Room temperature ferromagnetism in two-step-prepared Co-doped ZnO bulks

T. Zhu and W. S. Zhan
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, People’s Republic of China

W. G. Wang and John Q. Xiao
Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716

(Received 26 February 2006; accepted 10 June 2006; published online 14 July 2006)

We have prepared Co-doped ZnO bulks with a two-step method. The bulk samples are sintered at the temperature above 1000 °C to get pure single phase and then treated by Zn vapor in a vacuum. Based on such two-step preparation, clear carrier induced ferromagnetism is found in Zn treated Co-doped ZnO bulks, which suggests that the magnetism mechanism can be of codoping effect. The onset of ferromagnetism is associated with the further increase of the hybridization of the impurity band with 3d states near the Fermi level when additional carrier induced to let the Stoner criterion for ferromagnetism to be satisfied. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2221881]

Recently, study on room temperature ferromagnetic semiconductors has become an attractive topic for many research groups due to their promising potential in spintronic applications.1–3 High Curie temperature (Tc) ferromagnetism (FM) in oxides such as TiO2, SnO2, or ZnO doped with transition metals (TM)s has been reported.4–7 In addition to the understanding of different results sensitively depending on the sample forms and their preparation methods, it is of utmost importance to clarify whether the observed FM is truly intrinsic or related to secondary phases such as magnetic clusters.8–10 For example, the absence of FM in ZnO:Co has been reported in bulk ferromagnetic semiconductors by standard solid-state reaction method, although the samples are of pure single phase.11–13 In some special reaction conditions, particularly with low sintered temperature, ferromagnetism has been reported in Mn-doped14 or Fe- and Cu-doped ZnO (Ref. 15) bulk samples, although other groups claimed secondary magnetic phase for the FM behavior in these bulks.10,16 Hence, it is still an issue how to prepare highly reproducible room temperature magnetic semiconductors with pure single phase.

In this letter, we report a two-step preparation process to obtain pure single phase Co-doped ZnO ferromagnetic semiconductors. We prepared the Co-doped ZnO bulk samples at high sintered temperature to produce pure single phase and then adjusted the carrier concentration to achieve high reproducible FM well beyond room temperature. The carrier concentration is controlled by doping interstitial Zn (Zni), similar to methods reported by Schwartz and Gamelin on Co2+:ZnO thin films.17 Although this is a simple process to prepare single phase magnetic semiconductor, it clearly shows how carrier concentration controls the magnetism in ZnO based semiconductors. This capability to fabricate ferromagnetic ZnCoO semiconductor with high reproducibility promises new spintronic devices in the future.

ZnCoO polycrystalline samples were fabricated by the standard solid-state reaction method. High purity ZnO (99.9%) and CoO (99.999%) powders (Alfa Aesar, USA) were mixed thoroughly and sintered at 1050 °C in the air for 12 h, which produced single phase ZnCoO, evidently from x-ray diffraction (XRD) using a D/Max-2400 (Cu Kα source). These samples were then annealed at 500 °C for 8 h and exposed to zinc vapor by heating Zn metal in a quartz tube at 0.5 Pa to get interstitially Zn-doped bulk ZnCoO (hereafter called as Zn treatment). The Co concentrations of the samples with and without Zn treatment have been measured by using an inductively coupled plasma atomic emission spectroscopy, which matched the nominal composition very well. The room temperature magnetic properties of the samples were measured using an alternating gradient magnetometer (AGM, MicroMag™ 2900) with a resolution of 1×10−8 emu. The temperature dependence of the magnetic properties was measured using a superconducting quantum interference device (SQUID, Quantum Design™ MPMS-7).

Typical powder XRD pattern of Zn1−xCoO for x=0.05 is shown in Fig. 1. When x ≤ 0.07, all the peaks can be indexed with hexagonal lattice of ZnO, and there is no indication of secondary phases. When x > 0.1, minor cubic phase (CoO) appears in dominating hexagonal ZnCoO matrix. Similar results can be found in Refs. 11–13. The solubility range changed a little in different references, but it is no doubt that pure single phase ZnCoO bulks can be obtained.

FIG. 1. (Color online) The XRD pattern of Zn1−xCoO with x=0.05.

---

aElectronic mail: tzhu@aphy.iphy.ac.cn
when the sinter temperature is higher than 1000 °C. Also from XRD measurements, no change in the lattice and no secondary phase have been observed after Zn treatment.

Figure 2 shows the magnetization (M) hysteresis loops of the ZnCoO samples treated with Zn vapor, indicating a ferromagnetic behavior at room temperature. As shown in the inset of Fig. 2(a), the magnetization increases with the increase of Co concentration but the coercivity (Hc) changes little. ZnCoO bulks without Zn treatment show no FM, which are the same as all previous results.

Figure 3 shows a typical temperature dependence of magnetization for bulk Zn0.95Co0.05O sample measured in an applied field of 1 kOe. ZnCoO bulks without Zn treatment exhibit antiferromagnetism, whereas the ferromagnetic behaviors can be clearly seen with additional interstitial Zn. The temperature dependence of susceptibility χ in as-sintered samples can be described by the diluted Heisenberg antiferromagnet theory by the formula,11,12,18

$$\chi = C_M(x)/(T - \Theta(x))$$

where the $C_M(x) = C_0x$ is the molar Curie constant and $\Theta(x) = \Theta_0x$ is the Curie-Weiss temperature, respectively. By fitting the temperature dependence of susceptibility with the modified Curie-Weiss law, we obtained Curie-Weiss temperature $\Theta_0 = 59 \pm 4$ K, indicating antiferromagnetic (AF) coupling in the as-sintered ZnCoO sample.

On the other hand, there is still an antiferromagnetic contribution in the Zn treated ZnCoO. This may be related with the carrier diffusion nature in the semiconductor. It is well known that, during the exposure of Zn vapor, Zn diffuses into bulk ZnO interstitially, but with concentration variation. In this simple experiment, the concentration and depth of interstitial Zn have not been well controlled. It is quite possible to have some areas where no enough interstitial Zn exists, resulting in antiferromagnetic behavior. Carrier doping is still a critical issue in the magnetic semiconductor studying. For example, even in well-grown GaMnAs, some Mn atoms occupy interstitial sites to induce an antiferromagnetic contribution.

The ZnCoO bulks treated with Zn vapor exhibit reversible ferromagnetic ordering. Heating the Zn treated bulk sample in air at 500 °C rapidly destroys its ferromagnetism, but the ferromagnetic state recovers when the same sample is exposed to Zn vapor again. The typical results are shown in Fig. 4. Similar reversible ferromagnetic ordering has also been observed in ZnCoO thin films treated by Zn.17 Hence, it suggests that ferromagnetic states will only be achieved when other carriers are induced. The ferromagnetic reversible behavior also exhibits the high reproducibility in ferromagnetic ZnCoO bulks.

Compared with the insulating as-sintered ZnCoO bulk sample, Zn treated ZnCoO bulk was highly conductive. The carrier density was estimated as $1 \times 10^{20}$ cm$^{-3}$ by using Hall measurement with Van der Pauw configuration. However, the nature of n-type carrier is the obstacle for the well-known magnetic contribution.19

FIG. 2. (Color online) The magnetization hysteresis loops for Zn0.95Co0.05O bulks (a) with and (b) without Zn treatment, respectively. The inset of (a) shows estimated saturation magnetization ($M_s$) and the coercivity ($H_c$) as a function of Co concentration. The lines are guides of eye.

FIG. 3. (Color online) Temperature dependence of the magnetization in an applied field of 1000 Oe for Zn0.95Co0.05O bulks with and without Zn treatment, respectively. The line plots the modified Curie-Weiss behavior for Zn0.95Co0.05O bulk without Zn treatment (see text).

FIG. 4. (Color online) Magnetic hysteresis loops for Zn0.95Co0.05O bulk prior to Zn vapor treatment (down triangles), after first Zn vapor treatment (squares), annealed in air after first Zn vapor treatment (up triangles), and after second Zn vapor treatments (circles), respectively.
hole-mediated mechanism in the ferromagnetic semiconductors.\textsuperscript{29} Several models have been presented to explain the FM origin in those ferromagnetic TM-doped ZnO semiconductors.\textsuperscript{7,21-23} Recently, Coey \textit{et al.} presented spin-split impurity-band model\textsuperscript{12} to explain the variation of the magnetic moment across Zn\textsubscript{1-x}TM\textsubscript{x}O series. From this model, the ZnO based semiconductors exhibit FM behavior only when they are doped by some 3d atoms, such as Co, which induced strong hybridization of 3d impurity band near the Fermi level, $N(E_F)$. However, in the case of as-sintered Co-doped ZnO bulk sample, it is clear that the Co\textsuperscript{2+} ions distributed in the ZnO matrix antiferromagnetically interact with each other. In other words, the contribution of 3d impurity band is important but is not enough for FM behavior in ZnCoO bulks. The carrier characteristic in ZnO should be considered. ZnO is very easily and naturally n-type semiconductor with O vacancies ($V_O^-$) and Zn interstitials ($Zn^+_{\text{i}}$).\textsuperscript{24} The Fermi level sensitively depends on the dopant types and concentration. For example, Zn has a shallow level while $V_O^-$ has a deep level.

Hence, we suggest that Stoner criterion for ferromagnetism should be the key point for the FM origin in TM-doped ZnO bulk samples. The onset of ferromagnetism is associated with the additional carriers induced, which increase $N(E_F)$ to satisfy the Stoner criterion for ferromagnetism, $N(E_F)/I > 1$ ($I$ stands for the Stoner parameter). In order to satisfy such Stoner criterion, we emphasize a codoping effect consisting of 3d atoms and additional carriers for the FM mechanism. First, it needs suitable 3d atoms, such as Co, with strong impurity band near the Fermi level. Second, it still needs additional treatment for increasing carrier concentration to further increase the $N(E_F)$. According to this codoping effect model, we can easily explain our experimental results. Only Zn-doped ZnCoO bulks exhibit FM behavior. As for other TM ions, for example, Mn, the hybridization of the impurity band near the Fermi level is very weak. So, we cannot observe FM behavior in Mn-doped ZnO bulks even they were treated by the Zn vapor.

The above explanation partially consists with the first principles calculation by Lee and Chang.\textsuperscript{7} From their calculation, there is no FM in normal Co-doped ZnO. Most recently, Sluiter \textit{et al.}\textsuperscript{25} fabricated ferromagnetic Li and Co codoped ZnO with low temperature process. However, the low temperature processing can easily introduce second phase,\textsuperscript{10,16} raising the doubt of intrinsic ferromagnetism in (LiCoZn)O. In our experiments, we separated the preparation into two clear steps to prevent second phase in the samples. The original antiferromagnetic-coupled Co\textsuperscript{2+} ions become ferromagnetic coupled when enough carriers doped after Zn vapor treatment. Our results exhibit that the combination of the 3d impurity band and the additional carriers are the keys to achieve FM behaviors. Zn interstitials dominate the transport, which will be reported elsewhere, and are finally responsible for the highly reproducible FM.

In summary, Co-doped ZnO bulks were prepared with a two-step process. The samples were sintered above 1000 °C to obtain single phase and then treated by Zn vapor in a vacuum to induce FM well beyond room temperature. Our results suggest that the ferromagnetism originates from the codoping effect of combination of Co dopant and additional carriers. This easy and high reproducible two-step preparation will be useful in further devices based on ferromagnetic ZnCoO semiconductors.

This work was supported by Chinese Academy of Sciences, NSFC, and NSF DMR Grant No. 0405-136. One of the authors (T.Z.) also thanks for the partial financial support from Alexander von Humboldt foundation and Dr. H. Braak in Juelich research center, Germany, for the help on Hall effect measurements.

\begin{thebibliography}{99}
\end{thebibliography}