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The effect of Cu on O adsorption on a ZnO(0001) surface: a first-principles study

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Abstract

Density functional theory and a pseudopotential plane-wave approach are employed to study the effect of Cu on the adsorption of O on a ZnO(0001) surface. The results show that the Cu adlayer enhances the adsorption of O on ZnO(0001). The energetically favored configuration for Cu and O co-adsorption on ZnO(0001) is that the Cu adatoms are located at the face-centered cubic (fcc) hollow sites, while O adatoms are at the top site of the Zn-terminated ZnO(0001) surface. The possible interchange between Cu adatoms and substrate Zn atoms in the ZnO(0001)-(2 × 2) ideal surface is also examined. The result suggests that the diffusion of Cu into the ZnO substrate is not favorable under equilibrium conditions.

1. Introduction

ZnO has become an intensively studied material because of its wide range of technological promises. ZnO is the basic material for varistors, thyristors, and optical coatings. In addition, its wide band gap makes it an attractive candidate for blue and ultraviolet (UV) light-emitting diodes and laser diodes [1].

Recently, nanostructured ZnO materials have received broad attention due to their distinguished performances in electronics, optics and photonics. The demonstrations of room temperature ultraviolet lasers [2], field effect transistors [3] and field emission arrays [4] based on ZnO nanowires have stimulated greater interest in developing functional nanodevices. The metal-catalyzed vapor-liquid-solid (VLS) process has been widely used to synthesize ZnO nanowires. The use of metal catalysts has allowed a significant increase in control over the processes governing the growth of ZnO nanowires [5]. Cu is one of the most active metal catalysts for ZnO nanowire synthesis by the VLS process [6, 7]. Experimentally, by using high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED),

Li *et al* showed that Cu-catalyzed ZnO nanowires with a high-quality wurtzite (hexagonal close packed, or hcp) structure grew vertically on a p-type Si(100) substrate [6]. It was further shown that Cu catalyst-assisted fabrication of ZnO nanowires contained no copper contamination when the thickness of the copper film was less than 70 Å [7]. Cu particles were only found at the tips of the ZnO nanowires [6, 7]. On the other hand, Geng *et al* observed no catalyst particles at the tip of the nanowire [8]. Other studies further showed that metal catalyst might not be necessary for nanowire growth [9]. From the above, one may see that the particular roles of Cu in ZnO growth and of the atomic structure of Cu in ZnO are still poorly understood. Such knowledge, however, will be of fundamental importance for the better understanding and control of the growth processes.

A few theoretical studies of metallic adlayers on polar ZnO surfaces have highlighted the importance of the surfactant effects during ZnO nanostructure growth. Using first-principles calculations based on density functional theory, Wei *et al* examined Au adatoms on polar ZnO surfaces [10]. Northrup *et al* investigated an In surfactant layer on ZnO(0001) using first-principles total energy calculations [11]. However, a study of a Cu catalytic layer on ZnO is not yet available.

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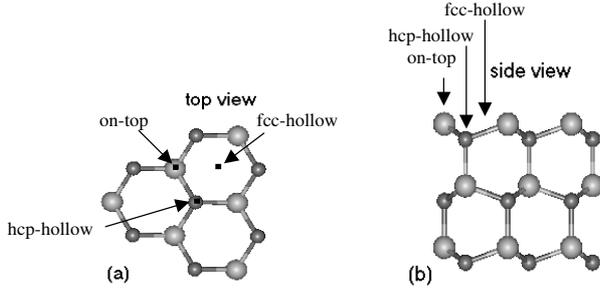


Figure 1. Top view (a) and side view (b) of the ZnO(0001) surface, indicating the highest-symmetry adsorption sites: fcc-hollow, hcp-hollow, and on-top. Light gray and gray balls represent Zn and O atoms, respectively.

In this paper, we investigate the adsorption of Cu and O on a ZnO(0001) surface. In particular, the effect of Cu on the adsorption of oxygen during ZnO(0001) growth is revealed. The calculations employ the density functional theory and first-principles pseudopotential method. Experimentally, it has been found that the growth of ZnO by molecular-beam epitaxy typically takes place on the (0001) or the (000 $\bar{1}$) surfaces [12]. We focus here on the ZnO(0001) surface which, in the absence of reconstruction, would be terminated by three-fold coordinated Zn atoms. In order to investigate whether or not the Cu adatoms diffuse into the ZnO substrate, a structure with Cu and Zn atoms exchanging sites on a ZnO(0001)-(2 \times 2) surface (referred to as the ‘exchange’ structure hereafter) is also considered. Computational details are presented in section 2. The calculated results and discussion are given in section 3, and a summary is given in section 4.

2. Methods

The present calculations are performed within the generalized-gradient approximation (GGA) framework, as implemented within the Vienna simulation package (VASP) [13, 14], employing the projector augmented wave (PAW) method [15]. The Zn 3d4s, O 2s2p and Cu 3d4s electrons are treated as part of the valence band. A cutoff energy of 400 eV is employed throughout this investigation.

For the study of Cu and O adsorption and their co-adsorption on a ZnO(0001) surface, we employ a slab model with a 1 \times 1 surface unit cell consisting of eight Zn–O bilayers and a vacuum layer of 15 Å separating the slabs. The top three Zn–O bilayers as well as the adatom layer are allowed to relax while the bottom five bilayers of ZnO are fixed at their bulk positions to mimic the bulk substrate. For the ‘exchange’ model, a ZnO(0001)-(2 \times 2) surface with a smaller thickness of six ZnO bilayers is used. Only adatoms are allowed to relax, while the others are frozen at the bulk positions. The dangling bonds at the bottom layer are saturated with pseudo-hydrogens with a fractional charge of $e/2$ in order to prevent unphysical charge transfer between the top and bottom slab surfaces. Surface unit cells with (1 \times 1) and (2 \times 2) periodicity are employed, with Gamma centered grids of (4 \times 4 \times 1) and (2 \times 2 \times 1) special k points, respectively, for the Brillouin zone integration.

Table 1. Lattice constants of wurtzite ZnO.

Lattice constant	a (Å)	c (Å)	u
Our results	3.287	5.303	0.378
PAW [18]	3.287	5.279	0.381
Experiment [17]	3.250	5.207	0.382

Table 2. Vertical distance d_0 and formation energy E_f of Cu and O adatoms for different adsorption sites considered on the ideal ZnO(0001)-(1 \times 1) surface.

Adsorption site	Cu/ZnO		O/ZnO	
	d_0 (Å)	E_f (eV)	d_0 (Å)	E_f (eV)
fcc-hollow	1.891	-2.54	0.794	0.03
hcp-hollow	1.887	-2.50	0.805	0.48
on-top	2.440	-2.39	1.860	0.92

Three different high-symmetry adsorption sites are considered on the polar ZnO(0001) surface. These are the on-top site, the hcp-hollow site and the fcc-hollow site (see figure 1). The formation energies E_f for the different surface atomic configurations were calculated according to [16]

$$E_f = E_{\text{tot}} - E_{\text{ref}} - \Delta n_{\text{Cu}} u_{\text{Cu}} - \Delta n_{\text{O}} u_{\text{O}}$$

where E_{tot} is the total energy of the ZnO(0001) slab with adlayers, E_{ref} is the total energy of a clean, relaxed ZnO(0001) slab, and Δn_{Cu} and Δn_{O} represent the numbers of Cu and O adatoms, respectively. u_{Cu} is the chemical potential of the Cu atom, and this is equal to the energy of the single Cu atom calculated in a large cubic cell (~ 0.067 eV). The chemical potential of O is equal to one half of the ground-state energy of an oxygen molecule in the gas phase, i.e. $u_{\text{O}} = \frac{1}{2}E(\text{O}_2)$, which is 4.41 eV.

3. Results and discussion

Before investigating different atomic structures with Cu or O adatoms, we first optimized the lattice structures of bulk wurtzite ZnO. The calculated lattice parameters are summarized in table 1 and show good agreement with the previous experimental [17] and theoretical values [18]. In the following calculations, the lattice constants of the substrate are assumed to take the calculated values.

3.1. Cu and O on the ZnO(0001) surface

The formation energies as well as the vertical distances (denoted as d_0) for Cu and O adatoms on the ZnO(0001) surface are calculated for different adsorption sites, and the results are summarized in table 2. Among the different adsorption configurations considered, the two most energetically favored structures for the Cu/ZnO(0001) system are the adsorptions of Cu at the fcc- and the hcp-hollow sites. The formation energy difference between these two is only 45 meV/atom. We therefore consider that Cu may be adsorbed either at the fcc-hollow site or at the hcp-hollow site. The vertical distances between Cu adatoms and the top Zn layer

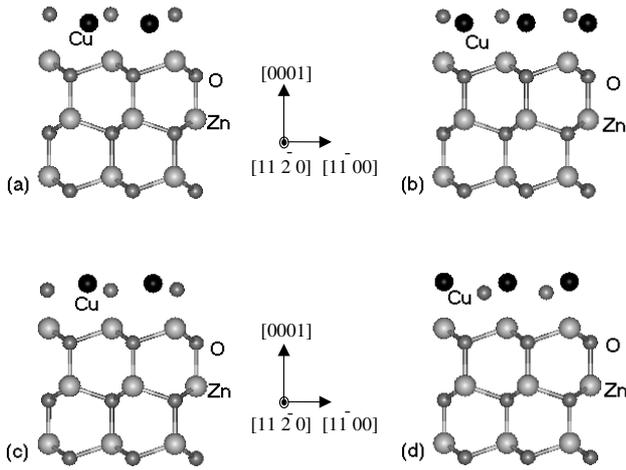


Figure 2. Schematic side views for co-adsorption of Cu and O adatoms on a ZnO(0001)-(1 × 1) surface with: (a) on-top O and fcc-hollow Cu adatoms structure; (b) on-top O and hcp-hollow Cu adatoms structure; (c) fcc-hollow Cu and on-top O adatoms structure; (d) on-top Cu and fcc-hollow O adatoms structure. Dark balls represent Cu adatoms.

are measured to be the same (within 0.01 Å) for adsorption at the fcc- and the hcp-hollow sites, which is in good agreement with the findings of Meyer and Marx [19]. The relatively small energy difference between the two configurations is a consequence of the fact that the surface Cu–Zn bonds are non-polar [20]. Thus, the Cu atoms are charge-neutral on ZnO(0001) and do not experience a large electrostatic attraction from the second layer O atoms. As for O adsorption, we find that the O-adsorbed ZnO(0001) does not present stable structures (refer to table 2). The lowest formation energy of O atoms adsorbed at the fcc-hollow site is 0.03 eV/atom. O adsorption at the hcp-hollow site is much less favorable than that at the fcc-hollow site, with an energy difference of ~0.45 eV/atom. This may be understood from the fact that O atoms adsorbed at the hcp-site sit directly above the second-layer O atoms of the ZnO substrate. Since the latter is partly ionic, this leads to electrostatic repulsion between these O atoms [21]. Note that the epitaxial sites for O atoms on ZnO(0001) are the on-top sites. However, from table 2, we find that such sites are energetically unfavorable. Thus, O adatoms on ZnO(0001) would avoid the epitaxial on-top sites during the initial stage of deposition of ZnO. Similar behavior has been found by Ishii for the epitaxial growth of GaN(0001) [22].

It should be pointed out at this stage that the positive formation energy of O on ZnO-(1 × 1) would suggest that the O₂ would not be dissociatively adsorbed on ZnO(0001). On the other hand, If we consider the surface adsorption of atomic O, the resulting formation energy would be that of the E_f listed in table 1 minus half of the binding energy of O₂ (~2.62 eV), which becomes negative, meaning that the adsorption of oxygen atoms is strongly favorable on ZnO surfaces. Even for dissociative adsorption of O₂, we found that at lower coverage (e.g. 1/3 and 1/4 monolayer), the formation energy can also be negative, and so the dissociative adsorption of O₂ may be preferable at the initial stage.

Table 3. Calculated formation energy E_f of Cu and O adatom co-adsorption on ZnO(0001) at full coverage.

Structure	E_f (eV)
O(on-top)/Cu(fcc-hollow)/ZnO(0001) (a)	-3.27
O(on-top)/Cu(hcp-hollow)/ZnO(0001) (b)	-3.20
Cu(fcc-hollow)/O(on-top)/ZnO(0001) (c)	-6.05
Cu(on-top)/O(fcc-hollow)/ZnO(0001) (d)	-4.71

3.2. Effect of Cu on the adsorption of O on ZnO(0001)

In the following, we shall investigate whether Cu may serve as a catalyst so as to enhance O adsorption on ZnO(0001). To do so, we compared two hypothetical geometric structures, i.e. O adsorption on ZnO with Cu adatoms present at the fcc- and the hcp-hollow sites, respectively. These structures are depicted in figures 2(a) and (b). The formation energies for O atoms being adsorbed at the surface high-symmetry sites of the Zn-terminated ZnO surface are calculated, and the stable configurations (with low formation energies) are listed in table 3. The formation energy of O adsorption at the on-top site on a surface with Cu atoms being pre-adsorbed at the fcc-hollow site (figure 2(a)) is lower than that on a surface with Cu being pre-adsorbed at the hcp-hollow site (figure 2(b)) by 0.07 eV/atom. Compared to O adsorption on a clean ZnO(0001) surface described earlier, the presence of Cu on ZnO(0001) lowers the formation energy by as much as 3.30 eV/atom. So, Cu greatly enhances the adsorption of O on ZnO(0001).

For completeness, we also examined Cu adsorption on O pre-adsorbed ZnO(0001) surfaces, where the O adatoms are located at the on-top site and the fcc-hollow site, respectively (see figures 2(c) and (d)). The formation energies for Cu adsorption at high-symmetry surface sites are calculated, while the results with low formation energies are given in table 3. Comparing all configurations, Cu adsorption at the fcc-hollow sites on a surface with O atoms being pre-adsorbed at the on-top sites (figure 2(c)) appears to be more favorable. For such a configuration, the adsorbed oxygen atoms would have chemical bonds closer to those of the substrate and thus energetically more stable. In combination with the earlier result for O adsorption on Cu pre-adsorbed ZnO(0001), we reach the conclusion that if there exist Cu atoms on the surface, which would preferably occupy the fcc-hollow sites, then O adsorption at the on-top sites (which are the epitaxial sites of ZnO) will become energetically favorable, in contrast to the case of O adsorption on clean ZnO(0001) surfaces. This is analogous to that of N adsorption on the truncated GaN(0001) surface [23]. This confirms that metal Cu can be advantageous to the epitaxial growth of high-quality ZnO crystals, which is consistent with the experiment involving high-quality ZnO nanostructures being grown on a p-type Si(100) substrate per catalysis by Cu [6].

Recent experimental investigations demonstrated that Cu particles are only found at the tips of ZnO nanowires based on VLS processes [6, 7]. These phenomena indicate that the Cu particles serve as a catalyst during growth of the ZnO nanowires. In order to achieve a better understanding of these peculiar phenomena, we may compare the formation

energies of O adsorption on Cu pre-adsorbed ZnO(0001) and Cu adsorption on O pre-adsorbed ZnO(0001) (figures 2(a) and (b) versus figures 2(c) and (d)). One notes that the latter configurations (figures 2(c) and (d)) are more favorable. The energetically favored configuration of Cu and O co-adsorption on a ZnO(0001) surface is thus that Cu adatoms are located at the fcc-hollow sites and O adatoms are located at the on-top Zn-site, with the position of the Cu adatoms being higher than that of the O adatoms. The result is again consistent with the finding by field emission scanning electron microscopy (FE-SEM) where Cu is only found at the tips of the nanowires [6, 7].

To gain insight into the possible precipitation of Cu in ZnO, the ‘exchange’ configuration, where Cu adatoms takes the place of Zn atoms in the ZnO(0001)-(2 × 2) surface, is examined. Regarding the case of 1/4 ML (monolayer) of Cu on the ZnO(0001)-(2 × 2) surface, various high-symmetry adsorption sites are tested. It is found that these Cu adatoms prefer to be located at the fcc-hollow site to the hcp-hollow site, and the energy is lower by 0.14 eV/(2 × 2). The least favored adsorption position is at the on-top site. If Cu adatoms interchange with Zn atoms in the ZnO ‘substrate’ surface, the energy is increased by 0.61 eV/(2 × 2). This suggests that Cu incorporation and becoming a contaminant in ZnO is not favorable during the growth of ZnO crystals using Cu as the catalyst, which agrees with the experimental finding of [7].

4. Summary

We have studied the role of copper in the adsorption of oxygen on a ZnO(0001) surface using first-principles density functional theory slab calculations. The results show that the most stable position of a Cu adatom on ZnO(0001) is at the fcc-hollow site, whereas O adsorption on a clean ZnO(0001) surface is unstable. On the other hand, the adsorption energy for O on a Cu pre-adsorbed ZnO(0001) surface can be decreased by 3.30 eV/atom, suggesting that Cu enhances the adsorption of O on ZnO(0001). For the latter case, the energetically favored configuration of Cu and O co-adsorption is that Cu adatoms are adsorbed at the fcc-hollow site while O atoms are at the on-top site, with the position of the Cu adatoms being higher than that of the O adatoms. The atom ‘exchange’ configuration, where Cu and Zn atoms interchange positions, also shows a high energy, indicating that it is unlikely for Cu atoms to be incorporated in ZnO during its growth by the catalysis of Cu.

Acknowledgments

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