APPLIED PHYSICS LETTERS **94**, 142502 (2009)

Magnetism and band gap narrowing in Cu-doped ZnO

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(Received 19 February 2009; accepted 12 March 2009; published online 6 April 2009)

First-principles calculations based on density functional theory are performed to study the magnetic, electronic, and optical properties of ZnO doped with 6.25%, 12.5%, and 18.75% of Cu. The Cu dopants are found spin polarized, and a net magnetic moment of $0.57\mu_B$ is found for Cu at a composition of 6.25%. The calculations confirm an appreciable band gap reduction in ZnO in agreement with recent experimental results. The analysis of the partial density of states reveals that ferromagnetism and narrowing of ZnO band gap are due principally to the strong *p*-*d* mixing of O and Cu. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3112603]

Spintronics, the recent field of science, allows one to explore the physics of previously unavailable combinations of electronic, optical, and magnetism in semiconductors, in which the spin[1] (electrons or holes) is exploited to provide new functionality such as spin based information storage, data processing, spin-polarized laser, etc. Among the most promising candidates for this task, transition metal (such as V, Cr, Mn, Fe, Co, and Ni) doped III-V and II-VI diluted magnetic semiconductors (DMSs) as a particular example, was the discovery of ferromagnetism in Mn-doped GaAs (Ref. 2) observed at temperatures in excess of 100 K. An ideal DMS should exhibit ferromagnetism at room temperature for practicable applications and have a homogeneous distribution of the magnetic dopants. The presence of any magnetic precipitation in the host semiconductors in forms of clusters or secondary phases of the magnetic impurities is crucial to the applications of DMS and therefore should be avoided. To solve the magnetic precipitation obstacle, alternative dopants which are intrinsically nonmagnetic but can be incorporated into semiconductors to form DMS are desired, their precipitation does not contribute to ferromagnetism since such dopants are naturally and intrinsically nonmagnetic. Cu is such a dopant for III-V and II-VI semiconductors that has recently attracted both theoretical and experimental attention.

Among DMS II-VI compounds doped with Cu, ZnO with a large gap of 3.2 eV has attracted great attention, both theoretically and experimentally, because of its potential application for next-generation short-wavelength optoelectronic devices such as light emitting diodes and laser diodes.[3] Moreover, the interest in doping ZnO is to explore the possibility of tailoring its magnetic and optical properties. However, the band gap of ZnO (3.3 eV) is too large to effectively use visible light (the solar spectrum has a maximum intensity at about 2.7 eV), and as a native *n*-type semiconductor, it is known to be difficult to make as a *p* type.[4] Therefore, it is important to have both *p*-type and band gap reduction in ZnO.

A large work exists in the literature concerning several aspects of Cu-doped ZnO from both theory and experiments. Recently room temperature ferromagnetism of Cu-doped ZnO was reported in several experiments,[5–12] whereas the absence of ferromagnetism also exists,[13,14] and first-principles calculations[15–19] has showed that Cu dopants in ZnO favor a spin polarization and a ferromagnetism ground state. The origin of the observed ferromagnetism still remains controversial, whether it is an intrinsic or extrinsic property of the material.

The ternary nature of the DMS offers the other possibility of tuning the band gap by varying the *x* composition of the material. Very limited research exists on band gap narrowing of ZnO by impurity incorporation. In the case of $Zn_{1-x}Cu_xO$ system, an increasing Cu composition leads to the reduction in the gap. In recent experimental investigation, Ahn *et al.*[20] reported that the band gap of ZnO can be reduced by 0.21 eV for low Cu composition ($x \sim 10\%$), revealing relatively important band gap reduction, inconsistent with an assumed simple linear dependence of the band gap over this composition range, as is expected on the basis of the virtual crystal approximation.

From the theoretical and experimental points of view, there are a lot of open questions regarding the magnetism and the optical properties of these materials. In this letter, we report on our first-principles calculations in doping ZnO with Cu. We study the magnetism and explore the possibility of band gap narrowing in Cu-doped ZnO.

The calculations were performed in the framework of density functional theory. We have employed the full potential linearized augmented plane wave method as implemented in the WIEN2K code.[21] The muffin-tin radii of Cu, Zn, and O were chosen to be 2.0, 2.1, and 1.4 a.u., respectively. We expand the basis function up to $R_{MT}K_{MAX}=6.5$. The maximum value of partial waves inside atomic sphere is $l=10$. Fully relativistic approximations are used for core electrons, and scalar relativistic approximations are used for valence electron. Brillouin zone integrations were performed with the special *k*-point method over a $3\times3\times2$ Monkhorst–Pack mesh.[22]

The calculations were done using the generalized gradient approximation (GGA),[23] which is supposed to be superior for magnetic system. The supercell employed contains 32 atoms, which corresponds to a $2\times2\times2$ supercell of ZnO.

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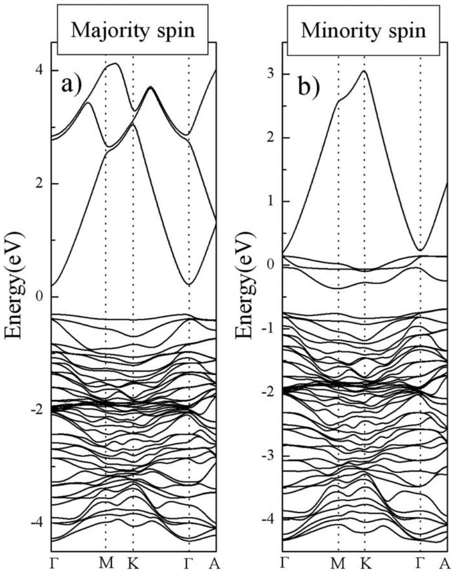

FIG. 1. Band structure of the majority spin (a) and the minority spin (b) of ZnO doped with 6.25% of Cu. Fermi level is set to zero.

Three doping levels were checked: $x=0.0625$, 0.125, and 0.1875. The doped structures were then optimized with respect to both optimized lattice constants and the relaxation of atomic positions. These parameters ensure a convergence better than 2 meV for total energy. The relaxation of lattices was stopped until the maximum force on single atom is less than 0.02 eV/Å. All calculations are done for the ferromagnetism case since theoretical calculations[17,18] show high stability of ferromagnetism. The calculated lattice constants a and c of wurtzite ZnO are 3.28 and 5.29 Å, respectively, which are in good agreement with the experimental values.

We focus first on the magnetic properties of the Cu-doped ZnO. For one Cu, i.e., $x=0.0625$, we found a total magnetic moment of $0.92\mu_B$ per supercell, the local moment at Cu is about $0.57\mu_B$, and the four surrounding O atoms in the CuO_4 tetrahedron are polarized with a magnetic moment of $0.05\mu_B$ for the top site O and $0.08\mu_B$ for the other three O in the basal plane. These results are very similar to the one reported by Ye *et al.*,[17] where the authors found for $x=0.125$ a magnetic moment of $0.58\mu_B$ for Cu, $0.04\mu_B$ for the top site O, and $0.08\mu_B$ for the other three O.

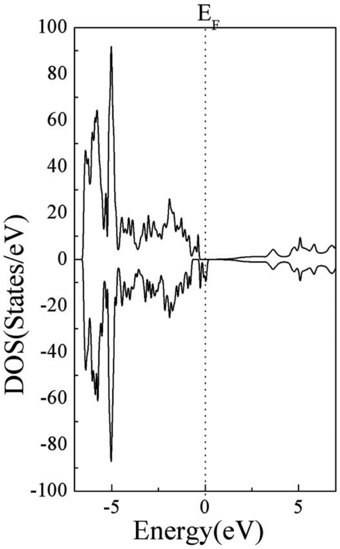

FIG. 2. Total density of states of ZnO doped with 6.25% of Cu. Fermi level is set to zero. Positive (negative) values correspond to the majority (minority) spin.

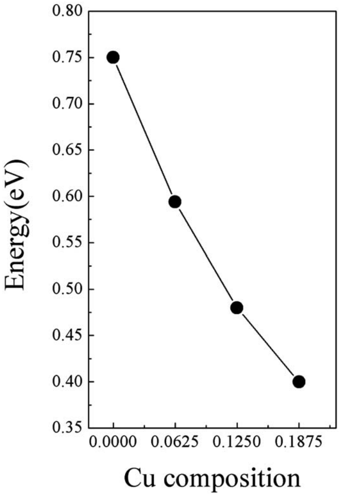

FIG. 3. Cu content dependence of the band gap energy.

Furthermore for $x=0.125$, we found a total magnetic moment of $1.87\mu_B$ per supercell. The local moment at Cu is about $0.55\mu_B$ and remains relatively constant for all compositions study. The calculated local moment of Cu is similar to the theoretical works of Huang *et al.*[18] and Ye *et al.*,[17] who found a magnetic moment of $0.55\mu_B$ and $0.58\mu_B$, respectively, which are weaker than the one of Park and Min[15] who obtained a magnetic moment of $0.81\mu_B$.

Moreover for $x=0.0625$, we found that the substitution of Zn by Cu is a p-type doping, as found theoretically,[17,19] which supports recent experimental observation.[7,13] The calculated holes in the Cu site and in the interstitial region are $0.11e$ and $0.6e$, respectively, indicating that the charge redistribution mostly happens in the interstitial region.

To illustrate the corresponding electronic properties, the spin-resolved band structures, and total density of states of Cu-doped ZnO for $x=0.0625$ are given in Figs. 1 and 2, respectively. A half-metallic behavior is shown with the majority being semiconducting and minority spin being metallic. The 100% polarization of conduction carriers, which is required in spin injection, suggests that Cu-doped ZnO can be used efficiently in injection of spin-polarized charge carriers into the nonmagnetic ZnO. The Zn, O, and Cu contri-

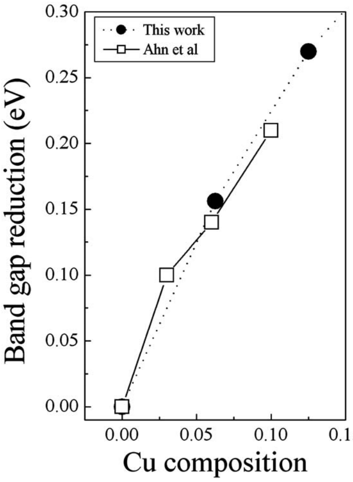

FIG. 4. Cu content dependence of the band gap reduction (solid circle) compared with experimental results (Ref. 20, open square).

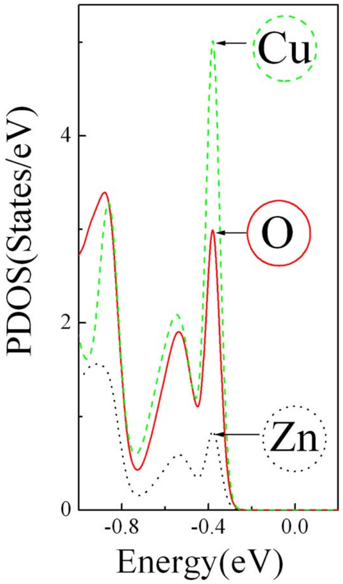

FIG. 5. (Color online) Partial DOS of ZnO doped with 6.25% of Cu (Zn atom in dotted line, O atom in solid line, and Cu atom in dashed line). Fermi level is set to zero.

butions of the majority-spin system can be divided into three parts. The states in the energy region form −7 to −3 eV arise primarily form the Zn 3*d* states, the states in the energy range from −3 to −1 eV come mainly from the O 2*p* bands, while the states near E_F are composed mostly of Cu 3*d* bands.

An important consequence of the inclusion of Cu atoms in ZnO is the reduction in the band gap. Figure 3 shows the variation of the band gap of Cu-doped ZnO for the majority-spin case as function of Cu compositions. As found experimentally,[13] our results show that band gap of Cu-doped ZnO decreases considerably with increasing Cu concentrations. Since GGA underestimates the band gaps, it is useful to compare our calculated band gap reduction $\Delta E_g = E_g(\text{ZnO}) - E_g(\text{Cu}-\text{ZnO})$ with the experiment. Figure 4 shows the comparison of band gap reduction as function of Cu compositions. Our results are in perfect agreement with the experimental data (for example for $x=6\%$, we found a band gap reduction of 0.15 eV, which compared favorably with the measured value of 0.14 eV) showing a relatively large reduction in the band gap of ZnO. This reduction is inconsistent with an assumed simple linear dependence of the band gap over this composition range as expected for highly "well-matched" alloys, where the substituted atom induces weak perturbation in the host material. The calculated band gap reduction in Cu-doped ZnO follows the simple fitted formula: $\Delta E_g = 1.4x^{0.8}$. To have more insight into the common physical relationships between alloys, heavily charge doped semiconductors and heavily electronically doped semiconductors, a scaling rule was recently observed by Zhang *et al.*,[24] $\Delta E_g = \beta x^{\alpha}$. For highly matched semiconductor alloys, such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$, the scaling exponent of x is close to unity, while for heavily-doped alloys (e.g., GaAs-doped N), this scaling factor is close to 2/3.[24] The results suggest an appreciable band gap bowing of the band gap of ZnO-doped Cu, and explicitly demonstrate the nonlinear behavior of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ band gap at low Cu doping compositions. The main contribution to the band gap reduction in the Cu-doped ZnO system comes from chemical and magnetic effects, since Zn and Cu atoms have strong (weak) mismatch in electronegativity (size).

Figure 5 shows the partial density of states of Zn, O, and Cu around the Fermi level for $x=0.0625$. The origin of the reduction in the band gap of the Cu-doped ZnO is mainly due to the large hybridization of the Cu 3*d* bands with the O 2*p* bands. This *p*-*d* exchange mechanism, which is also responsible for ferromagnetism in Cu-doped ZnO, is large for this system, since the *p* orbital energies of O are very close to that of Cu. Clearly, this strong $\text{O}(p) - \text{Cu}(d)$ exchange interaction play a role in narrowing the band gap of the Cu-doped ZnO system.

In summary, we have performed first-principles calculations of Cu-doped ZnO with 6.25%, 12.5%, and 18.75% of Cu composition. It is revealed that because of the strong coupling between O 2*p* and Cu 3*d* bands, this system which does not contain any magnetic ion is found as half-metallic material. Furthermore we found that the *p*-*d* repulsion mechanism is also responsible for the relatively appreciable reduction in the band gap of Cu-doped ZnO as found experimentally.

We acknowledge the VR-SIDA for financial support and high performance computing in Uppsala University for computational facilities.

[1] H. Ohno, Science **281**, 951 (1998).
[2] H. Ohno, A. Sher, F. Matsuka, A. Oiwa, and A. Eudo, Appl. Phys. Lett. **69**, 363 (1996).
[3] D. M. Bagnall, Y. V. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **70**, 2230 (1997).
[4] K. Kakiuchi, E. Hosno, and S. Fujihara, J. Photochem. Photobiol., A **179**, 81 (2006).
[5] K. Ando, H. Saito, Z. Jin, T. Fukumura, M. Kawaski, Y. Matsumoto, and H. Koinuma, J. Appl. Phys. **89**, 7284 (2001).
[6] H.-J. Lee, B.-S. Kim, C. R. Cho, and S.-Y. Jeong, Phys. Status Solidi B **241**, 1533 (2004).
[7] D. B. Buchholz, R. P. H. Chang, J. H. Song, and J. B. Ketterson, Appl. Phys. Lett. **87**, 082504 (2005).
[8] D. Chakraborti, J. Narayan, and J. T. Prater, Appl. Phys. Lett. **90**, 062504 (2007).
[9] X. Wang, J. B. Xu, W. Y. Cheung, J. An, and N. Ke, Appl. Phys. Lett. **90**, 212502 (2007).
[10] M. S. Seehra, P. Dutta, V. Singh, Y. Zhang, and I. Wender, J. Appl. Phys. **101**, 09H107 (2007).
[11] A. Tiwari, M. Snure, D. Kumar, and J. T. Abiade, Appl. Phys. Lett. **92**, 062509 (2008).
[12] C. Sudakar, K. Padmanabhan, R. Naik, G. Lawes, B. J. Kriby, S. Kumar, and V. M. Naik, Appl. Phys. Lett. **93**, 042502 (2008).
[13] D. J. Keavney, D. B. Buchholz, Q. Ma, and R. P. H. Chang, Appl. Phys. Lett. **91**, 012501 (2007).
[14] Q. Xu, H. Schmidt, S. Zhou, K. Potzger, M. Helm, H. Hochmuth, M. Lorenz, A. Setzer, P. Esquinazi, C. Meinecke, and M. Grundmann, Appl. Phys. Lett. **92**, 082508 (2008).
[15] M. S. Park and B. I. Min, Phys. Rev. B **68**, 224436 (2003).
[16] X. Feng, J. Phys.: Condens. Matter **16**, 4251 (2004).
[17] L.-H. Ye, A. J. Freeman, and B. Delley, Phys. Rev. B **73**, 033203 (2006).
[18] L. M. Huang, A. L. Rosa, and R. Ahuja, Phys. Rev. B **74**, 075206 (2006).
[19] D. Huang, Y.-J. Zhao, D.-H. Chen, and Y.-Z. Shao, Appl. Phys. Lett. **92**, 182509 (2008).
[20] K.-S. Ahn, T. Deutsch, Y. Yan, C.-S. Jiang, C. L. Perkins, J. Turner, and M. Al-Jassim, J. Appl. Phys. **102**, 023517 (2007).
[21] P. Blaha, K. Schwarz, and J. Luitz, WIEN2K, University of Technology, Vienna, 1997; [improved and updated Unix version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990)].
[22] H. J. Monkhorst and J. D. Park, Phys. Rev. B **13**, 5188 (1976).
[23] J. P. Perdew, K. Burke, and M. Enrzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[24] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. B **63**, 161303(R) (2001).