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Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Comparative study of Fe doped ZnO based diluted and condensed magnetic semiconductors in wurtzite and zinc-blende structures by first-principles calculations



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ARTICLE INFO

Article history:

Received 1 October 2015

Received in revised form

5 December 2015

Accepted 9 December 2015

Available online 17 December 2015

Keywords:

DFT

Half metallic materials

Magnetic materials

FP-LAPW

Electronic band structure

ABSTRACT

Magnetic semiconductors with simultaneous semiconducting and magnetic characteristics are significant for applications in next generation spintronic devices. However, efficiency of these materials strongly relies on the selection of the proper host and dopant/alloying materials. In this work, we explore magnetic semiconductors based on the most appropriate materials namely ZnO doped with Fe in wurtzite (*w*) and zinc-blende (*zb*) structures. For comprehensive analysis, Fe has been doped into ZnO for several Fe concentrations such as 6.25%, 12.5%, 18.5% and 25%. Investigations are achieved using density functional theory (DFT) based full potential linearized augmented plane wave plus local orbital FP-L (APW+*lo*) method. The exchange correlation energy has been determined using Perdew et al. proposed generalized gradient approximations (GGA) with additional Hubbard (*U*) parameter as well. Our results show that; in *w*-structure, Fe:ZnO favors antiferromagnetism (AFM) at ground state, whereas in *zb* structure, ferromagnetism (FM) is dominated at 6.25% and 12.5% dopant concentration. However, for 18.75% and 25% dopant concentration, AFM interactions are dominated over FM, possibly is caused by the occurrence of anti-ferromagnetic secondary phases. Moreover, effect of mismatching ionic radii of Fe and Zn atoms, and formation of secondary phases is noticed on lattice parameters of Fe:ZnO with Fe concentration. The electronic and magnetic properties of Fe:ZnO endorse them suitable for applications in spin based electronic devices.

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1. Introduction

Diluted magnetic semiconductors (DMS) with allied semiconducting and magnetic characteristics have been extensively studied for the past few years. The main motivation behind this is to investigate suitable materials/composition of the magnetic semiconductors with enhanced processing speed and data storage for spintronics [1–3]. DMSs are designed by doping magnetic elements particularly transition metals (TM) in host semiconductor matrix. Therefore, search for appropriate host

semiconductor is crucial alongside dopant element. In this regard, ZnO is considered one of the excellent host semiconductor [4], as ZnO exhibit important features like wide and direct band gap, abundant availability and easy fabrication [2,5–9].

ZnO that naturally exist in *w*-structure, now is getting equal importance in meta-stable *zb* geometry for fabrications of DMSs [10–22]. Although considerable research work is available in literature on DMS, there are certain key issues in realizing of DMS for their practical use in devices, like, synthesis of homogeneous DMS, with high T_c . The embedded nano-crystals exhibit different structural geometry than that of host materials. Similarly many TMs display extremely low thermodynamic miscibility in semiconductors and have maximum tendency of impurity dopant aggregation.

By employing advanced characterization tools, it has also been proven that the robust FM in certain DMS can be correlated to the

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existing nano-scale regions with rich magnetic cations, referred to as condensed magnetic semiconductors (CMS) buried in the matrix of the host [23]. In CMS, the FM clusters can be combined together, resulting in significantly higher total magnetic moment (MM) and stable spin state. This higher MM, from three or four times larger than the MM of a single dopant atom, is due to the alignment of FM clusters [24]. The combined effect of the nanocomposites in magnetic semiconductors, resulting in higher MM, has attracted considerable researcher's attention [23–29].

Among TMs, one of the most important and suitable dopant element to be used in ZnO is the Fe^{2+} for fabrication of ZnO-based DMS for spintronic applications [22,30]. However, there exist certain conflicts between the results that rationalize their practical applications for efficient DMS based on Fe:ZnO. For instance, the experimental studies of Han et al. [31] have reported room temperature FM (RTFM) in Fe:ZnO, which was contradicted soon after by Yoon et al. [32] while predicting that; Fe–Fe interactions are dominated by AFM ordering in Fe:ZnO. Yoon et al. predictions were supported by other researchers as well via first-principles studies at the level of LDA+U [33] and GGA+U [34]. In addition, DFT based hybrid functional calculations performed by Xiao et al. [35] reported antiferromagnetic ordering for Fe^{2+} substituted ZnO materials where the origin of magnetic ordering have been attributed directly to the local ordering of Fe in the ZnO matrix. Similarly in a GGA based first-principles study, McLeod et al. [36] reported that the observed ground state antiferromagnetic ordering was dominated by FM because of secondary phase formation (i.e. ZnFe_2O_4). On the other hand, Lin et al. [37] achieved FM in Fe:ZnO above room temperature in an experimental study. In a mixed experimental and theoretical study, Karmakar et al. [38] observed RTFM in Fe:ZnO nanocrystals alongside transformation to spin glass at low temperature, and paramagnetic above 450 K. The corresponding RTFM in Fe:ZnO was reported to be originated from the unequal antiferromagnetic Fe^{3+} ions [39]. Similarly, the experimental investigations of Karamat et al. [40] regarding the magnetic properties of Fe:ZnO have revealed FM nature at 300 K. The investigations of Wang et al. [41], regarding the room temperature ferromagnetic ordering, highlight that the magnetization in Fe:ZnO is strongly dependent on the concentration of the Fe impurities. The concentration of dopant atoms play important role in tuning the properties of magnetic semiconductors as well as in the formation of secondary phases and clusters. Hence increase in concentration of dopant atoms favor to cluster in the matrix of the host semiconductor materials, has become an important question in the study of magnetic semiconductors [42]. To resolve this issue, therefore, the investigations concerning the site preferences in Fe doping ZnO are essential. Moreover, mostly studies reported in literature are focused on the *w*-structure of Fe:ZnO. Fe doped *zb*-structure of ZnO is scarcely explored to our knowledge [22].

In this work, we perform first-principles calculations comprehensively to investigate the structural, electronic and magnetic properties of Fe:ZnO based diluted and condensed magnetic semiconductors in both *w* and *zb* geometry. The well established density functional theory (DFT) based FP-L(APW+*lo*) methodology was used within generalized gradient approximations (GGA) and GGA+Hubbard (*U*) parameter as exchange correlation potentials.

2. Computational method

For the present first-principles calculations of Fe:ZnO, the DFT based FP-L(APW+*lo*) method has been used as implemented in the WIEN2k package [43]. In FP-L(APW+*lo*) method, the unit cell is divided into two regions namely the non-overlapping atomic spheres or core region, and interstitial regions, where different

basis sets are used in both the regions to expand the Kohn–Sham wave functions, charge density and potential. Inside the core region, a linear combination of radial functions times spherical harmonics is used, and in the interstitial region a plane wave expansion is used [43]. In this work to treat the exchange correlation energy, Perdew et al. proposed GGA [44] and GGA+*U* [45–47] has been used. The criteria of choosing *U*-parameter has been discussed in detail in the section describing the electronic properties. The muffin-tin radii (RMT) values for Zn^{2+} , Fe^{2+} are selected as 1.78 a.u and 1.5 a.u for O^{2-} atoms. A dense *k*-mesh with 72*k*-points is employed in the special irreducible Brillouin zone (BZ). Energy cutoff is taken as $K_{\text{max}}=8.0/R_{\text{MT}}(R_{\text{yd}})^{1/2}$. The Fourier expanded charge density was truncated at $G_{\text{max}}=16 \text{ a.u}^{-1}$.

3. Results and discussion

Results of our calculations are given in Table 1 for the ground state total energies of Fe:ZnO in *w* and *zb* structures. It is noted that the total energies of the investigated structures of Fe:ZnO exhibited marginal difference in both *w* and *zb* structures. These minor differences in *w* and *zb* structures reflecting the equivalent stability of *zb*-Fe:ZnO to that of *w*. Because except the difference in their stacking direction (111) both the structures present similar local tetrahedral bonding and carry the same atomic coordination through the second nearest neighbors as in the case of undoped ZnO [22].

By adopting the approach of Gopal et al. [33], two different spatial arrangements, referred as C1 and C2 based on the Fe substitution sites, are considered for the investigations of the clustering preference, ground state magnetic stability and short range/long range magnetic interactions. In C1 spatial arrangement, the Fe^{2+} dopant atoms are placed at a minimum distance to neighboring Fe^{2+} atoms separated by an oxygen atom i.e. Fe–O–Fe. While in C2 spatial arrangement, the Fe^{2+} atoms are placed far apart from other Fe atoms separated by two oxygen atoms and one Zn atom like Fe–O–Zn–O–Fe. For both arrangements, a marginal difference in the total energies of the two spatial arrangements is noticed. For example, at 12.5% dopant concentration, the total energy values are -3611.9631 and $-3611.9599R_y$ respectively for *w*-Fe:ZnO, and for *zb*-structure, are -3611.9617 and $-3611.9579R_y$ respectively for C1 and C2 arrangements. However comparatively lower energy of the C1 configuration than in the corresponding C2 configuration is noted for all the studied compositions. This trend is analogous for both *w* and *zb* geometries, showing that Fe:ZnO-based DMS favors short-range Fe–Fe magnetic coupling and have a tendency to cluster together. Our results of clustering tendency in *w*-Fe:ZnO are in agreement to Ref. [33].

To investigate the effect of Fe^{2+} on the structural properties of ZnO, lattice parameters are evaluated by minimizing the total energy of the unitcell/Supercell volume through the Murnaghan's equation of state [48]. The results, as presented in Fig. 1, show that there is variation in the lattice parameters for different dopant concentrations. The lattice parameters of Fe:ZnO in *w*-structure do not reveal a significant change for 6.25% and 12.5% of the Fe^{2+} concentration, whereas a drastic decrease in the lattice parameters

Table 1

Summary of the calculated ground-state total energies (in Ry) per formula unit of Fe:ZnO in *w* and *zb* structures.

Composition	<i>w</i>	<i>zb</i>
$\text{Zn}_{15}\text{Fe}_1\text{O}_{16}$	–3677.3845	–3677.3802
$\text{Zn}_{14}\text{Fe}_2\text{O}_{16}$	–3611.9631	–3611.9617
$\text{Zn}_{13}\text{Fe}_3\text{O}_{16}$	–3546.4452	–3546.3838
$\text{Zn}_{12}\text{Fe}_4\text{O}_{16}$	–3480.9988	–3480.9970

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