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Energy Stabilities, Magnetic Properties, and Electronic Structures of Diluted Magnetic Semiconductor Zn$_{1-x}$Mn$_x$S(001) Thin Films

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We investigate the electronic and magnetic properties of the diluted magnetic semiconductors Zn$_{1-x}$Mn$_x$S(001) thin films with different Mn doping concentrations using the total energy density functional theory. The energy stability and density of states of a single Mn atom and two Mn atoms at various doped configurations and different magnetic coupling state were calculated. Different doping configurations have different degrees of p-d hybridization, and because Mn atoms are located in different crystal-field environment, the 3d projected densities of states peak splitting of different Mn doping configurations are quite different. In the two Mn atoms doped, the calculated ground states of three kinds of stable configurations are anti-ferromagnetic state. We analyzed the 3d density of states diagram of three kinds of energy stability configurations with the two Mn atoms in different magnetic coupling state. When the two Mn atoms are ferromagnetic coupling, due to d-d electron interactions, density of states of anti-bonding state have significant broadening peaks. As the concentration of Mn atoms increases, there is a tendency for Mn atoms to form nearest neighbors and cluster around S. For such these configurations, the antiferromagnetic coupling between Mn atoms is energetically more favorable.

Key words: Zn$_{1-x}$Mn$_x$S(001) thin film, Electronic structure, Diluted magnetic semiconductor

I. INTRODUCTION

Manganese-doped II-VI and III-V diluted magnetic semiconductors (DMS) have recently attracted a great deal of attention as a new class of semiconductors. DMSs have been considered of tremendous scientific and technological importance [1, 2]. This is essentially due to the combination of ferromagnetism with semiconductor properties in the same host material, which enable the use of the spin degree of freedom to process, to transfer as well as to store information, giving rise to the emerging field of spintronics [3–6], which are essential for future generation spintronic device applications [1, 7–9]. The replacement of the cations in the II-VI semiconductors yields unusual magneto-transport and magneto-optical properties [10, 11].

Among DMSs materials, ferromagnetic (Zn, Mn)S has attracted considerable attention. Substitution of Mn for Zn in ZnS introduces local spin 5/2 magnetic moments. Therefore, it is of great importance for practical applications to clearly understand the role of Mn-dopant in determining the magnetic and electronic properties. The electronic and magnetic properties of wurtzite [12] and zinc blende [13] ZnS semiconductor doped with transition metal atoms have been studied. The results showed the ZnS bulk materials doped with Cr, Fe, and Ni are determined to be half-metallic, while those doped with Mn and Co impurities are found to be semiconducting. But Guo et al. showed ZnTe:Mn has different ground state for ZnTe doped with 12.5% and 6.25% [14]. The Co-doped zinc-blende ZnO exhibits the antiferromagnetism (AFM) ground state [15]. Although ZnS-based and ZnO-based diluted magnetic semiconductors has been studied a lot, their thin film materials are not much reported. However, the diluted magnetic semiconductor thin films have more important applications. Doping in thin films is more complex than that in the bulk since the bonding environments of dopants vary from the surface layer to the subsurface and inner layers due to different coordination number and different bond-length contraction.

In this paper, we study calculations of total energies, electronic structure, and magnetic properties of Mn-doped(001) ZnS thin film based on density functional theory (DFT) and the generalized gradient approximation for exchange and correlation [16]. We focus our attention on the impurity interstitial surface configurations. Some researchers studied the energetic preference in Zn$_{1-x}$Mn$_x$S, demonstrating that the interstitial sites...
in \(\text{Zn}_{1-x}\text{Mn}_x\text{S}\) were energetically favored compared to the substitutional counterparts [17, 18]. Furthermore, Bernardini et al. showed that the dimers formed by two nearest neighboring Mn ions in \(\text{Zn}_{1-x}\text{Mn}_x\text{S}\) were energetically preferable and brought much larger local spin moments [19], which is similar to the prediction for III-V DMSs by using first principles calculations [20]. However, these results are difficult to accurately explain the complex observations in experiments.

II. COMPUTATIONAL DETAILS

In this work, we have studied the magnetic properties of \(\text{Zn}_{1-x}\text{Mn}_x\text{S}\) in thin film forms by allowing full structural relaxation. Using DFT with generalized gradient approximation for exchange and correlation, we have calculated the total energies, electronic structure, and magnetic coupling for ferromagnetism (FM) and AFM states in \(\text{Zn}_{1-x}\text{Mn}_x\text{S}(001)\) thin films.

The \(\text{ZnS}(001)\) thin film with S-terminated surface was modeled by a slab of eight layers containing a total of 32 atoms. Each slab was separated from the other by a vacuum region of 12.2 Å. The bottom layer of atoms is fixed. The geometry after relaxation of the supercell (\(\text{Zn}_{16}\text{S}_{16}\)) consisting of 16 Zn and 16 S atoms is given in Fig.1. A systematic “polydoping” study of DMS inevitably involves a large number of geometrical configurations and possible magnetic states.

Calculations of the total energies and forces, and optimizations of geometry, were carried out using a plane wave basis set with the projector augmented plane-wave (PAW) method [21] as implemented in the Vienna \textit{ab initio} simulation package (VASP 4.6) [22]. The DFT calculations were performed using PW91 exchange and correlation functional. The particular advantage of the PAW method over the conventional pseudopotentials and ultrasoft pseudopotentials is that it can improve the accuracy, especially for magnetic systems and for materials including d-electron or f-electron elements. The energy cutoff was set to 350 eV, and the convergence in energy and force were 100 μeV and 0.01 eV/Å, respectively.

We begin the calculations with a bulk zinc blende structure. To investigate Mn distribution, a supercell of \(\text{Zn}_{1-x}\text{Mn}_x\text{S}\) thin film with the calculated lattice constants (5.41 Å), and \(2\times2\times2\) supercell of 32 atoms was used. The internal parameters were fully relaxed. The Monkhorst-Pack scheme [23] was used for the generation of special k points in the Brillouin zone. The convergence was checked carefully with respect to the number of k points used. For example, a \(6\times6\times1\) mesh for k points was used for the unit cell containing 32 atoms for the accurate calculation of density of states (DOSs).

We calculate the formation energy to determine the relative stability of different configurations, for which the formation energy is calculated as \(E_F=E_{\text{ZnMnS}}-m\mu_{\text{Mn}}+n\mu_{\text{Zn}}\), where \(E_{\text{ZnMnS}}\) and \(E_{\text{ZnS}}\) are the total energies of Mn-doped \(\text{ZnS}(001)\) thin film and the relaxed pure \(\text{ZnS}(001)\) thin film (as calculated with the same size supercell), respectively, \(\mu_{\text{Mn}}\) and \(\mu_{\text{Zn}}\) are atom chemical potentials of Mn and Zn, while \(m\) and \(n\) are the numbers of doped Mn atoms and substituted Zn atoms. Particularly, we have used the bulk fcc Mn and bulk hcp Zn as the source of the Mn atoms and Zn atoms, respectively [24].

We study the energetic stabilities in the case of single doping, and then based on that, the two Mn atoms doping are investigated systematically. The energetically favorable configurations are schematically investigated. The associated formation energies spin moments and magnetic states are also discussed. We have performed the calculations of electronic properties. The obtained DOSs of \(\text{Zn}_{1-x}\text{Mn}_x\text{S}(001)\) thin films with the presence of varying stable doping configurations are discussed.

III. RESULTS AND DISCUSSION

A. Structural and magnetic properties

1. Single Mn doping

To study the properties of Mn-doped \(\text{ZnS}\) thin film, we determine the preferred site of Mn atoms and how these sites change as the concentration of Mn is increased. For the doping of a single Mn atom in \(\text{ZnS}\) slabs, nine high symmetry sites, including three substitutional \(\text{MnZn}\) and six interstitial sites \(\text{MnT}\) are considered. These correspond to Mn concentration of 6.25%. Three substitutional sites correspond to surface Zn site (Zn13 in S-1), subsurface Zn site (Zn11 in S-2), and third layer Zn site (Zn5 in S-3), respectively. Two kinds of interstitial sites (T-1 sites and T-2 sites) are considered. For T-1 site, the Mn atom is located at the center of the same closest four layer S atoms. T-2 site corresponds to below the middle of two nearest S atoms. Three T-1 sites correspond to the center of the closest
FIG. 2 Structurally optimized geometries for the three most energetically stable configurations of single Mn doping configurations. (a) S-2, (b) S-4, and (c) S-7. The red atoms are Mn, the blue atoms are Zn, and the yellow atoms are S. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

TABLE I Formation energies $E_F$ and magnetic moments at each Mn atom for all single doping configurations.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Structure</th>
<th>$E_F$ (eV)</th>
<th>Magnetic moment ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>Mn$_{16}$</td>
<td>$-4.648$</td>
<td>1.37</td>
</tr>
<tr>
<td>S-2</td>
<td>Mn$_{11}$</td>
<td>$-6.196$</td>
<td>4.94</td>
</tr>
<tr>
<td>S-3</td>
<td>Mn$_{5}$</td>
<td>$-3.456$</td>
<td>2.49</td>
</tr>
<tr>
<td>S-4</td>
<td>Mn$_{7.1}$</td>
<td>$-7.010$</td>
<td>3.81</td>
</tr>
<tr>
<td>S-5</td>
<td>Mn$_{7.1}$</td>
<td>$-4.308$</td>
<td>3.32</td>
</tr>
<tr>
<td>S-6</td>
<td>Mn$_{7.1}$</td>
<td>$-3.915$</td>
<td>4.51</td>
</tr>
<tr>
<td>S-7</td>
<td>Mn$_{7.2}$</td>
<td>$-6.776$</td>
<td>4.98</td>
</tr>
<tr>
<td>S-8</td>
<td>Mn$_{7.2}$</td>
<td>$-3.531$</td>
<td>3.27</td>
</tr>
<tr>
<td>S-9</td>
<td>Mn$_{7.2}$</td>
<td>$-4.950$</td>
<td>4.85</td>
</tr>
</tbody>
</table>

**2. Two Mn doping**

For the doping of two Mn atoms in ZnS slabs, there are many configurations can be achieved, including...
two Mn atoms in the same layer of the substitutional and interstitial doping, the two Mn atoms in different layers of the substitutional and interstitial doping. We have considered all representative doping configurations, including seventeen different configurations, which correspond to nine substitutional-substitutional Mn doping, six interstitial-substitutional Mn doping and two interstitial-interstitial Mn doping, are given in Table II. These correspond to Mn concentration of 12.5%. For substitutional-substitutional Mn doping, we have replaced the nearest-neighbor and second-nearest-neighbor Zn sites by Mn atoms on the surface layer marked configuration D-1 and D-2. D-3 and D-4 correspond to the replacement of the nearest-neighbor and second-nearest-neighbor Zn sites on subsurface layer. D-5 and D-6 correspond to the substitution of Zn atoms at the third layer. D-7 represents the substitution of two nearest Zn sites by Mn with one belonging to the surface and the other to the subsurface plane. D-8 corresponds to the replacement of two nearest-neighbor Zn atoms by two Mn atoms with one belonging to the subsurface and the other to the third layer. D-9 corresponds to the replacement of two Zn atoms by two Mn atoms with one belonging to the surface and the other to the third layer. In D-10, D-11, and D-12, one Mn atom is T-1 site (interstitial site) and the other Mn atom is substitutional site corresponding to the nearest-neighbor Zn site on the same layer. Two Mn atoms in configuration D-10, D-11, and D-12 belong to surface, subsurface, and third layer respectively. In D-13, D-14, and D-15, one Mn atom is T-2 site (interstitial site) and the other Mn atom is substitutional site corresponding to the nearest-neighbor Zn site on the same layer. Two Mn atoms in D-13, D-14, and D-15 belong to surface, subsurface and the third layer respectively. D-16 and D-17 correspond to two interstitial sites on surface layer and subsurface layer respectively.

We calculated the total energy, the formation energy, magnetic moment and structure of the ferromagnetic and anti-ferromagnetic state of all 17 configurations. These results were shown in Table II. According to the calculation result of formation energy, the energy stable doping configuration was able to determine. Formation energies of various configurations were shown in Fig. 3. The distance between the two Mn atoms in configuration D-9 is 7.59 Å, which is enough large and AFM and FM is basically degenerate, so the interaction can be ignored.

The II-VI and III-V semiconductors incorporation of Mn can be a source of magnetic properties, new electronic and optical properties, and energy band gap tuning. The main benefits of the incorporation of Mn in II-VI and III-V semiconductors are the formation of Mn acceptors and donors and the magnetic properties of the doped materials.

**Table II: Formation energies difference \( \Delta E \), magnetic moments, the optimized Mn–Mn distances \( d_{\text{Mn-Mn}} \), and ground states for each configuration.**

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \Delta E / \text{meV} )</th>
<th>Magnetic moments/( \mu_B )</th>
<th>( d_{\text{Mn-Mn}} )(AFM, FM)/Å</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1(Mn(<em>{Zn16}), Mn(</em>{Zn15}))</td>
<td>95</td>
<td>2.75, 2.95</td>
<td>3.83, 3.83</td>
<td>FM</td>
</tr>
<tr>
<td>D-2(Mn(<em>{Zn16}), Mn(</em>{Zn14}))</td>
<td>82</td>
<td>2.71, 2.93</td>
<td>5.41, 5.41</td>
<td>FM</td>
</tr>
<tr>
<td>D-3(Mn(<em>{Zn11}), Mn(</em>{Zn10}))</td>
<td>-124</td>
<td>4.02, 4.14</td>
<td>3.83, 3.83</td>
<td>AFM</td>
</tr>
<tr>
<td>D-4(Mn(<em>{Zn11}), Mn(</em>{Zn9}))</td>
<td>-72</td>
<td>4.19, 4.13</td>
<td>5.41, 5.41</td>
<td>AFM</td>
</tr>
<tr>
<td>D-5(Mn(<em>{Zn8}), Mn(</em>{Zn7}))</td>
<td>48</td>
<td>3.98, 4.00</td>
<td>3.83, 3.83</td>
<td>FM</td>
</tr>
<tr>
<td>D-6(Mn(<em>{Zn8}), Mn(</em>{Zn6}))</td>
<td>70</td>
<td>4.04, 3.97</td>
<td>5.41, 5.41</td>
<td>FM</td>
</tr>
<tr>
<td>D-7(Mn(<em>{Zn16}), Mn(</em>{Zn11}))</td>
<td>-596</td>
<td>4.16, 2.92</td>
<td>3.81, 3.77</td>
<td>AFM</td>
</tr>
<tr>
<td>D-8(Mn(<em>{Zn11}), Mn(</em>{Zn8}))</td>
<td>-51</td>
<td>4.05, 4.11</td>
<td>3.62, 3.72</td>
<td>AFM</td>
</tr>
<tr>
<td>D-9(Mn(<em>{Zn16}), Mn(</em>{Zn6}))</td>
<td>7</td>
<td>3.14, 3.16</td>
<td>7.59, 7.59</td>
<td>FM</td>
</tr>
<tr>
<td>D-10(Mn(<em>{T-1}), Mn(</em>{Zn16}))</td>
<td>-177</td>
<td>3.41, 3.70</td>
<td>2.50, 2.73</td>
<td>AFM</td>
</tr>
<tr>
<td>D-11(Mn(<em>{T-1}), Mn(</em>{Zn11}))</td>
<td>-285</td>
<td>4.03, 4.10</td>
<td>2.99, 4.89</td>
<td>AFM</td>
</tr>
<tr>
<td>D-12(Mn(<em>{T-1}), Mn(</em>{Zn8}))</td>
<td>1087</td>
<td>3.47, 4.04</td>
<td>2.83, 3.91</td>
<td>FM</td>
</tr>
<tr>
<td>D-13(Mn(<em>{T-2}), Mn(</em>{Zn14}))</td>
<td>-159</td>
<td>3.45, 3.80</td>
<td>2.70, 2.94</td>
<td>AFM</td>
</tr>
<tr>
<td>D-14(Mn(<em>{T-2}), Mn(</em>{Zn11}))</td>
<td>735</td>
<td>3.83, 4.16</td>
<td>2.73, 3.99</td>
<td>FM</td>
</tr>
<tr>
<td>D-15(Mn(<em>{T-2}), Mn(</em>{Zn6}))</td>
<td>-122</td>
<td>3.80, 3.97</td>
<td>2.75, 3.04</td>
<td>AFM</td>
</tr>
<tr>
<td>D-16(Mn(<em>{T-1}), Mn(</em>{T-2}))</td>
<td>-53</td>
<td>4.01, 4.12</td>
<td>2.98, 3.50</td>
<td>AFM</td>
</tr>
<tr>
<td>D-17(Mn(<em>{T-1}), Mn(</em>{T-2}))</td>
<td>420</td>
<td>4.01, 3.92</td>
<td>2.83, 3.21</td>
<td>FM</td>
</tr>
</tbody>
</table>
transition magnetic ions may show ferromagnetic or spin glass state [28]. Ferromagnetic state is the electron spin parallel, the other is the spin-glass state, the electron spin orientation is random, and each has 50% probability of upward or downward. Comparison of total energy of ferromagnetic state and spin glass state, the ground state of the system will be able to determine. Two-state energy difference represents the stability of the ferromagnetic state and the corresponding Curie temperatures are high or low.

D-16 has the lowest formation energy. The structure of D-16 after relaxation was shown in Fig.4(a). D-16 and D-17 have similar structures. D-16 correspond to the two Mn atoms which were in the surface T-1 site and the surface T-2 sites respectively, while the D-17 correspond to the two Mn atoms which were in the sub-surface T-1 site and sub-surface T-2 site. We found that the formation energy is the lowest when two Mn atoms are interstitial sites near the location of the surface. Formation energies of D-16 anti-ferromagnetic state and the ferromagnetic state were −5.690 and −5.637 eV. The formation energy of anti-ferromagnetic state is lower by 53 meV than that of the ferromagnetic state. In anti-ferromagnetic coupling of D-16, the average magnetic moment per Mn atom is 4.01 µB/Mn. For ferromagnetic coupling, the average magnetic moment per Mn atom is 4.12 µB/Mn. As can be seen in the three stable configurations, anti-ferromagnetic state formation energy lower than the ferromagnetic state, the ground state is anti-ferromagnetic state. This is because the electronic configuration of Mn$^{2+}$ is $d^9$, exactly half filled d band. The antiferromagnetic super-exchange interaction between Mn ions stabilizes the spin glass state. It was obtained that D-10 and D-11 have also relatively low formation energies from the calculated results. Two kinds of stable configurations correspond to a surface interstitial Mn atom, and the other Mn replaces the neighboring surface Zn atoms or neighboring sub-surface Zn atoms. Formation energies of anti-ferromagnetic state and the ferromagnetic state of configuration D-10 and D-11 were $-5.433$, $-5.348$, and $-5.256$, $-5.063$ eV, anti-ferromagnetic state energy lower than the ferromagnetic state energy of 177 and 285 meV respectively. Formation energy differences between anti-ferromagnetic coupling and ferromagnetic coupling of configuration D-10 and D-16 are larger than that of configuration D-11. According to the above results of formation energy, we found that films have low formation energy when two Mn atoms tend to close to the surface and the neighbor doping. The ferromagnetic coupling of the two Mn atoms is generally long-range exchange interaction, in which the interstitial Mn atoms move more easily to the near-surface position. The anti-ferromagnetic coupling is the short-range super-exchange interaction, so the two Mn atoms would tend to close to each other. The ground states of the three lowest energy configurations are also anti-ferromagnetic coupling.

Formation energy differences of the ferromagnetic coupling and the anti-ferromagnetic coupling of D-12 and D-14 are larger than that of other configuration. Ferromagnetic states of two configurations have lower formation energy. Formation energies of anti-ferromagnetic configuration state and ferromagnetic state of configuration D-12 and D-14 were $-4.051$, $-5.139$, and $-4.457$, $-5.192$ eV. The formation energy of ferromagnetic state is lower by 1088 and 735 meV than that of anti-ferromagnetic state. When the two Mn atoms of D-12 configuration are anti-ferromagnetic and ferromagnetic coupling, respectively, average magnetics per Mn atom are 3.47 and 4.04 µB/Mn. The two Mn atoms of D-14 are anti-ferromagnetic and ferromagnetic coupling respectively, and average magnetic per Mn atom are 3.83 and 4.16 µB/Mn. Doping structures of the configuration D-12 and D-14 after the relaxation were shown in Fig.4. Obviously the anti-ferromagnetic
coupling of two Mn atoms is also essential to maintain an interstitial site and the other is substitutional site. But the structures of the ferromagnetic coupling of two kinds configurations have great changes that interstitial Mn atoms replace Zn atoms in position, while Zn atoms are excluded to the film surface location, so that the system can get a lower total energy.

B. Electronic structures

For spintronic applications, both magnetic and electrical properties are important. The Mn atoms have been shown to be magnetic dopants and can enhance the ferromagnetism of the material under particular conditions. We calculated DOSs of a single and two Mn atoms doped ZnMnS(001) film. Figure 5 shows the total density of states of the Zn\textsubscript{1-x}Mn\textsubscript{x}S and the projected densities of states (PDOS) onto the Mn 3d orbitals of S-2. The feature at the energy from \(-14\) eV to \(-12\) eV reflects the S-states. The large sharp peaks at the energy from \(-8\) eV to \(-6\) eV are the Zn\textsubscript{d} states, the broad feature between the Zn\textsubscript{d} states and Fermi energy (set to 0 eV) is composed of Zns, Mnd, and Sp states of bonding. The unoccupied states above the Fermi energy are also hybridized mixtures of Zns and Sp states. Figure 6 gives DOSs of Mn atom 3d states and the neighboring S atom 3p state for three energy stable single Mn-doped configuration. The Mn atom 3d PDOS and the adjacent S atoms 3p PDOS of S-2, S-4, and S-7 were shown in Fig.6). Note from Fig.7 near the valence band edge, there was significant overlap for Mn spin-up 3d states and S\textsubscript{3p} states, while great difference was observed for S atom 3p states of spin-down and the 3p state of spin-up. It is shown that a strong hybrid between spin-up states of Mn3d and states of S\textsubscript{3p}, the basic ferromagnetism is induced by Mn\textsubscript{d} and Sp hybridized band. And three kinds of doped configuration have different strength of p-d hybridization, the Mn3d states and the S\textsubscript{3p} states in the valence band near the top almost completely overlap for S-2 (substitutional site) and the S-7 (T-2 site), which have relatively strong degree of p-d hybridization. There was a large difference between Mn3d states and S\textsubscript{3p} states in the DOSs near the top of valence band for S-4 (T-1 site), which show configuration S-4 has relatively weak degree of p-d hybridization.

Note that the DOSs for S-2, S-4, and S-7 are different, as those three configurations have different crystal field symmetry. Configuration S-2 is substitutional doping, which correspond to tetrahedral environment. Since the cations are under the tetrahedral environment, the d states of Mn atoms are split into t\textsubscript{2g} and e\textsubscript{g} states and e\textsubscript{g} states lie lower in energy than t\textsubscript{2g} states. As seen from Fig.6, the t\textsubscript{2g} state hybridizes only with the Sp state while the e\textsubscript{g} states do not take part in the hybridization, this p-d hybridization makes the electrons prefer to occupy t\textsubscript{2g} states rather than Mn\textsubscript{d} or e\textsubscript{g} states. The densities of 3d states for configuration S-7 are similar to that of S-2, except the band of t\textsubscript{2g} split into two peaks, it is affected by a nontetrahedral crystal field splitting. Due to that S-7 (Mn\textsubscript{T-2}) is basically tetrahedral interstitial site, it is located near surface of the thin film, which has only a little distortion. On the other hand, noted that S-4 (Mn\textsubscript{T-1}) have more change in the densities of 3d states than S-2 (MnZn) and S-7 (Mn\textsubscript{T-2}). This is because Mn\textsubscript{T-2} site is not tetrahedral interstitial sites. We found that interstitial Mn (S-2) compared to substitutional Mn (S-7), the energy gap between t\textsubscript{2g} bonding state and e\textsubscript{g} anti-bonding state (Fermi level near 0 eV) decreases. The t\textsubscript{2g} anti-bonding state is below the Fermi level, but in S-4, the t\textsubscript{2g} anti-bonding state was pushed to the band gap of the non-doped ZnS (001) films above the Fermi level. As can be seen from Fig.6, S-4 (Mn\textsubscript{T-1}), compared with the other two configurations p-d hybridization is the weakest. The magnetic moments of S-2, S-4, and S-7 were 4.94, 3.81, and 4.98 \(\mu_B\)/Mn respectively, which decrease compared...
to the magnetic moment of a single free Mn atom with 5 \( \mu_B \)/Mn due to hybridization between the Sp and Mnd states.

The 3d PDOS diagrams of two Mn ions corresponded to three kinds of lowest energy configurations (D-10, D-11 and D-16) in different magnetic coupling states were shown in Fig.7. Figure 7(c) corresponds to 3d PDOS diagram of Mn\(_{\text{T-1}}\) atoms and Mn\(_{\text{T-2}}\) atom in the configuration D-16. When the two Mn atoms are the anti-ferromagnetic coupling, the 3d DOSs diagram of the two Mn atoms are basically similar to 3d DOSs of a single Mn atom which is located at T-1 site and T-2 site. When the two atoms are ferromagnetic coupling, the 3d densities of states of the two Mn atoms are very different with 3d DOSs of a single Mn at the same location doped. Figure 7 (a) and (b) correspond to the 3d PDOS of the two Mn atoms in configuration D-10 and D-11, respectively, it can be also seen when the two Mn atoms are the anti-ferromagnetic coupling, 3d density of states of Mn atoms are similar to the 3d DOSs of a single doped Mn at the same location. When the two atoms are ferromagnetic coupling, densities of states of the anti-bonding state correspond to significant broadening peaks.

Anti-ferromagnetic coupling is the result of short-range super-exchange interaction and holes transition from one Mn-ion to the other Mn ions must have a spin-flip, so d-d interaction is very weak, which lead to DOSs of anti-bonding is similar to density of states of a single Mn-doped. However, ferromagnetic coupling is the result of the long-range double exchange interaction, the d-d interaction between two Mn atoms increases, and energy band of anti-bonding state widens, the energy difference between occupying state and unoccupied states decreases. As the d-d electron interactions of the ferromagnetic state make DOSs of anti-bonding state have significant broadening peaks. When the impurity valence electrons partially filled d band, it will be allowed that valence electrons transition between the 3d orbits of the neighboring electronic impurity ions, reducing its kinetic energy, which is in ferromagnetic state. If valence electron spins anti-parallel arrangement between the adjacent ions, there will not be the energy gain. In general, there is ferromagnetic double exchange interaction and the anti-ferromagnetic super-exchange interaction in DMS, a kind of DMS material is ferromagnetic state or spin-glass state, depending on the result of competition between two mechanisms.

IV. CONCLUSION

The electronic structure and magnetic properties of Zn\(_{1-x}\)Mn\(_x\)S thin films have been investigated systematically using first-principles calculations based on the gradient corrected density-functional theory and supercell slab model.

The Mn atoms prefer to occupy closer to the thin film surface. The surface T-1, surface T-2 site and sub-surface Zn site are three most stable single doping configurations. For the two Mn atoms doping, the most stable configuration correspond to a surface T-1 site (Mn\(_{\text{T-1}}\)), while the other neighbor surface T-2 site (Mn\(_{\text{T-2}}\)). In addition, an interstitial site and a substantial site are located near surface and they are the nearest neighbor corresponding to more stable configurations.

When doping concentration is low, that is, two Mn atoms away from each other, the ferromagnetic state and anti-ferromagnetic state in energy is almost degenerate. When the doping concentration increased, it is a trend that Mn atoms form clusters around the S atoms.

The result of DOSs shows the hybridization between Mn spin-up 3d states and the 3p states of S atoms. The strong p-d hybridization between Mn-3d states of substitutional Mn (MnZn) and T-2 site (Mn\(_{\text{T-2}}\)) states and the weak p-d hybridization between Mn3d states of T-1 site and S3p states were observed.

Different doping configuration with different crystal field environment of Mn atoms, so that different configurations of the Mn doping of the 3d PDOS are very
different.

For a pair of Mn ions, in the three stable configurations, the ground states are AFM state, formation energy of anti-ferromagnetic state are lower than that of ferromagnetic states.

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