Magnetic Properties of Co doped ZnS Diluted Magnetic Semiconductor

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Abstract. The magnetic properties of Zn0.9Co0.1S nanoparticles synthesized by solid state reaction method are presented. The nanoparticles are crystallized with zinc-blende structure. The variation of magnetic properties stems from the changes of the local structure around Co ions and the distribution of Co ions, given by X-ray absorption fine structures.

1. Instruction

Doped transition metal II–VI semiconductors have been investigated extensively due to various optoelectronic applications, such as optical sensors, light emitting displays, electroluminescence devices, etc [1, 2]. Zinc sulfide (ZnS), a II–VI compound semiconductor with wide band gap of 3.67 eV when crystallized with zinc-blende structure and of 3.90 eV for wurtzite structure [3, 4], is an attractive material for current research. Theoretical studies have shown that wide band gap semiconductors may be representative materials for ferromagnetism at room temperature or higher temperature modulated by carriers [5]. It is reasonable to speculate that there most likely exists ferromagnetism in ZnS-doped materials.

As far as the magnetic properties of ZnS doped with cobalt (Co) are concerned, most of the theoretical and experimental studies show that this material has a spin glass or anti-ferromagnetic behavior, paramagnetic and ferromagnetic behaviors [6, 7, 8]. However many experimental results are contradictory [9, 10, 11]. The bound magnetic polaron (BMP) model is based on the fact that when carrier concentration exceeds a certain value an impurity band is formed and the magnetic dopants couple with localized carriers [12, 13]. Lots of observations on magnetic moments in oxide diluted magnetic semiconductor (DMS) materials, such as ZnO–based DMS, support this theory. However, only a few indirect experiments support this model in ZnS-based DMS. In this work, we analyzed the influence of interactions between magnetic ions and defects on the magnetic properties and the influence of annealing temperature on the crystal structure and magnetic properties.

2. Samples and experiments:

In this work, the synthesis of Zn0.9Co0.1S nanoparticles was carried out by solid state reaction. The high-purity reactants with stoichiometric ratio zinc acetate, cobalt acetate and sodium sulfide were mixed together and the mixtures were thoroughly ground with adding sodium chloride and Isopropanol. After the reactions were completed, the Zn0.9Co0.1S nanoparticles were then separated...
from the reactants by centrifugation, and washed several times with deionized water and ethanol. Finally, the Zn_{0.9}Co_{0.1}S nanoparticles were dried in a desiccator for 10 h at 80 °C. Then the samples were divided into 3 parts and were marked as A, B, C. The sample A was without any treatment, sample B was calcined at 120 °C in vacuum environment for 10 hours and sample C was calcined at 200 °C in vacuum environment for 10 hours.

3. Results and discussions:

The XRD patterns of the samples are shown in Fig. 1. The XRD patterns for Zn_{0.9}Co_{0.1}S samples match well to ZnS with zinc-blende (ZB) structure. This result illustrates that the stable and high quality Zn_{0.9}Co_{0.1}S samples with zinc-blende (ZB) structure were synthesized. The fact that XRD does not show existence of the Co-related phase indicates that Co ions are oxidized in the ZnS matrix and substitute into the ZnS lattice at the Zn^{2+} site. According to Scherer’s formula \( D = \frac{0.9\lambda}{B\cos\theta} \), the size of all samples is almost the same, which is about 3 nm. Shiv P. Patel proposes that the ferromagnetism in diluted magnetic semiconductors is related to the surface area of grains [14]. And the ferromagnetism can be enhanced by increasing the area of grain boundary and reducing the volume of grains [15]. All of our samples are basically the same size, so we can rule out the possibility that the variation of magnetism stems from the surface size.

The M-H loops of all samples measured at 300K are shown in Fig. 2. It appears clearly that the magnetization of all the samples is the superimposition of ferromagnetic and paramagnetic components. Obviously, the magnitudes of paramagnetic components are almost the same which we can obtain from the slope of the paramagnetic component at high magnetic field. The magnitudes of ferromagnetic components change with increasing annealing temperature (saturation magnetizations \( M_S \) of A, B and C are 0.005emu/g, 0.02emu/g, 0.01emu/g, respectively). The remanent magnetization of the samples A, B, C is 0.0005emu/g, 0.002emu/g and 0.001emu/g respectively.

Co K-edge XANES spectra of Zn_{0.9}Co_{0.1}S nanoparticles are shown in Fig. 3. There are two peaks (M, N) in all samples below the energy of 7730 eV. The peak M is the absorption edge and the peak N is the pre-edge peak, which is ascribed to the transition of the 1s electron of the absorber to the bound state induced by hybridization of the cation and anion states. The M peak of sample C shifts to low energy side by about 4 eV compared with samples A and B, which indicates the valence state variation of Co ions or the changes of local environment around Co ions. The distance between the pre-edge and
edge position remains the same in sample A and sample B, while the distance decreases in sample C, which also can be due to the changes of local environment around Co ions.

Fig. 3. Co K-edge XANES spectra of Zn$_{0.9}$Co$_{0.1}$S nanoparticles.

Fig. 4. The Fourier Transform (FT) curves of the Co K-EXAFS of Zn$_{0.9}$Co$_{0.1}$S nanoparticles.

Fig. 4 shows the radial structure function for each sample. It can be seen from the above figure that it displays two main peaks below 0.3 nm in sample A and B. The position of the first peak (O) is almost coincident at 0.16 nm, while the second peak (P) of sample B shifts to higher distance. This is not surprising if the distribution of Co ions is taken into account. The ionic radii of Co$^{2+}$ and Zn$^{2+}$ are 0.72 Å and 0.74 Å respectively [8]. Sample B was calcined at 120 ºC in vacuum environment for 10 hours, so the distribution of Co ions in the lattice becomes more uniform in sample B than that in sample A. The $\sigma$ (disorder factor) of sample A and B we get by fitting the data is 0.1037 and 0.09 respectively. Therefore, the shift of the second peak is ascribed to redistribution of Co ions with more uniformity after annealing. Besides, as shown in Fig. 4 the sample B has a higher long-range structural order than sample A. When the annealing temperature is raised to 200 ºC, the local structure around Co ions has changed. It can be clearly seen that the radial structure function of sample C is largely different from those of sample A and B. The Co K-edge XANES and Co K-EXAFS spectra are compared of possible impurities such as CoO, CoS and Co$_2$O$_3$ with those of sample C. We get that a part of Co ions have been oxidized to Co$_2$O$_3$ after annealing at 200 ºC because of the low degree of vacuum. The experimental data presented here are consistent with the results obtained from Fig. 3.

The PL spectra of all the samples are shown in Fig. 5. The presence of sulfur vacancies is confirmed based on the results of photoluminescence (PL, the excitation wavelength is 325 nm). Results indicate that all samples exhibit broadening and stable blue emission peaks centered at around 400 nm, which can be assigned to the sulfur vacancies [16]. In order to study the influence of Co-doping on luminescence, the PL spectra of ZnS are presented here for comparison. By comparison, we can clearly find that the doping of Co$^{2+}$ into ZnS does not import new energy bands or defect states that can produce new emission peaks. It is certain that anion vacancies produce defect states which are responsible for the observed photoluminescence. With annealing of the sample, these defect states induced by S vacancies decrease in amount and the photoluminescence intensity diminishes.

The concentration of delocalized free carriers is so low that they do not have the capacity to induce room-temperature ferromagnetism by RKKY mechanism. Hence, this ferromagnetism does not arise from the RKKY mechanism, and our results argue for the BMP mechanism, in which S vacancies (V$_s$) play an important role. Shallow donors such as V$_s$ are energetically aligned with the Co$^{2+}$ leading to effective dopant-defect hybridization as described by perturbation theory. Formation of such a band upon coalescence of bound magnetic polarons in DMSs has been described theoretically [17].
We consider three possible types of magnetic states for Co in the ZnS matrix: (a) isolated PM Co due to small doping concentrations; (b) antiferromagnetic (AFM) exchange coupling between Co atoms through S; (c) FM exchange coupling (the cobalt ions form bound magnetic polarons). If two cobalt ions are separated by only one S ion, the spin of the two cobalt ions is in antiferromagnetic arrangement by the coupling with the excited states of S ions. According to previous analysis, the distribution of Co ions in sample B is more uniform than that in sample A, leading to the number of the antiferromagnetic Co ions decreases and the number of isolated cobalt ions and the Co ions which form bound magnetic polarons increases. So the $M_S$ of sample B is larger than that of sample A, and the remanent magnetization of sample B ($0.002$emu/g) is larger than that of sample A ($0.0005$emu/g). The local structure around Co ions of the samples has changed and a part of Co ions have been oxidized to $\text{Co}_2\text{O}_3$ after annealing at $200 \, ^\circ\text{C}$, which displays antiferromagnetism with the Neel temperature $40K$ [18]. Therefore, the $M_S$ and remanent magnetization of sample C become smaller than those of sample B, but still larger than those of sample A. With annealing of the sample, defect states induced by S vacancies decrease in content and the photoluminescence intensity diminishes, indicating the number of S vacancies becomes smaller with increasing annealing temperature. However, the number of S vacancies is still large enough to form bound magnetic polarons with Co ions. So the ferromagnetism of our samples mainly depends on the distribution of Co ions, rather than the number of S vacancies.

4. Conclusion:
High quality $\text{Zn}_{0.9}\text{Co}_{0.1}\text{S}$ samples with zinc-blende (ZB) structure were successfully synthesized by solid state reaction at RT. According to Scherer’s formula, the size of all samples is almost the same, which is about $3$ nm. The ferromagnetism in our samples mainly depends on the distribution of Co ions, rather than the number of S vacancies. When the temperature is raised to $200 \, ^\circ\text{C}$, the stability of the lattice becomes weaker and a part of Co ions have been oxidized to $\text{Co}_2\text{O}_3$.

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