Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2015, Article ID 329570, 8 pages
http://dx.doi.org/10.1155/2015/329570

Research Article

Electronic and Magnetic Properties of Rare-Earth Metals Doped ZnO Monolayer

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Received 24 March 2015; Revised 29 June 2015; Accepted 2 July 2015

Academic Editor: Chaochao Dun

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The structural, electronic, and magnetic properties of rare-earth metals doped ZnO monolayer have been investigated using the first-principles calculations. The induced spin polarization is confirmed for Ce, Eu, Gd, and Dy dopings while the induced spin polarization is negligible for Y doping. The localized f states of rare-earth atoms respond to the introduction of a magnetic moment. ZnO monolayer undergoes transition from semiconductor to metal in the presence of Y, Ce, Gd, and Dy doping. More interestingly, Eu doped ZnO monolayer exhibits half-metallic behavior. Our result demonstrates that the RE-doping is an efficient route to modify the magnetic and electronic properties in ZnO monolayer.

1. Introduction

ZnO is a wide band gap II–VI semiconductor which has several favorable properties, such as wide band gap, good transparency, and large exciton binding energy. It has been used for solar cells, light emitting devices, and transparent electrodes [1–9]. Recently, the interest in ZnO nanostructures has significantly increased owing to their specific structures and properties differ from bulk counterparts, leading to many potential applications. Several ZnO nanostructures have been synthesized and characterized [10–18], in particular in the form of ultrathin nanosheets. The two-dimensional layered phase of ZnO was firstly predicted by Freeman that ZnO film prefers a graphitic-like structure when the number of ZnO(0001) layers is reduced due to the depolarization of the surface [19, 20]. Tusche et al. were the first to synthesize two-monolayer-thick ZnO(0001) films deposited on a Ag(111) surface, where Zn and O atoms are arranged in planar sheet like in the hexagonal BN monolayer [21]. Furthermore, graphene-like honeycomb structures of ZnO have been successfully prepared on Pd(111) substrate [22].

In order to design ZnO-based devices, one of the most relevant issues is doping in pure ZnO. Extensive studies have been conducted on the electronic and magnetic properties of the ZnO monolayer doped with foreign atoms for nanoelectronic and spintronic applications [23–27]. So far, it is well know that, by doping with nonmetal (B, C, and N) species in the graphene-like ZnO monolayer, or adsorptions of an Mn atom on a ZnO sheet, the tunable electronic and magnetic properties and ferromagnetic coupling can be realized. Very recently, a transition-metal-doped two-dimensional ZnO monolayer has been investigated by first-principles calculations [26]. The results show that electronic and magnetic properties of ZnO monolayer can be modified by such doping. On the other hand, compared with $3d$ transition metals, $4f$ rare-earth (RE) metals have larger magnetic moments. Furthermore, the electrons may mediate the FM coupling between the RE ions due to the coupling between f electrons and host s electrons. So far, although the doping of RE atom in ZnO bulk has been studied previously [28–32], the electronic and magnetic properties of RE-doped ZnO monolayer remain unclear. Thus, it is important to understand the electronic structure and magnetic properties of RE-doped ZnO monolayer due to its potential application in nanoelectronic and spintronic devices.

In this study, the structural, electronic, and magnetic properties of the RE-doped (RE = Y, Ce, Eu, Gd, and Dy) ZnO monolayer with Zn atoms substituted by RE atoms have been

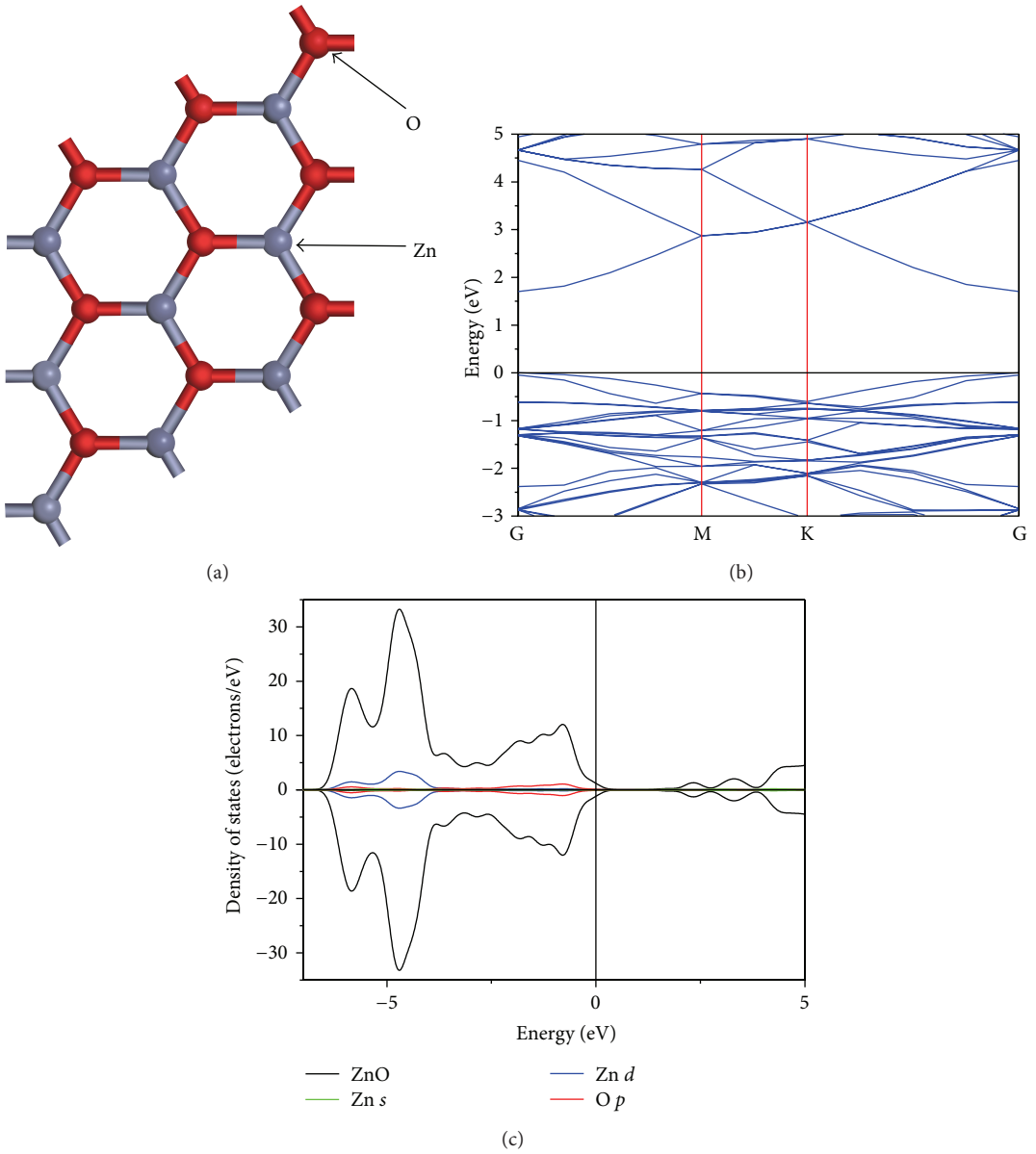

FIGURE 1: (a) Relaxed structure, (b) band structure, and (c) DOS of ZnO monolayer. The Fermi level is set to zero.

systematically studied by using first-principles calculations. It is found that the RE doping is an efficient route to tune the magnetic and electronic properties in ZnO monolayer and may provide a reference for its nanoelectronic and spintronic applications.

2. Computational Methods

First-principles calculations are performed within the framework of density functional theory (DFT) using the DMol^3 package [33, 34]. We used the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional to explain the exchange and correlation terms [35]. The geometry optimization is carried out with all atoms free to move and full cell optimization. The convergence criteria are of 1.0×10^{-5} Hartree in energy, 0.002 Hartree/Å in maximum force, and 0.005 Å in maximum displacement. We set the orbital cutoff globally with a parameter of 4.2 Å, and smearing is 0.035 Hartree. The brillouin zone is sampled with $4 \times 4 \times 1$ k-points. The models of 3×3 supercells for ZnO monolayer with one Zn atom substituted by one RE (RE = Y, Ce, Eu, Gd, and Dy) atom are considered. The vacuum region of 15 Å along the nonperiodic directions is employed to avoid interactions between two neighboring layers. All the calculations are carried out with spin polarization.

3. Results and Discussion

To investigate the properties of RE-doped ZnO monolayer, it is worth to mention the structural and electronic properties

of the pristine ZnO monolayer. The initial structure of the ZnO monolayer is cleaved from a bulk wurtzite ZnO with (0001) polar surface. After full optimization, the pristine ZnO monolayer transforms from initial wurtzite structure with a rippled surface into a graphene-like plane structure, as shown in Figure 1(a). The relaxed bond length of Zn-O in ZnO monolayer is 1.91 Å, which is shorter than its wurtzite bulk value of 2.01 Å. The contraction of the Zn-O bond length is attributable to the fact that the sp^2 hybridization in two-dimensional honeycomb structure is stronger than the sp^3 hybridization in wurtzite crystal. The geometric structure of the pristine ZnO monolayer agrees well with previous experimental and theoretical values [20, 21, 23, 36]. The band structure and density of states (DOS) of the pristine ZnO monolayer are calculated after structural optimization and present in Figures 1(b) and 1(c), respectively. The calculated band structure indicates that pristine ZnO monolayer is a semiconductor with direct band gap of 1.70 eV, consistent with previous theoretical calculations [21, 23]. The spin-up and spin-down components of the DOS are totally symmetric, indicating that the pristine ZnO monolayer is nonmagnetic. Moreover, it is found that the valence bands are dominated by O 2*p* and Zn 3*d* states, whereas the conduction bands are mainly ascribed to the O 2*p* and Zn 4*s* states.

In the following, considering spin polarization, we optimized the structures of RE-doped ZnO monolayer. The average bond lengths for the Y, Ce, Eu, Gd, and Dy atoms to their nearest-neighbor O atoms are 2.10, 2.19, 2.18, 2.14, and 2.16 Å, respectively. From the bond lengths, it can be seen that the RE-O bond is expanded a little compared to the Zn-O of the pristine ZnO monolayer. The RE-O-Zn bond angles for the Y, Ce, Eu, Gd, and Dy atoms are 117.03, 115.06, 113.79, 115.87, and 115.20°, respectively. Considering the Zn-O-Zn bond angle is 120° in the pristine ZnO monolayer, it can be known that RE doping distorts the bond angle. From these results, we can find that compared to the pristine one, the RE-doped ZnO systems are distorted. The main reason is the different atomic radius between doping RE atoms and Zn atom.

The formation energy of the RE-doped ZnO monolayer has been calculated for the understanding of its relative stability. The definition of formation energy is given as $E_f = E_{\text{tot}}$ (RE-doped ZnO) $-E_{\text{tot}}$ (ZnO) + $\mu_{\text{Zn}} - \mu_{\text{RE}}$, where E_{tot} (RE-doped ZnO) and E_{tot} (ZnO) are the total energies per supercell of the relaxed RE-doped and pure ZnO monolayer, respectively. The μ_{Zn} and μ_{RE} represent the chemical potential of Zn and RE species, respectively [37]. Figure 2 presents the results of calculated formation energies of the RE-doped ZnO monolayer. As displayed in the figure, the formation energies of all the doped systems are found to be negative. The smaller the formation enthalpy is, the easier the dopant incorporates into the ZnO sheet. The obtained results of the formation energies indicate that the RE atoms of Y, Ce, Eu, Gd, and Dy are suitable to dope into ZnO monolayer. This is also demonstrated by the experiment. Being directly related to the present work, successful Eu doping in ZnO nanowires has been experimentally achieved by ion implantation.

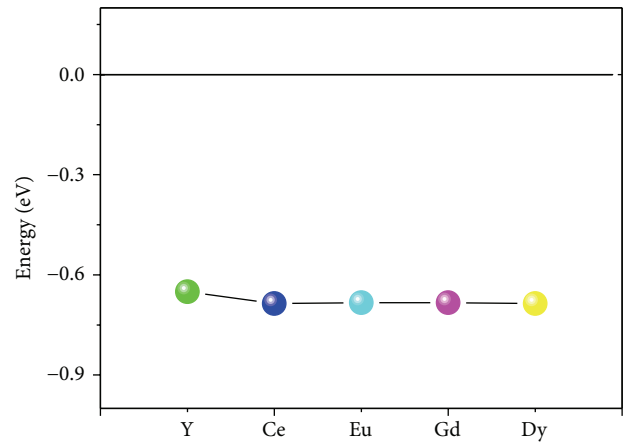

Figure 2: The formation energies of the RE-doped ZnO monolayer.

The incorporated RE atoms were found to replace Zn in the ZnO lattice [13].

An important aspect of RE-doped ZnO monolayer is the magnetic behavior of the system. From our calculation, it is found that no magnetism is observed when Y atom is doped in the ZnO monolayer. In the case of Ce, Eu, Gd, and Dy doped system, the induced spin polarization is observed. The total magnetic moments and local magnetic moments of RE, Zn, and O atoms in the considered systems are plotted with respect to a series of RE atoms as shown in Figure 3. The total magnetic moments of ZnO monolayer doped by Ce, Eu, Gd, and Dy are −0.76, 3.43, 3.78, and 2.28 μ_{B}, respectively. In the above case, the magnetic properties of the systems are mainly attributed to the contribution of doped RE impurities because of the nonmagnetic character of pristine ZnO monolayer. Moreover, one can see from Figure 3 that RE atoms have major contributions to the total magnetic moment and the nearest-neighbor O atoms only have very minor contribution to the total magnetic moment. This phenomenon is similar to the cases of 3*d* TM-doped ZnO sheet and BN sheet [38], which was also observed in 3*d* TM-doped ZnO nanotubes [39].

The magnetism distributions of RE-doped ZnO monolayer can be studied by the analysis of the spin density as shown in Figure 4. It can be seen that Ce, Eu, Gd, and Dy doped ZnO monolayers exhibit similar distribution phenomenon that is magnetic moments mainly concentrated on the RE atoms and nearest-neighbor O atoms contributed slightly. This is consistent with above calculated local magnetic moments of RE and O atoms.

In order to further investigate the effects of RE doping and the origins of the magnetic properties, the spin polarized band structures and projected density of states of RE-doped ZnO monolayer have been calculated. The spin polarized band structures have been presented in Figure 5. From Figure 5(b), it can be seen that the majority and minority band structures of ZnO monolayer doped by Y are identical with zero magnetic moment of Y atoms. Moreover, the system of Y doped ZnO monolayer is nonmagnetic metallic, which is well consistent with highly conductive films of Y doped

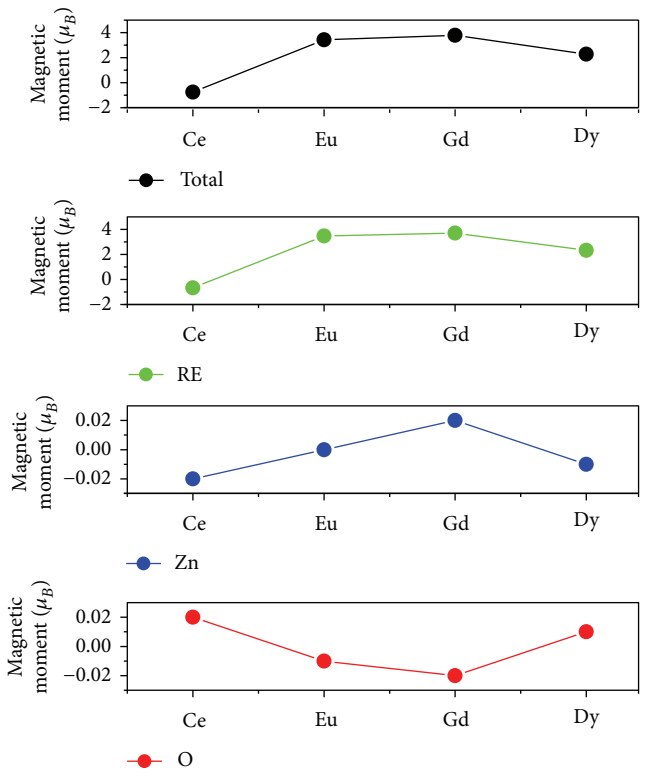

Figure 3: The total and local magnetic moments of RE, Zn, and O atoms in the RE-doped ZnO monolayer.

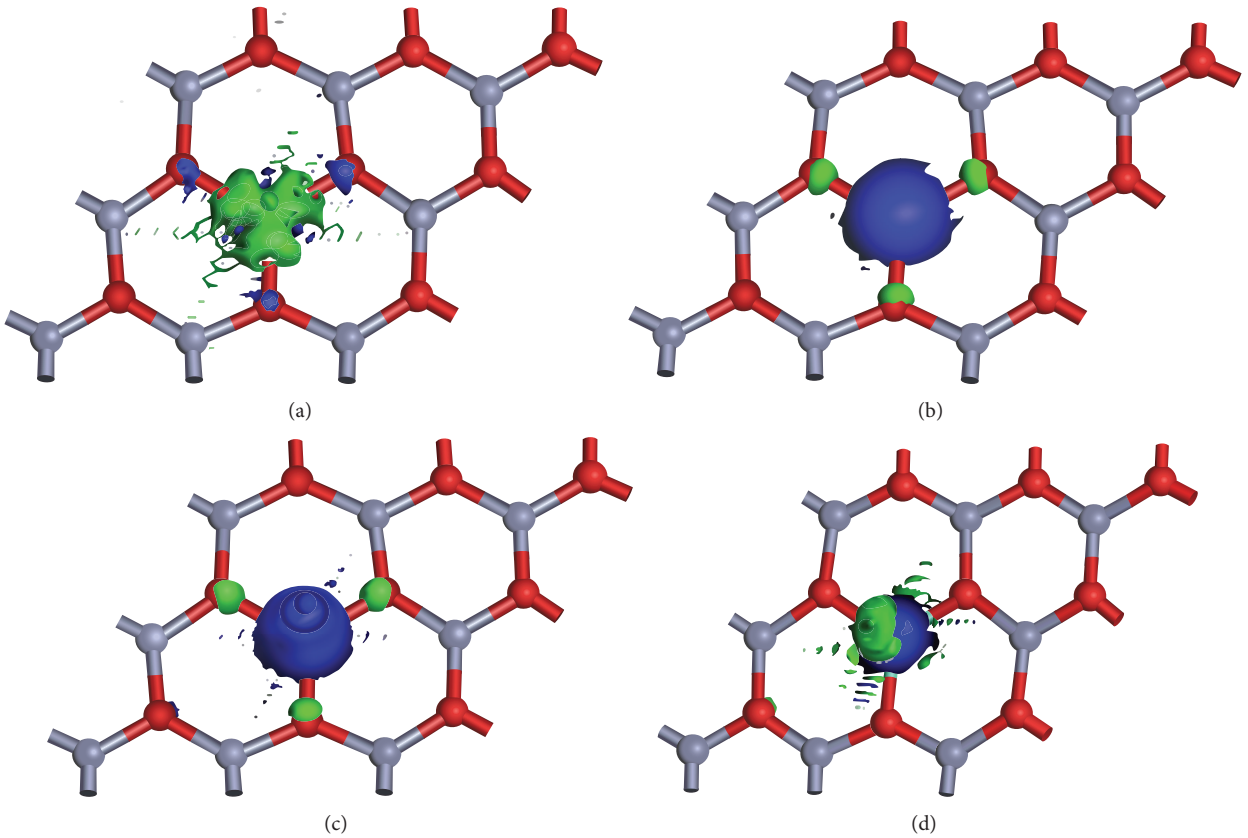

Figure 4: The spin charge density distribution of (a) Ce, (b) Eu, (c) Gd, and (d) Dy doped ZnO monolayers. The blue and green colors represent spin-up and spin-down values, respectively.

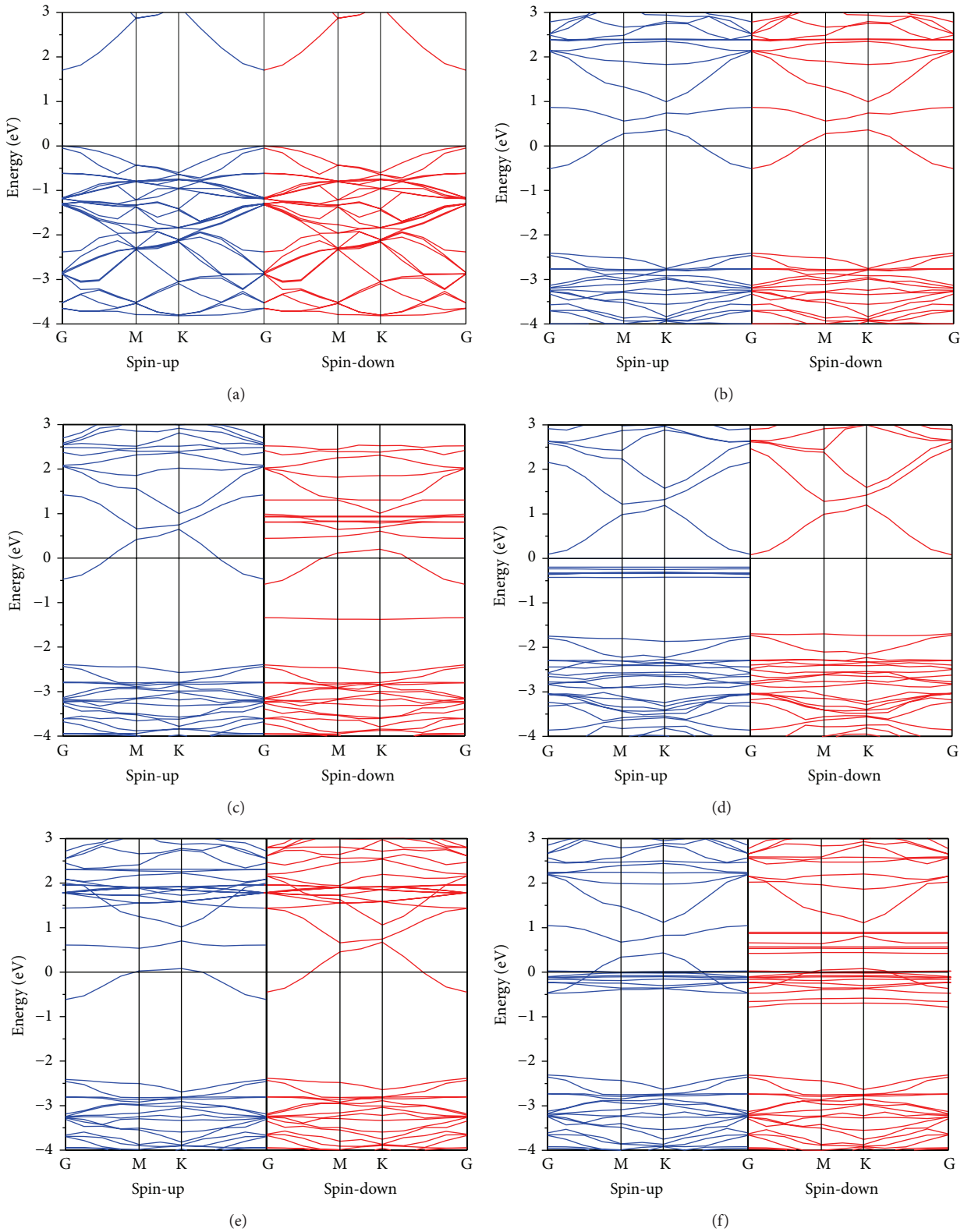

Figure 5: The spin polarized band structures of (a) pristine and (b)–(f) a single Y, Ce, Eu, Gd, and Dy doped ZnO monolayers. The horizontal dash line indicates the Fermi level.

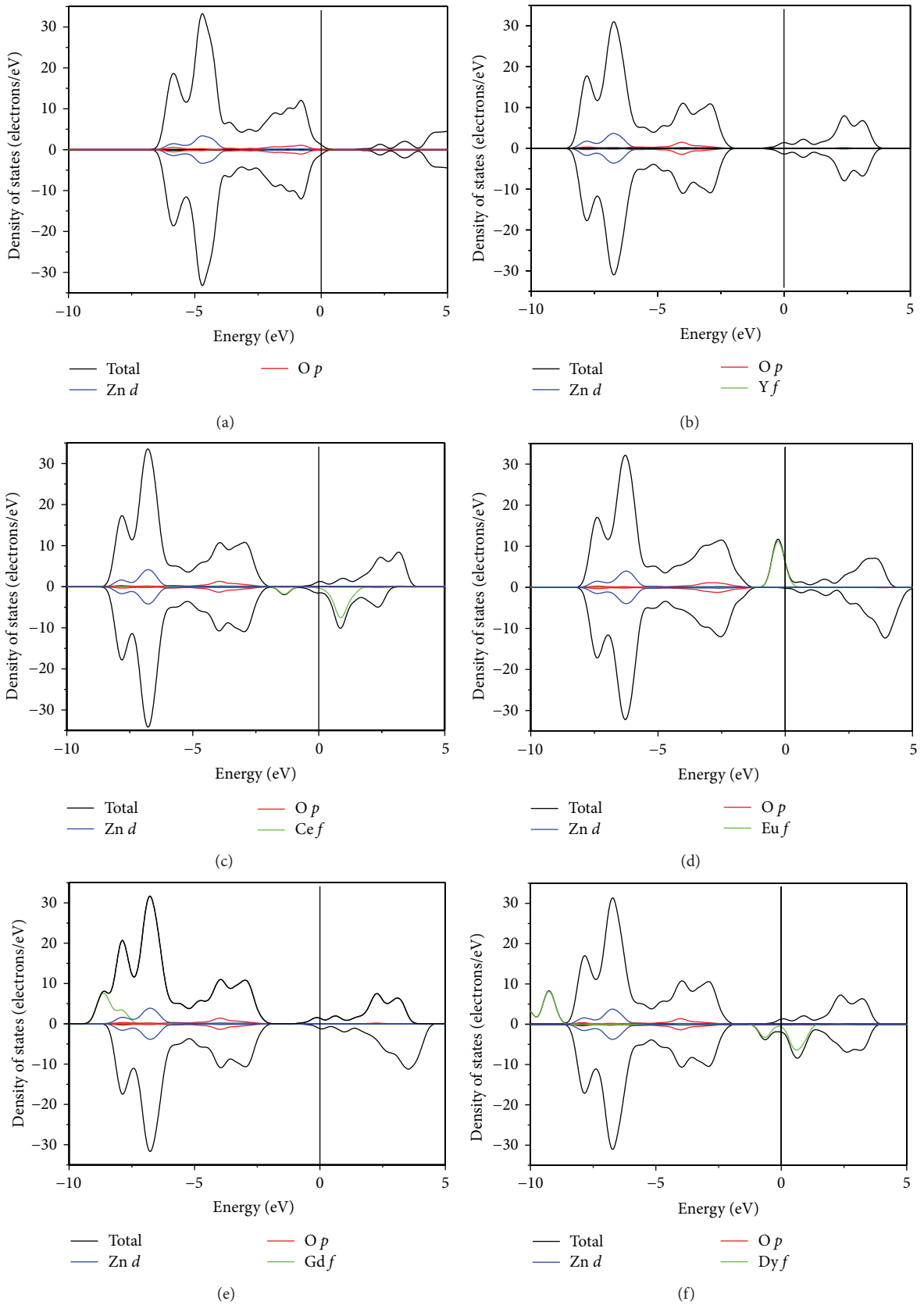

FIGURE 6: The total and partial DOS of (a) pristine and (b)–(f) a single Y, Ce, Eu, Gd, and Dy doped ZnO monolayers. The vertical dash line indicates the Fermi level.

ZnO reported by Minami et al. [40]. In the case of ZnO monolayer doped by Ce, Gd, and Dy, the calculated band structure as shown in Figures 5(c), 5(e), and 5(f) indicates that these systems are magnetic metallic with spin polarized bands cross the Fermi level for both spin-up and spin-down channels. Meanwhile, the majority bands in the vicinity of the Fermi level are different from the minority bands in which several nearly flat bands appear near 1.0 eV below the Fermi level. The band structure of Eu doped ZnO monolayer is shown in Figure 5(d). It is worth noting that the spin-down channel is semiconducting with a direct band gap of 1.8 eV, whereas it is important that the spin-up channel is metallic with impurity bands induced by Eu dopant crossing the Fermi level. As a result, the one Eu doped ZnO monolayer is magnetic half-metallic. The half-metallic nature with a 100% spin polarization at the Fermi level is considered as an optimal candidate for spintronic devices.

Figure 6 shows the total and partial DOS of RE-doped ZnO monolayer. As shown in Figure 6(b), for the Y doped ZnO monolayer, it can be seen that the spin-up and spin-down DOSs are completely symmetrical, indicating the nonmagnetic states of the system. And it can also be seen that the Ce, Eu, Gd, and Dy doped ZnO monolayers are magnetic because there is a clear spin polarization between the DOSs of the two spin channels near the Fermi level. The analyses of the total DOSs are consistent with those of calculated magnetic properties. Furthermore, for the ZnO monolayer doped by Ce, Eu, Gd, and Dy, partial DOS indicates that f electrons of RE atoms are responsible for the induced magnetic moments. Although the p orbits of O atoms and $3d$ orbits of Zn atoms also exhibit spin polarization, their contribution to the magnetic moment of the systems is small. Therefore, the origin of magnetism in RE-doped ZnO monolayer resides on unpaired f electrons of dopant RE atoms.

4. Conclusions

In summary, we have performed a comprehensive investigation of the structural, electronic, and magnetic properties of ZnO monolayer doped by RE (RE = Y, Ce, Eu, Gd, and Dy) using first-principles calculations. The doping of Ce, Eu, Gd, and Dy in ZnO monolayers is found to be magnetic. Y doped ZnO monolayer exhibits no magnetism. The magnetic moment of RE-doped ZnO monolayer is mainly contributed from localized f states of rare-earth atoms. Substitution doping of the RE atoms for Zn atom has significant effect on the electronic properties of ZnO monolayer. ZnO monolayer undergoes transition from semiconductor to metal in the presence of Y, Ce, Gd, and Dy doping. More interestingly, Eu doped ZnO monolayer exhibits half-metallic behavior with a 100% spin polarization at the Fermi level. Our results may provide a reference for modifying the material property of ZnO monolayer and designing nanoelectronic and spintronic devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors acknowledge the support of National Natural Science Foundation of China (Grant nos. 51471064 and 51301054), the Program for New Century Excellent Talents (Grant no. 1253-NCET-009), and Program for Youth Academic Backbone in Heilongjiang Provincial University (Grant no. 1251G022).

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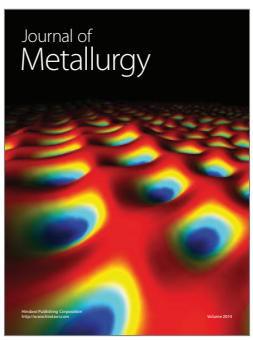

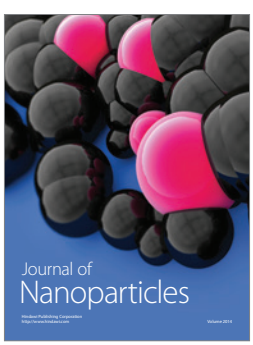

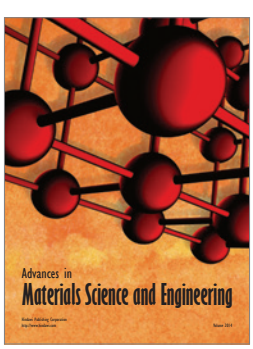

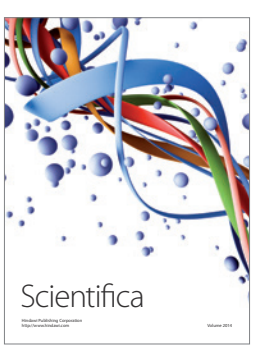

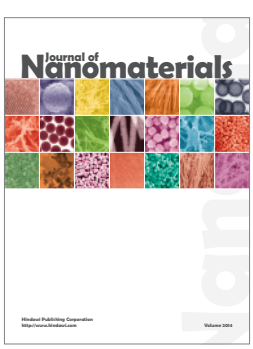

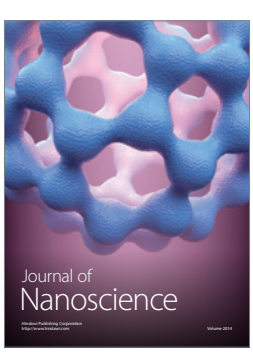

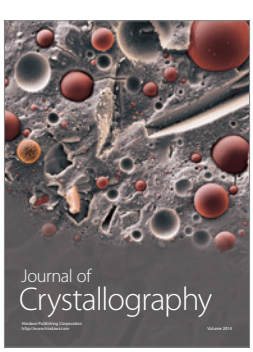

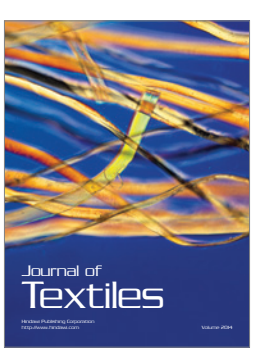

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