eV (DFT-GGA).

B. Cu atoms on ideal polar surfaces

For a long time it was believed that the polar ZnO surfaces exist in an unreconstructed, truncated-bulk-like state.^{23,38} If no reconstruction by loss of surface atoms and no adsorption of charged species occurs, the polar surfaces are inevitably stabilized by partially filled surface states with a 3/4 and a 1/4 filled band for the O and the Zn termination, respectively.^{22–24,38}

Assuming such a situation in our DFT calculations we find a very strong binding of Cu atoms on both polar ZnO surfaces (see Table II). The Cu binding energies are much larger than what is found for the finite Zn_4O_4 cluster (see Table I) and, more importantly, for the nonpolar ZnO(10 $\bar{1}$ 0) surface.³⁹ In addition, it is also larger than what is typically known from other oxide surfaces.¹⁶ The reason for this behavior is that at low copper coverages, the 4s electrons of the Cu atoms fill the partially occupied surface bands and thereby stabilize the polar surfaces. The same mechanism was found for the adsorption of atomic hydrogen on the polar O-terminated surface (see Ref. 24): at low H coverages the binding energy of an H atom relative to a reference of isolated H_2 molecules is more than 2 eV. However, as soon as a H coverage of 1/2 monolayer is reached, the surface bands are filled and the adsorption energy for additional H atoms decreases rapidly. As a consequence, surface structures with more than 1/2 monolayer of H are not stable in thermodynamic equilibrium with a H_2 gas phase at any temperature and partial pressure.²⁴ Therefore, we can expect that the strong binding of copper on the polar ZnO surfaces is only possible as long as the surface bands are not fully occupied. If the bands are filled, either by higher copper coverages or by the presence of coadsorbates such as hydrogen, the Cu adsorption properties may change drastically. However, for copper there is one significant difference compared

to hydrogen: at higher Cu coverages strong Cu-Cu bonds will form so that Cu will also adsorb at coverages exceeding 1/2 monolayer.

C. Cu atoms on adsorbate precovered polar surfaces

Several very recent studies have created considerable doubt that the polar ZnO surfaces really exist as ideal, truncated-bulk-like surfaces. With scanning tunneling microscopy (STM) nanoscaled island and pit structures were found at the Zn-terminated face⁴⁰ which lead to an overall loss of roughly 1/4 of the surface Zn atoms. Such a stabilization mechanism was confirmed in DFT calculations^{40,41} which furthermore predict high concentrations of adsorbed OH groups in hydrogen-rich environments. For the O-terminated surface it was shown by He atom scattering,⁴² in a study of the CO adsorption energetics,⁴³⁻⁴⁵ and also by DFT calculations²⁴ that they are H covered for a wide range of temperatures and H partial pressures. Both mechanisms, loss of Zn atoms and adsorption of hydrogen, lead to a filling of the surface bands. The filling need not be perfect, however, in order to study the consequences of such a stabilization of the polar surfaces on the Cu (co)adsorption properties and also in order to support our prediction from the last subsection, we have considered four idealized surface structures of the polar ZnO surfaces for which the surface bands are fully occupied.

In the first two structures surface band filling was realized by removing 1/4 of the surface atoms. For both the O- and the Zn-terminated surface one surface atom was taken out of a (2×2) surface unit cell, thereby creating a regular (2×2) vacancy pattern. In the third and fourth surface structure we considered that band filling occurs by adsorbates. For the O- and the Zn-terminated surface we assumed that 1/2 monolayer of H atoms and OH groups, respectively, is present. The most stable adsorption sites for H atoms (OH groups) on the O(Zn)-terminated surface are the on-top position (fcc-hollow sites). Therefore, to form 1/2 monolayer coverages, we placed the H atoms (OH groups) on every second atomic row (every second row of fcc-hollow sites) at the surface.

For all four surfaces the Cu adsorption energy was computed as described in Sec. III B for all different adsorption sites between the vacancies and at the adsorbate-free rows between the H/OH adatoms. The results for the most stable adsorption positions are given in Table III. The adsorption energies for Cu atoms placed into the vacancies are added for comparison. We find indeed that the Cu binding energy is significantly reduced compared to the result of the ideal surface termination with partially occupied (“metallized”) surface bands. The favored adsorption site and the Cu adsorption energy basically do not depend on how the surface band filling was achieved. The adsorption energy of roughly 1 eV of Cu atoms on the H covered and vacancy-stabilized O-terminated surface is only slightly larger than what was found for the finite closed-shell Zn_4O_4 cluster and for the nonpolar ZnO surface (having fully occupied bands, i.e., nonmetallic character).³⁹ In addition, a similarly small value was also found in a quantum-chemical embedded cluster

TABLE III. Equilibrium distances d_0 and binding energies E_{ad} of single Cu atoms on polar ZnO surfaces with vacancy and adsorbate structures to fill the surface bands (which results in “insulating surfaces” for Cu coadsorption). Same slabs as in Table II were used.

Adsorption site	d_0 [Å]	E_{ad} [eV]
(000 $\bar{1}$)-O surface with 1/4 O vacancies		
on top	1.91	1.13
vacancy	0.71	1.58
(000 $\bar{1}$)-O surface covered with 1/2 monolayer of H		
on top	1.91	1.12
(0001)-Zn surface with 1/4 Zn vacancies		
fcc hollow	1.79	0.82
vacancy	0.22	2.53
(0001)-Zn surface covered with 1/2 monolayer of OH		
fcc hollow	1.75	0.94

study of the polar O-terminated surface²⁶ in which the embedding scheme was chosen in such a way that it leads to fully occupied surface bands, similar to our hydrogen covered surface.

D. Cu monolayers on polar surfaces

We turn now to the study of Cu monolayers on the polar ZnO surfaces. ZnO and bulk Cu have very different lattice constants. The equilibrium distance of the surface atoms at the polar surfaces is computed to be 3.28 Å (experimentally: 3.25 Å), and for the Cu bulk lattice constant we found 3.65 Å which corresponds to a nearest-neighbor separation between the Cu atoms of 2.58 (experimentally: 3.615 Å and 2.56 Å, respectively). Epitaxial growth with a (111) orientation of copper would therefore lead to a lattice mismatch of 21%. Thus, we cannot expect that epitaxial growth occurs. Experimentally it was found that Cu on the polar surfaces is basically unstrained, even at very low coverages.⁸ Exclusively (111) Cu planes were observed with a fixed orientation given by the ZnO substrate.

The realistic treatment of such unstrained copper layers on the ZnO surfaces would be computationally very demanding since we would have to use prohibitively large surface unit cells for our slab. However, in order to get a first idea on how the Cu adsorption strength and the preferred adsorption sites change if a high concentration of copper is present on the polar surfaces we have nevertheless studied ideal epitaxial Cu (111) monolayers on the ZnO surfaces. For such hypothetical films we have calculated the equilibrium distance and the work of separation which is defined by

$$E_{\text{sep}} = E_{\text{slab}}^{\text{ZnO}} + E_{\text{layer}}^{\text{Cu}} - E_{\text{Cu/ZnO}}, \quad (1)$$

where $E_{\text{slab}}^{\text{ZnO}}$ is the total energy of the relaxed ZnO slab in absence of Cu, $E_{\text{layer}}^{\text{Cu}}$ is the total energy of the Cu(111) layer(s) in their relaxed geometry but with the lattice spacing of ZnO, and $E_{\text{Cu/ZnO}}$ is the total energy of the Cu/ZnO system. The results for E_{sep} are given in Table IV. For the O-terminated surface we find that Cu preferentially binds on

TABLE IV. Equilibrium distances d_0 and work of separation E_{sep} (per surface atom) of a Cu monolayer for different adsorption sites on the polar ZnO surfaces, with and without atomic relaxation of the slab.

Adsorption site	Rigid slab		Full relaxation	
	d_0 [Å]	E_{sep} [eV]	d_0 [Å]	E_{sep} [eV]
(000 $\bar{1}$)-O surface				
on top	1.98	1.02	1.94	1.23
hcp hollow	2.21	0.38	1.71	0.66
fcc hollow	1.75	0.58	1.36	0.90
(0001) Zn surface				
on top	2.56	0.54	2.50	0.62
hcp hollow	2.13	0.63	1.88	0.84
fcc hollow	2.12	0.66	1.89	0.87

top of the oxygen atoms. The equilibrium distance and the binding energy of 1.23 eV per Cu atom are very similar to the results obtained for single atoms on the finite Zn_4O_4 cluster and the surface with filled surface states. Also for the Zn-terminated surface we find a good binding of the copper monolayers with a work of separation of almost 0.9 eV per Cu atom. This is in agreement with experiment where a good adhesion of Cu on both polar surface terminations was found.^{5,6,9} In contrast to the O-terminated surface, the hollow positions for the Cu atoms are more stable than the on-top site. The two hollow positions are very similar in energy and may both be populated for nonepitaxial films. This may explain the experimental observation that the orientation of deposited Cu relative to the substrate is less strict for the Zn-terminated face than for the O termination.^{6,8} Importantly, we also find that the structural relaxation of the ZnO substrate cannot be neglected. The relaxation energy contributes 20 to 30 % to the binding energy of these copper films.

E. Cu films on polar surfaces

Finally, we briefly study the effect higher copper coverages than full monolayer on the bonding at the Cu/ZnO interface. This will give some insight into the nature of the chemical bond at the interface. The higher coverages were simulated by adding a second and a third monolayer of Cu on top of the polar surface. For the two and three layer films different stacking sequences are possible. As shown in Tables V and VI, the energy differences between different stacking sequences turn out to be very small so that the specific stacking does not play a role in the following arguments.

Overall we find that the same adsorption sites as for the monolayer coverage are the most stable ones for the thicker Cu films: the on-top position for the O-terminated surface and the hollow sites for the Zn-terminated face. For the O-terminated surface the work of separation increases with the thickness of the copper film, whereas for the Zn termination a small decrease in the binding energy is observed. This behavior as well as the preferred adsorption sites can be explained as follow: For the O-terminated surface the first copper layer adopts the role of the missing next Zn layer.

TABLE V. Equilibrium distances d_0 and work of separation E_{sep} (per surface atom) of Cu double layers for different adsorption sites on the polar ZnO surfaces and different stacking sequences. The slabs were fully relaxed.

Adsorption site	Sequence	d_0 [Å]	E_{sep} [eV]
(000 $\bar{1}$)-O surface			
on top	hcp	1.96	1.50
	fcc	1.96	1.50
(0001)-Zn surface			
hcp hollow	hcp	1.86	0.94
	fcc	1.87	0.93
fcc hollow	hcp	1.90	0.91
	fcc	1.93	0.90

Therefore the on-top position, which is the next regular lattice site of the wurtzite structure, is preferred. Charge is donated to the surface O ions to fill the partially occupied surface bands, which can more easily occur for thicker copper films, and a partially ionic/covalent bond as in bulk ZnO is formed.

On the other hand, for the Zn-terminated surface, the topmost Zn layer behaves more similar to the first layer of the adsorbed metal film. Therefore the hollow positions, which correspond to an extension of the metal film, are the low-energy adsorption sites. The 4s electrons of the partially filled Zn surface band contribute to the metallic state of the metal film so that the Zn-Cu bond is more metallic in character. However, the “integration” of the topmost Zn layer becomes weaker for thicker copper films.

Figure 3 depicts the charge redistribution which takes place when the Cu/ZnO interface is formed from the two free surfaces. The valence electron density of the free Cu and ZnO surfaces was determined in separate slab calculations and subtracted from the density distribution of the interface. The different behavior of the Cu-O and the Cu-Zn chemical bonds can be clearly distinguished in Fig. 3. For the O-terminated ZnO surface, shown in panel (a), a strong directional redistribution of charges between the surface Cu and O atoms takes place, as it is typical for ionic/covalent bonds. Furthermore, a small charge density increase between the surface O and the second-layer Zn atom is visible, indicating that the additional charge coming from the metallic

TABLE VI. Equilibrium distances d_0 and work of separation E_{sep} (per surface atom) of Cu triple layers on the polar ZnO surfaces for different stacking sequences. The slabs were fully relaxed.

Adsorption site	Sequence	d_0 [Å]	E_{ad} [eV]
(000 $\bar{1}$)-O surface			
on top	hcp	1.96	1.33
	fcc	1.96	1.32
(0001)-Zn surface			
hcp hollow	hcp	1.87	0.76
	fcc	1.88	0.76

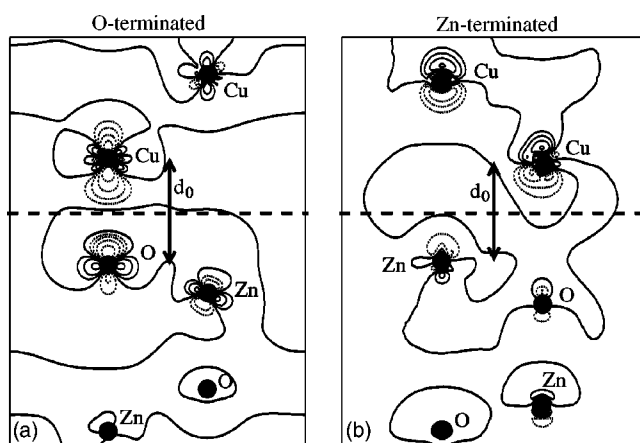


FIG. 3. Contour plot of the difference in the valence electron density between a slab calculation with the Cu/ZnO interface and the superposition of the electron density of the separated Cu film and ZnO surface, shown in (a) for the O-terminated and in (b) for the Zn-terminated polar ZnO surface. The cut was taken perpendicular to the interface along the $[10\bar{1}0]$ direction. Contours start from $0.01e/\text{bohr}^3$ and change successively by a factor of 2. The long dashed line indicates the position of the interface.

Cu film also leads to a strengthening of the binding in the topmost ZnO double layer. On the other hand, for the Zn-terminated slab in panel (b), hardly any change in the electron distribution of the ZnO slab can be seen. Charges that were spilling out into the vacuum for the isolated surfaces are mainly transferred into the metal layer, leading to a small increase in the charge density of the Cu film. Due to small rehybridizations of the Cu-3d electrons the additional charge is redistributed within the layer. Altogether the charge redistribution is very “diffuse” being typical for the formation of a metalliclike interfacial contact or bond.

IV. SUMMARY AND CONCLUSIONS

Using DFT calculations and periodically repeated slabs to represent the two polar ZnO surfaces, i.e., the $(000\bar{1})\text{-O}$ and $(0001)\text{-Zn}$ faces, we find a pronounced difference in the adsorption energy of Cu atoms depending on the coverage. Crucial to the proposed understanding of this phenomenon is the fact that the ideal, unreconstructed O- and Zn-terminated

surfaces feature partially filled surface states with a $3/4$ and a $1/4$ filled band, respectively (often referred to as “metallization” of the polar surfaces). Up to $1/2$ monolayer coverage the adhesion of copper on such polar surfaces is found to be very strong since the 4s electrons of the Cu atoms can fill these partially occupied bands and thereby stabilize the polar surface itself. However, as soon as these bands are filled due to copper (or due to coadsorbates) already present on the surface, the binding of additional Cu to the surface becomes weaker and less favorable in comparison to the cohesion energy of Cu in small Cu clusters and thin Cu films.

Considering the experimentally observed coverage-dependent change of the growth mode of copper on the polar ZnO surfaces in Refs. 4–7 (i.e., formation of two-dimensional islands until critical coverages of about 50 and 30 % for the O- and the Zn-terminated surface, respectively, is reached at which three-dimensional growth of Cu clusters sets in) it may very well be that this sudden change is not caused by *kinetic* limitations at low temperatures alone. Instead, it might also be driven *thermodynamically* by the significant change in the adsorption energetics of copper on such polar surfaces due to successive band filling, which in turn is directly coupled to increasing the surface coverage. The lower critical coverage found experimentally for the Zn-terminated surface may then be explained quite naturally by the lower adsorption energy of copper found for this particular surface. Additionally, the presence of coadsorbates during or prior to copper deposition may strongly influence both the critical coverage and the morphology of the grown Cu particles.

Thus, it becomes evident that the *polar* ZnO surfaces allow for a wealth of quite different adsorption scenarios depending on parameters such as coverage, defects, coadsorbates, etc. Since these parameters typically change in complex ways during catalytic cycles one is tempted to speculate that the polar character might be at the very heart of the catalytic activity of ZnO.

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