Structural stability and magnetic properties of Co-doped or adsorbed polar-ZnO surface

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ARTICLE INFO

ABSTRACT

The structural stability and magnetic properties of Co-doped or -adsorbed polar-ZnO surface systems are investigated using first-principles calculations. It is found that Co ions energetically prefer to substitute for Zn in the outermost layer of both Zn- and O-terminated surfaces. Substitutional Co ions are antiferromagnetically coupled at ideal ZnO surfaces, which indicates additional defects or strain played a critical role in the reported ferromagnetism of ZnO : Co system. In addition, it is found that the adsorbed Co ions are preferred to ferromagnetic coupling, which may provide a new approach for spin injection of a ZnO film.

1. Introduction

Dilute magnetic semiconductors (DMSs), obtained by introducing transition metals (TM) into conventional semiconductors, have attracted much interest for potential spintronic applications due to their novel magnetic, magneto-optical and magneto-electrical properties [1]. Since the theoretical prediction of room temperature ferromagnetism in wide gap semiconductors [2], increased efforts have been put into studies of TM-doped ZnO, a II–VI wide band gap oxide semiconductor. This is also stimulated by renewed application of the inexpensive ZnO material itself, such as in field emission devices, optoelectronics, transducers and resonators [3]. Among the TM-doped ZnO systems, distinct magnetic properties have been reported in ZnO : Co: while Co-doped ZnO samples were reported to be ferromagnetic [4–10], more recent calculations and experiments indicate competition between ferromagnetic and antiferromagnetic phases [11–17] due to its sensitivity to growth conditions. Furthermore, the origin of experimentally observed high-T_c phase is still unclear, which leads more attention to the disorder effects. It was found recently that the high-T_c phases in ZnO : Co may be resulted from the formation of nano-scale spinodal decomposition phases, which may enhance its

magnetic percolation [18,19]. It is noticeable that most of above studies are focused on ZnO : Co bulk systems. On the other hand, the structural stability of TM on the surfaces and their magnetic properties play a critical role in spintronic device fabrication, since most semiconductor devices are made from thin films [3,20]. It is important to have the TM ions uniformly distributed since electron transport may be diffracted at TM clusters, if they form. Meanwhile, investigation of the ZnO polar surface itself has also been revived due to the critical surface effects in the application of ZnO based electronic devices [21]. To our knowledge, few studies have been performed to examine the structural stability and magnetic properties of Co on the ZnO polar surface. Surface effects on the magnetic properties are not easy to tackle experimentally due to the difficulty in delicately controlling the distribution of Co atoms on surfaces. The following questions could naturally be raised for theoretical studies: (i) What is the preferred structure for Co ions on the ZnO surface? (ii) How are Co ions magnetically coupled for various possible surface configurations? (iii) What could be suggested for possible spintronic applications of ZnO : Co films from a theoretical point of view?

In this work, we calculate the magnetic properties of Co-doped or -adsorbed polar-ZnO surface systems using first-principles calculations. We find that Co ions energetically prefer to substitute Zn at the outermost layer on both Zn- and O-terminated surfaces. Substitutional Co ions are antiferromagnetically coupled at surfaces, indicating the critical role of additional defects or strain

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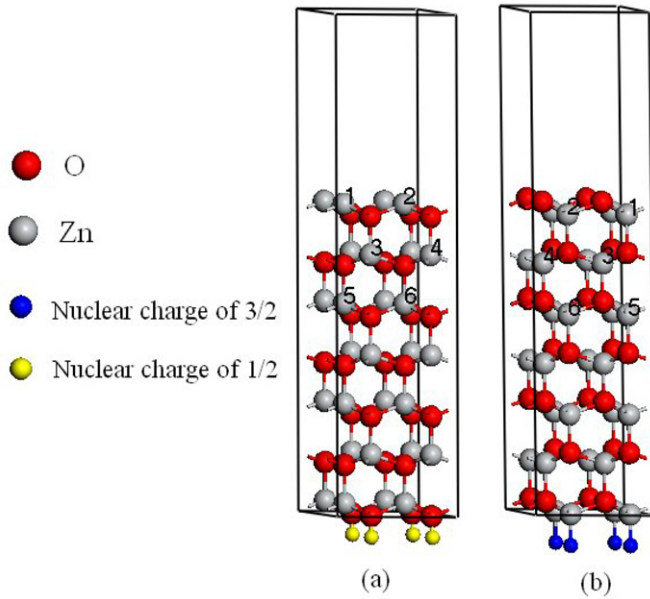*E-mail address:* zhaoyj@scut.edu.cn (Y.-J. Zhao).

Fig. 1. Wurtzite ZnO polar surfaces saturated with pseudo-hydrogen atoms: (a) Zn-terminated (0001) surface, (b) O-terminated (000$\bar{1}$) surface.

Table 1

The calculated formation enthalpies of the competing binary phases in ZnO : Co system.

	Formation enthalpy (eV)
ZnO	−3.541
CoO	−1.845
CoO$_2$	−3.738
Co$_2$O$_3$	−7.053
Co$_3$O$_4$	−9.476

to the reported ferromagnetism in the Co-doped ZnO system. We also find that the adsorbed Co ions are coupled ferromagnetically, which may be a novel approach for spin injection of ZnO films.

2. Computational details

Our density functional theory calculations were performed using Vienna ab initio simulation package (VASP) [22]. Exchange correlation interactions were described by the generalized gradient approximation (GGA) with the Perdew–Wang formalism (PW91) [23]. The projector-augmented wave (PAW) method [24] was used for the treatment of electron-core interactions since it is expected to have a better description of the interaction than ultrasoft-pseudopotentials [25]. A kinetic energy cutoff for plane waves of 400 eV was adopted for all systems. The total energy of Co-doped polar-ZnO surface systems was obtained using gamma centered Monkhorst–Pack k-point grids of $4 \times 4 \times 1$ [26]. In addition, the spin polarization scheme was adopted for all calculations.

Bulk ZnO consists of Zn and O slabs alternately placed along the $\langle 0001 \rangle$ direction, so its cross-sectional plane can be a Zn-terminated (0001) or an O-terminated (000$\bar{1}$) polar surface [27,28], as illustrated in Fig. 1. In the calculations, each slab consists of 2×2 surface unit cells and 7 Zn–O molecular layers with the 2 bottom layers fixed. The residual internal electric field in these thin slabs was quenched by saturating the broken surface bonds on the bottom side of the slabs with hydrogen-like atoms [21]. The artificial atoms with a nuclear charge of 1/2 and 3/2 were added for each surface atom at O- and Zn-terminated surfaces, respectively (cf. Fig. 1). This guarantees that the surface bands on the Co-free side are always fully occupied and that ideal charge neutralization

Table 2

Total energy E_{total} (eV), formation energy ΔE_{form} (eV) and total magnetic moment MM (μ_B) of single Co-doped polar-ZnO surfaces. The detailed Co doping configuration is shown in Fig. 1. Here the maximum Co chemical potentials of −3.738 eV and 0 are adopted for O-rich and O-poor conditions, respectively, with the restriction of avoiding competing Co oxides.

Co-doped position	E_{total} (eV)	Bond length of Co–O (Å)		ΔE_{form} (eV)		MM (μ_B)
		3-bond	1-bond	O-rich	O-poor	
O-terminated surface						
Co$_1$	−266.454	1.81	1.96	−0.328	–	4.972
Co$_3$	−265.441	1.85	1.95	0.685	–	4.465
Co$_5$	−264.857	1.90	1.95	1.269	–	3.948
Clean surface	−260.051					
Zn-terminated surface						
Co$_1$	−264.514	1.92	–	–	1.699	2.639
Co$_3$	−264.314	1.96	1.99	–	1.899	2.858
Co$_5$	−264.229	1.97	2.02	–	1.984	2.956
Clean surface	−260.336					

for this side of the slab is enforced [21]. The vacuum thickness is set to 12 Å. The polar-ZnO surface supercell consists of 28 Zn atoms and 28 O atoms. We also tried calculations for a slab of 10 Zn–O molecular layers with the 2 bottom layers fixed and found that there are no significant changes in the surface structure.

The structure preference of Co (doped or adsorbed) on the polar-ZnO surface was investigated by calculating the formation energy of the corresponding Co configuration at Zn-terminated and O-terminated surfaces. The formation energy of Co doped or adsorbed on the ZnO surface, ΔE_{form}, was calculated by [29]

$$\Delta E_{\text{form}} = E_{\text{Co}} - E_{\text{clean}} + n_{\text{Zn}}\mu_{\text{Zn}} - n_{\text{Co}}\mu_{\text{Co}} + q(E_{\text{VBM}} + E_f), \quad (1)$$

where E_{Co} is the total energy of the Co-doped or -adsorbed ZnO surface, and E_{clean} is the total energy of the clean polar-ZnO surface. μ_{Zn} and μ_{Co} are the chemical potentials of the Zn and Co atoms, respectively. The range of μ_{Zn} and μ_{Co} was obtained by avoiding the possible Co related competing phases (CoO, CoO$_2$, Co$_2$O$_3$, Co$_3$O$_4$, etc., with their calculated formation energy listed in Table 1). n_{Zn} and n_{Co} are the number of Zn and Co atoms involved in the given Co configuration, respectively. E_{VBM} represents the energy at the valence band maximum (VBM) of the defect free system. E_f is the Fermi energy relative to E_{VBM}. The charge state of defect atoms is denoted by q, which is set to zero here since no electron exchanges are expected for Co at the ideal ZnO polar surface.

3. Results and discussion

3.1. Co-doped polar-ZnO surfaces

The calculated formation energy of a single Co atom replacing a Zn atom in the slab model at different ZnO layers and its corresponding magnetic moment are listed in Table 2. The detailed Co configurations are shown in Fig. 1. Here, the maximum Co chemical potentials are used for the Co$_{\text{Zn}}$ defect formation energy listed in Table 2 with the restriction of avoiding possible Co oxides, i.e., −3.738 eV (dominated by Co$_2$O$_3$ compound) and 0 for O-rich and O-poor, respectively. The formation energies of Co$_{\text{Zn}}$ at the Zn-terminated surface under O-rich condition are not listed since O will exist on the ZnO surface when the environment is rich in oxygen. For a similar reason, data of the O-terminated surface under O-poor conditions are not listed, either. It is clear that the formation energy of substitutional Co defects increases significantly for a Co ion replacing a Zn ion at deeper layers for both of the polar-ZnO surfaces. Therefore, the doped Co atoms are expected to segregate to the outermost layers of the ZnO polar surfaces in equilibrium. The reduction of Co–O bond lengths as Co$_{\text{Zn}}$ forms in