Sains Malaysiana 43(6)(2014): 813–817

A Study of Cr doping on the Structural and Electronic Properties of ZnO: A First Principles Study

(Kajian Pengedopan Cr terhadap Sifat Struktur dan Elektronik ZnO: Kajian Prinsip Pertama)

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ABSTRACT

The central theme of nanotechnology to miniaturize devices has stimulated interest in diluted magnetic semiconductors (DMS). DMS that simultaneously exhibit magnetic and semiconducting behavior are capable of parting properties of two different function devices into one. In this research we present our first principles investigations related to the structural and electronic properties of, Cr doped zinc-blende (ZB) ZnO, DMS. These calculations are carried out using full potential linearized augmented plane wave plus local orbital (FP-L(APW+lo)) with generalized gradient approximations approach as implemented in WIEN2k code. In this study, the effect of Cr doping on lattice parameters, spin polarized electronic band structure, density of states (DOS) of ZnO is presented and analyzed in detail.

Keywords: Density functional theory; FP-LAPW; gradient and other corrections; local density approximation; magnetic semiconductors; transition metals and alloys; ZnO

ABSTRAK

Tema utama nano teknologi dalam pengecilan saiz peranti telah merangsang minat dalam semikonduktor magnet cair (DMS). DMS pada masa yang sama mempamerkan sifat magnet dan semikonduktor berkemampuan untuk menjadikan dua peranti yang mempunyai fungsi berbeza dalam satu. Dalam penyelidikan ini, kami membentangkan prinsip pertama penyelidikan yang berkaitan dengan sifat-sifat struktur dan elektronik, Cr didopkan zink-blend (ZB) ZnO, DMS. Pengiraan ini dijalankan dengan menggunakan keupayaan penuh linear gelombang satah terimbuh ditambah orbitan tempatan (FP-L(APW + lo)) dengan pendekatan anggaran kecerunan teritlak seperti yang dilaksanakan dalam kod WIEN2k. Dalam kajian ini, kesan pengedopan Cr pada parameter kekisi, struktur jalur elektronik spin terkutub dan ketumpatan keadaan (DOS) daripada ZnO dibentangkan serta dianalisis secara terperinci.

Kata kunci: FP-LAPW; kecerunan dan pembaikan lain; penganggaran ketumpatan tempatan; semikonduktor magnet; teori ketumpatan fungsian; transisi logam dan aloi; ZnO

INTRODUCTION

On hand electronic devices in today's information technology, such as computers and iPods are mainly consisting of two major elements, the logic gadgets and the data storage devices. Logic elements are usually composed of transistors based on semiconductor technology (as in integrated circuits and diodes) and are mainly used for communications and information processing, while data storage devices are made up of magnetic metals (as in magnetic hard drives and sensors). However, the rapid progress in the field of spintronics has made it possible to construct devices that would simultaneously exhibit magnetic and semiconducting behavior. An archetypal application of such phenomenon is giant magneto resistance (GMR) effect (Prinz 1998, 1995), where the magnetic field is used to change the electric resistance in a magnetic multilayer.

Although GMR sensors are almost commercially available for read heads in high density data storage devices, the complete potential of spintronics is still not exploited in current GMRs. The large mismatching between the resistivities of semiconductors and metals, in fact prevents the effective spin injection, which is considered as one of the major hurdles in the exploitation of these hybrid structures.

The dilemma in the applications of GMR is certainly resolved with the concept of diluted magnetic semiconductors (DMS). DMS are semiconducting materials where host cations are replaced by magnetic ions in a dilute range and thus introduce a strong magnetic effect to host material without deteriorating their electronic and optical properties. This possibility of combining both logic gadgets and data storage devices simultaneously into a single multifunctional spintronics device has dragged out rigorous attention of researchers, where their interest in this field were severely motivated with the discovery of ferromagnetism in DMSs based on Mn doped IV-VI (Story et al. 1986), III-V (Haury et al. 1997; Ohno et al. 1996, 1992; Van Esch et al. 1997) and II-VI (Ferrand et al. 2000; Ohno 1999). However, DMSs based on II-VI

compound semiconductors have attracted considerable attention due to their compatibility with existing II-VI semiconductors based technology. From II-VI compounds, ZnO is considered as one of the most promising candidate for the fabrication of DMSs. The importance of ZnO based DMSs is since the prediction of Dietl et al. (2000) based on Zener model, that transition metals could establish ferromagnetism above room temperature when doped (on the order of 5% or more) in p-type ZnO. Since then many studies have been carried out on ZnO doped with various transition metals (TM).

Among the TM, Cr is considered as more appropriate doping material, because of its large magnetic moment ($4\mu_B$) and small difference in ionic radii Cr (73 pm) to Zn (74 pm). The predicted stable ferromagnetic state (FM) than spin glass state (Sato & Katayama-Yoshida 2002, 2001) has made it more favorable for fabrication of DMSs based on ZnO. The FM state of Cr is energetically favorable than Co doped ZnO. However several experimental reports available on Cr:ZnO are in conflict with each other. For instance, the investigations of Ueda et al. (2001) and Venkatesan et al. (2004) reported no ferromagnetism Cr doped ZnO (Satoh et al. 2004) have experimentally reported ferromagnetic behavior of Cr: ZnO based on remanent magnetization. Roberts and Pakhomov (2005) have reported room temperature behavior of Cr: ZnO for 9.5% of Cr doping concentration. Sluiter et al. (2005) investigated the magnetic behavior of Cr doped ZnO both experimentally and with first principles approach and predicted the FM ordering in Cr doped ZnO. Recently, Chen et al. (2012) investigated the electronic structure and magnetic properties of Cr doped ZnO and reported magnetic moment 7.50 μ_B per supercell. They attributed the observed magnetic moment to the unpaired 3D electrons of Cr. The studies carried out Cr: ZnO are mostly focused on the wurtzite(WZ) phase of ZnO. To the best of our knowledge, Cr doped ZB-ZnO is scarcely studied, which is expected to exhibit p-type conductivity (Ashrafi & Jagadish 2007).

These studies motivated us to investigate the structural parameters and electronic properties of Cr doped ZnO in ZB phase. For calculations of these properties we used full potential augmented plane wave plus local orbital (FP-(APW+lo)) method based on density functional theory (DFT). The Perdew et al. (1996) generalized gradient approximations (GGA-PBE) have been adopted for the calculations of structural and electronic properties.

Method of Calculations

In the present work structural and electronic properties of Cr doped ZnO have been investigated using FP-(APW+lo) method. Perdew et al. (1996) proposed GGA has been adapted for the treatment of the exchange and correlation potential. Like our previous study (Bakhtiar et al. 2013, 2012), these calculations were done using WIEN2k code (Blaha & Schwarz 2001). In this scheme of computations, to investigate the structural and electronic properties of Cr:ZnO, unit cell is divided into two regions, interstitial region and non-overlapping atomic spheres. In both these regions, Kohn-Sham (Van Esch et al. 1997) wave functions, charge densities as well as potential are computed in a different way inside the unit cell. Inside the RMT (radius of muffin tin) spheres denoted usually by R_{MT} around the position of each atom, spherical harmonic expansion is used. Whereas in the interstitial space of the unit cell, the plane wave basis set is taken into account. R_{MT} values were chosen as 1.78 a.u for Zinc, 1.78 for Chromium and 1.58 a.u for oxygen. Charge density was Fourier expanded up to G_{max}= 16 au^{-1}. Plane wave cut-off K_{max} times MT radius was taken such that cut-off $K_{max} \times R_{MT}$ = 8. For well convergence of energy we used a 7 × 7 × 7 k points grid in the special irreducible Brillouin zone (BZ). To obtain better results, the total energy was converged to 10^{-5} Ryd/unit cell in the present self-consistent calculations.

Results and Discussion

In this work, for the investigations of structural and electronic properties of Cr:ZnO, the unit cell of ZnO containing two atoms was extended to a so called supercell with a configuration of 1×1×1. With this configuration the supercell contains 8 atoms of Zn and O. To dope 25% of Cr atoms in ZnO, one of Zn atom was replaced by Cr. The schematic view Cr: ZnO has been shown in Figure 1. The lattice parameters of Cr: ZnO in ZB phase have been calculated from the energy-volume curve (Figure 2). The calculated data have been listed in Table. 1. The value of our calculated lattice constant of $Zn_{0.75}Cr_{0.25}O$ is though closer to the experimentally measured value of un-doped ZnO, a small difference is because of the small mismatching in the ionic radii of Zn and Cr.

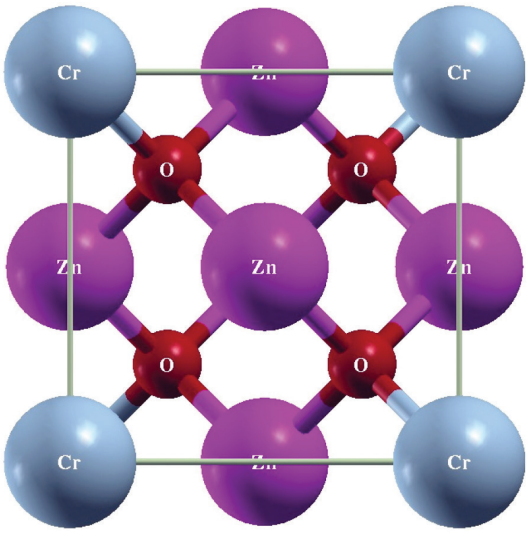

FIGURE 1. Schematic overview of structure of $Zn_{0.75}Cr_{0.25}O$ in zinc-blende phase

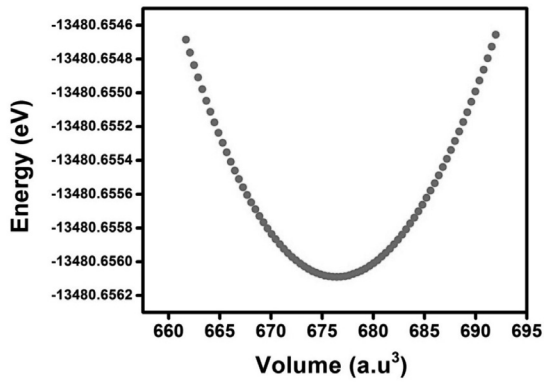

FIGURE 2. The schematic plot of cell volume against cell energy. The volume is calculated in atomic units

TABLE 1. The calculated optimized volume, lattice constant, total energy per formula unit and bulk modulus of $Zn_{0.75}Cr_{0.25}O$

$Zn_{0.75}Cr_{0.25}O$	Calculated values
Optimized volume (V_0)	656.6
Total energy (E_0)	-3370.1625
Lattice constant (a)	4.59
Bulk modulus (GPa)	123.14

The spin polarized electronic structures of Cr:ZnO in ZB phase have been presented in Figure 3. Cr:ZnO in ZB phase show metallic nature of these systems (Figure 3). For up spin channel, transition of electrons takes place from valence band to the unoccupied states in the conduction band in the vicinity of Fermi level. This is because of the strong hybridization among the O-p and Cr-d states. For down spin channel, the conduction band minimum which is mainly composed of Cr-d states, crosses the Fermi level at Γ- point of the BZ. The electronic structure profile is in good analogy to that reported by Chen et al. (2012). Splitting of up and down spin channels can be seen in

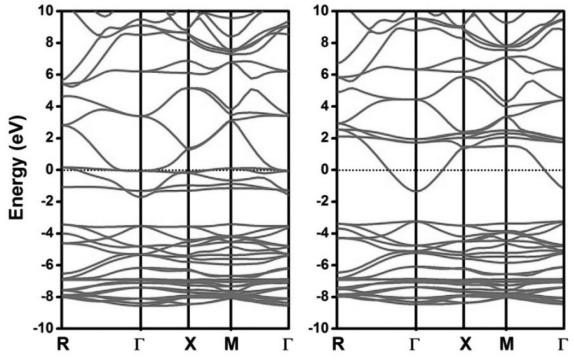

FIGURE 3. Schematic of spin polarized band structures of $Zn_{0.75}Cr_{0.25}O$

the vicinity of Fermi level that shows the doping Cr ions induce magnetism in ZB-ZnO. Our analysis showed the Cr atoms as the main contributor to the magnetism in Cr:ZnO system.

To further explain the contribution of states, we have calculated the spin polarized DOS of Cr:ZnO. The schematic overview of spin polarized DOS have been shown in Figure 4. In Cr:ZnO, for both up and down spin channels, the DOS in energy range -8.5 to -3.1 eV, are mainly contributed by Zn-3d states together with a weak effect of O-p and Cr d- states. For up spin channel, the DOS in energy -1.4 to 0.23 eV are mainly originated from Cr d-states, while in spin down case Cr d-states appear from 1.71 to 2.62 eV. Furthermore the up and down Zn-d and O-p spin states holds mirror symmetry (Figure 4). In the vicinity of Fermi level, the asymmetrical arrangement of Cr-d states for both up and down spin channels indicate the spin splitting that mainly result in the ferromagnetism.

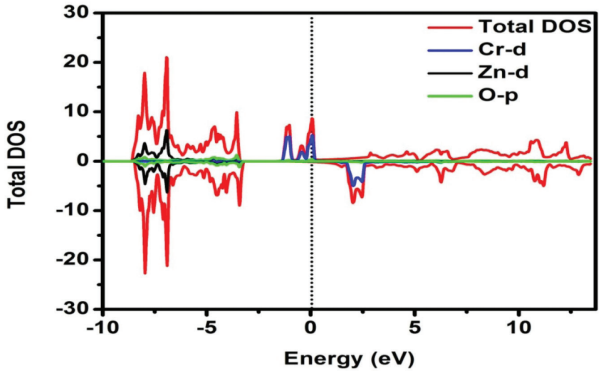

FIGURE 4. The calculated spin polarized density of states of Cr:ZnO. The DOS along positive Y-axis indicate the up spin DOS and the DOS along negative axis indicate down spin DOS

In ZB phase, each Cr atom (cation) in Cr:ZnO is tetrahedral connected to the nearest neighbor O^{-2} atoms (anion). As a result of anion environment, Cr^{2+} atoms experience a strong negative coulomb potential because of O^{2-} atoms that strongly affect the degeneracy of Cr d-band and split it into higher energy to t_{2g} and lower energy e_g states. The schematic of the spin polarized Cr d-band have been shown in Figure 5. This splitting of Cr d-band results in crystal field splitting effect. The crystal field splitting energies calculated for up and down spin states were found to be about 1.08 eV for up spin channel and 0.38 eV for down spin channel.

CONCLUSION

In this work, the structural and electronic properties of Cr doped ZnO in ZB phase have been investigated using FP-L(APW+lo) method structured within DFT. About 25% of Zn atoms were successfully replaced by Cr^{2+} atoms by using the so called supercell approach. The lattice constant

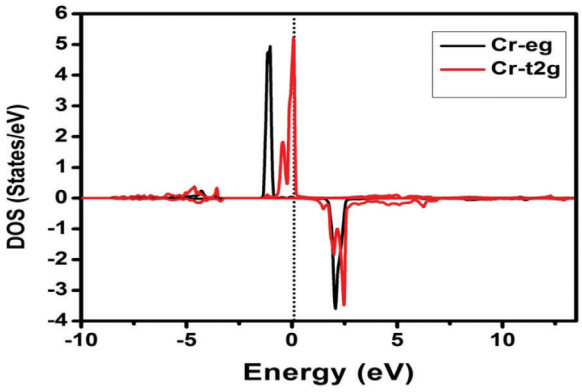

FIGURE 5. The splitting of d-band has been schematically shown. The states along positive Y-axis show the up spin Cr^{2+} d-band and the states along negative axis indicate down spin Cr^{2+} d-band

of Cr:ZnO was slightly reduced than pure ZnO because of the small mismatching in ionic radii of Zn^{2+} and Cr^{2+}. The DOS show splitting of Cr^{2+} d-band into higher energy t_{2g} and lower energy e_g states thus result in crystal field splitting effect.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Education (MOE), Malaysia/ Universiti Teknologi Malaysia (UTM) for the financial support of this research through grant nos. R.J130000.7826.4F113; Q.J130000.7126.00J33; R.J130000.7726.4D034 and Q.J130000.2526.02H89.

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Received: 13 March 2013
Accepted: 26 December 2013