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

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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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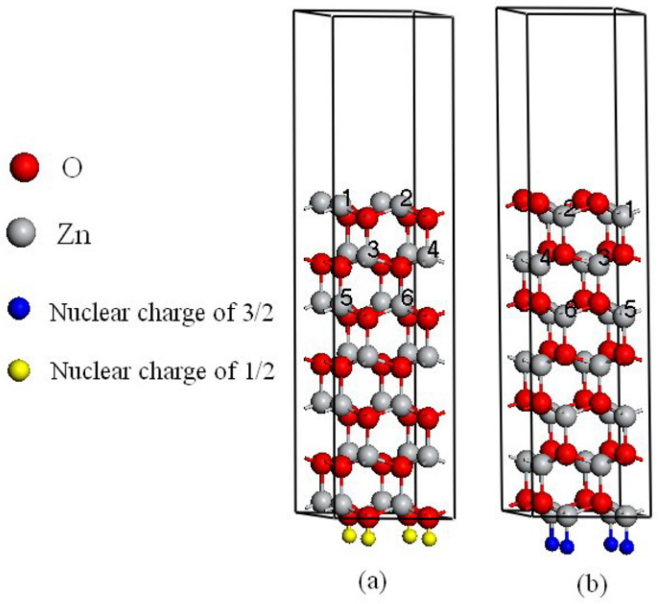

Fig. 1. Wurtzite ZnO polar surfaces saturated with pseudo-hydrogen atoms: (a) Zn-terminated (0001) surface, (b) O-terminated $(000\bar{1})$ surface.

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_2O_3	−7.053
Co_3O_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 ⟨0001⟩ 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 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.

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					

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]

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

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_2O_3, Co_3O_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_{Zn} defect formation energy listed in Table 2 with the restriction of avoiding possible Co oxides, i.e., −3.738 eV (dominated by Co_2O_3 compound) and 0 for O-rich and O-poor, respectively. The formation energies of Co_{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 CoZn forms in

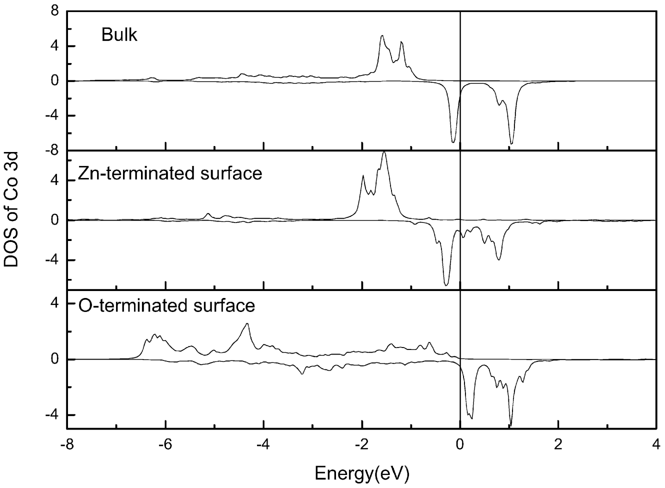

Fig. 2. The local density of 3d states on Co atoms, which are doped in the Co_1 position in the O-terminated surface, Zn-terminated surface and in $Zn_{0.96}Co_{0.04}O$ bulk.

the outer layers also reflects the stronger Co–O bonding of outer layers, where the lattice constraint is weaker.

On the other hand, the magnetic moment of Co in ZnO is also a matter of debate in the literature. Table 2 indicates that when Co replaces Zn in deeper layers of the Zn-terminated film, the magnetic moment of the Co ion decreases. In contrast, when Co replaces Zn in deeper layers in the O-terminated film, the magnetic moment of the doped film increases. In the Co_1 position on the O-terminated surface, Co has a spin magnetic moment ($4.972\mu_B$) larger than that on the Zn-terminated surface ($2.639\mu_B$). In order to compare the magnetic properties of Co on the surface and in the bulk, we also calculated the magnetic moment of Co in bulk ZnO (one Co atom in a 48-atom ZnO supercell). The calculated magnetic moment is $3.10\mu_B$ per Co ion, which is consistent with the value obtained in Ref. [30]. It is obvious that the magnetic moment of Co increases according to its environment along the series: Zn-terminated surface → bulk → O-terminated surface. Fig. 2 shows the Co-3d partial density of states of Co in the outermost layer of O- and Zn-terminated surfaces and ZnO bulk. It is also shown in Fig. 2 that crystal field splitting and the exchange splitting on the Co 3d states are noticeably greater at the O-terminated surface than at the Zn-terminated surface or in the bulk, which introduces a larger magnetic moment.

In order to study the magnetic interaction between Co ions at the polar-ZnO surfaces, we calculated the electronic structure of Co–Co coupling at the 2 × 2 polar-ZnO surfaces. The calculated magnetic moments in the Co–Co pair doped polar-ZnO surface and the formation energy of each slab with a Co–Co pair are listed in Table 3. E_{diff} is defined as the energy difference between the anti-ferromagnetic (AFM) and ferromagnetic (FM) states of the Co-doped polar-ZnO surface. This indicates that the AFM coupling between the Co ions is more stable than the FM coupling for doped Co ions at the ZnO surface. However, the strength of AFM coupling of doped Co at the surfaces is weaker than that in ZnO bulk, where the calculated energy difference is around 61 meV. This clear evidence of AFM coupling between Co in ZnO bulk and thin films indicates that additional crystal defects or strains play a critical role in the reported ferromagnetism in ZnO : Co. The conclusion on the segregation of Co ions to the outermost layer in equilibrium is also confirmed for the AFM coupled Co_{Zn} defect pairs, which have higher formation energy at the deeper layers as listed in Table 3. However, the Co_{Zn} defect formation energy increases as the concentration increases (cf. Tables 2 and 3). Thus, the Co atoms may not be clustering due to the repulsive interaction between the Co_{Zn} defects. We should also point out here that some calculations beyond LDA have been conducted on ZnO : Co system [31,32]. Although the electronic structures of ZnO : Co could be affected significantly due to the well-known LDA band gap problem, it is also confirmed that additional doping is necessary to achieve ferromagnetism, in good agreement with our results.

Table 3
Total energy E_{total} (eV), formation energy ΔE_{form} (eV/Co), energy difference between AFM and FM coupling ($E_{\text{diff}} = E_{\text{AFM}} - E_{\text{FM}}$ in eV/Co), and magnetic moment (MM in μ_B/Co) of Co–Co coupling doped polar-ZnO surface. 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)	E_{diff} (eV)	ΔE_{form} (eV)		MM (μ_B)
				O-rich	O-poor	
O-terminated surface						
Co_{12}	FM	−271.242	−0.060	0.479	–	3.97
	AFM	−271.361		0.420	–	0
Co_{34}	FM	−270.080	−0.107	1.060	–	3.94
	AFM	−270.294		0.953	–	0
Co_{56}	FM	−269.137	−0.058	1.532	–	3.56
	AFM	−269.252		1.474	–	0
Zn-terminated surface						
Co_{12}	FM	−268.799	−0.085	–	1.646	2.50
	AFM	−268.969		–	1.561	0
Co_{34}	FM	−268.359	−0.051	–	1.866	2.70
	AFM	−268.460		–	1.815	0
Co_{56}	FM	−268.234	−0.040	–	1.928	2.95
	AFM	−268.314		–	1.889	0

Table 4
The total energy E_{total} (eV), formation energy E_{form} (eV), energy difference between AFM and FM coupling ($E_{\text{diff}} = E_{\text{AFM}} - E_{\text{FM}}$ in eV/Co), and magnetic moment MM (μ_B/Co) of single Co atom and Co–Co coupling adsorbed on 2 × 2 polar-ZnO surfaces. Here the *absolute* chemical potential of Co is set to *zero* (i.e., atomic Co) because most adsorption occurs at low temperature.

		E_{total} (eV)	E_{diff} (eV)	E_{form} (eV)	MM (μ_B/Co)
Single Co adsorbed					
O-terminated (H_3)	FM	−267.680		−6.238	3.02
O-terminated (T_4)	FM	−265.545		−4.103	2.77
Zn-terminated (H_3)	FM	−264.732		−3.005	1.17
Zn-terminated (T_4)	FM	−264.744		−3.017	1.18
Co pair adsorbed					
O-terminated (H_3)	FM	−272.455	0.064	−5.502	2.12
	AFM	−272.328		−5.443	0
Zn-terminated (T_4)	FM	−269.311	0.053	−3.792	1.81
	AFM	−269.205		−3.739	0

3.2. Co adsorbed polar-ZnO surfaces

The total energy, E_{total}, surface formation energy, E_{form}, and magnetic moment of a single Co atom adsorbed on a polar-ZnO surface are listed in Table 4. Here, the *absolute* chemical potential of Co is set to zero (i.e., atomic Co is taken as a reference) considering the relatively low temperature for adsorption. Notably, this should not be considered an equilibrium condition. We wish to stress here that the formation energy of adsorbed Co is not appropriate to compare with that of doped Co directly due to the different values of Co chemical potential used here. We find that the Co atom is easily adsorbed at the H_3 site on the O-terminated surface, while it is only slightly preferred at the T_4 site on the Zn-terminated surface (cf. Fig. 3). This is in agreement with a previously reported result [33]. Our calculated result indicates that Co more easily adsorbs on the O-terminated surface than on the Zn-terminated surface (cf. Table 4). The magnetic moment of adsorbed Co on the O-terminated surface is greater than that on the Zn-terminated surface, which contradicts the result presented in Ref. [33]. Comparing this with the data in Table 2, we see that

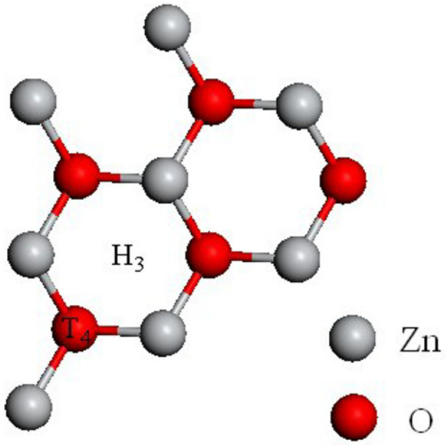

Fig. 3. Top view of polar-ZnO surface.

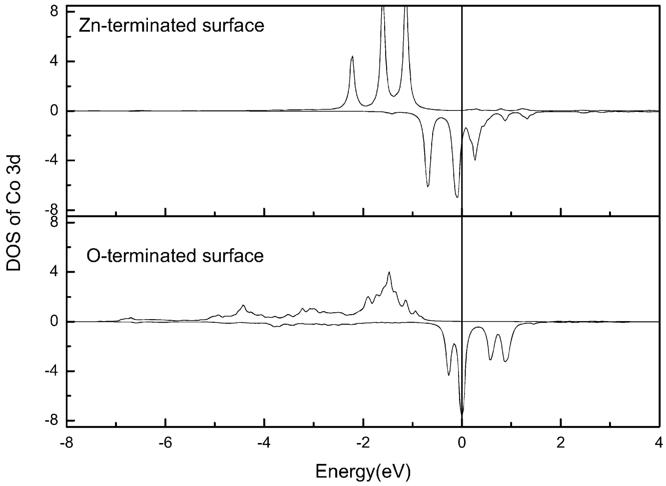

Fig. 4. The local density of 3d states on Co atoms, which are adsorbed on the O-terminated surface and Zn-terminated surface.

the magnetic moment of Co adsorbed on the polar-ZnO surface is smaller than that of Co doped in the polar-ZnO surface.

Fig. 4 shows the Co-3d partial density of states for adsorbed Co on the O-terminated surface and the Zn-terminated surface. It is clear that the majority spin density of Co 3d is more delocalized on the O-terminated surface than on the Zn-terminated surface. Similar to the doped Co case at the O-terminated surface, the stronger exchange splitting of Co 3d levels introduces a greater magnetic moment.

In order to evaluate the magnetic interaction between the adsorbed Co atoms on polar-ZnO surfaces, FM and AFM coupled Co pairs are studied on the polar-ZnO surface. The calculated energy difference between FM and AFM states, their magnetic moments and the formation energy of a Co pair adsorbed on the polar surfaces are listed in Table 4. It can be seen that the FM configuration is preferred to the AFM configuration when a Co–Co pair is adsorbed on polar-ZnO surfaces, in sharp contrast to the doped cases. We also find that the surface formation energy of a Co pair adsorbed on the O-terminated surface is lower than that on the Zn-terminated surface, but the magnetic moment of Co–Co coupling adsorbed on the O-terminated surface is larger than that on the Zn-terminated surface, which is consistent with the case of a single Co atom adsorbed on a polar-ZnO surface. The favored FM coupling on the polar surfaces are consistent with the results in Ref. [33]. However, the exchange energy between the adsorbed Co atoms (∼0.1 eV/pair in this work) are significantly smaller than the unexpectedly large values (∼1.0 eV) reported in Ref. [33]. This clear disagreement is expected because of the inappropriate saturation model for polar surfaces adopted in Ref. [33], where hydrogen atoms are deployed to terminate the bottom layers of the polar surfaces. Of note, it has been concluded in other studies that artificial hydrogen-like atoms with a nuclear charge of 1/2 and 3/2 are a more appropriate choice to saturate the surface bands [21].

4. Conclusion

We have performed a first-principles study of the structural stability and magnetic properties of Co-doped and -adsorbed polar-ZnO surface systems with an appropriate saturation model, which is critical for calculation of the magnetic coupling energy between Co atoms. It is found that Co ions energetically prefer to substitute Zn at the outermost layer on both Zn- and O-terminated surfaces. The substitutional Co ions are antiferromagnetically coupled in ideal ZnO bulk and surfaces, which clearly indicates ferromagnetism is unlikely in the Co-doped ZnO system unless additional defects or strains are introduced. In addition, it is found that the adsorbed Co ions are coupled ferromagnetically, which may be a novel approach for the spin injection of ZnO films.

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