Room Temperature Ferromagnetism in Co-doped ZnO Bulks

Long Peng, Huai-Wu Zhang, Qi-Ye Wen, and John Q. Xiao

Abstract—Pure single phase of Zn_{0.95}Co_{0.05}O bulks were successfully prepared by solid-state reaction method. The effects of annealing atmosphere and temperature on the room temperature ferromagnetic behavior were investigated. The results show that the air-annealed samples has similar weak ferromagnetic behavior with the as-sintered samples, but the obvious ferromagnetic behavior is observed for the samples annealed in vacuum or Ar/H_2 gas, indicating that the strong ferromagnetism is associated with high oxygen vacancies density. High saturation magnetization \( M_s = 0.73 \mu_B/Co \) and coercivity \( H_c = 233.8 \text{Oe} \) are obtained for the Ar/H_2 annealed samples with pure single phase structure when annealing temperature is 600 °C.

Index Terms—Co-doped ZnO, diluted magnetic semiconductors, ferromagnetism, spin electronics.

1. Introduction

Recently, diluted magnetic semi-conductors (DMSs) have been of great interest for the use of both charge and spin of electronics in semiconductors. TM-doped oxides (TiO, ZnO and SnO) have been investigated as a promising class of electronics in semiconducting band, which play an important role in the ferromagnetic origin. In addition to the magnetic doping effect, oxygen vacancies have been proposed to cause a marked change of the band structure of host oxides and make a significant contribution to the ferromagnetism on theory\(^6\),\(^7\). Accordingly, Hong et al.\(^8\) reported that remarkable room temperature ferromagnetism (RTFM) was observed in un-doped TiO_2, HfO_2, and In_2O_3 thin films. They proposed that the thin film form prepared by pulsed-laser deposition (PLD) method, which might create necessary defects or oxygen vacancies, would be reason for un-doped semi-conducting oxides to become ferromagnetic at room temperature. However, the oxygen vacancies could drastically vary with fabricating process and difficult to detect. In this paper, we investigated the effects of annealing atmosphere and temperature on RTFM for Co-doped ZnO bulks.

2. Experimental

The Co-doped ZnO bulks were prepared by solid-state reaction method. High pure (≥99.99%) ZnO and CoO were weighed in the composition of Zn_{0.95}Co_{0.05}O. These oxides were intimately mixed and milled. The ground powders were pre-sintering at 400 °C for 2 h and then further milled to homogenize the composition and improve reactivity by having a uniform small particle size. The powders, following the addition of polyvinyl alcohol (PVA), were granulated and formed into rectangle-shaped samples with the size of 15mm×10 mm×2 mm. Subsequently, these samples sintered from 800 °C to 1100 °C for 2 h in air, some of which annealed from 500 °C to 700 °C for 2 h in air, vacuum and mixed gas of Ar(90%)/H_2(10%), respectively. The magnetization versus magnetic field at room temperature for the samples was measured by a vibrating sample magnetometer (VSM) with a resolution of 1×10^{-8} emu at room temperature. The structure was studied by X-ray diffraction (XRD) with Cu K_a source.

3. Results and Discussion

Before annealing, the effects of sintering temperature on RTFM for Zn_{0.95}Co_{0.05}O bulks were investigated due to its important function on ferromagnetic behavior in TM-doped ZnO DMSs. We find out that ferromagnetic behavior can be detected only when sintering temperature is 800 °C. With increasing sintering temperature, the bulks show paramagnetic behaviors. It is well known that Co atoms diffuse into the ZnO matrix and partly substitute Zn atoms in the sintering process. With increasing sintering temperature, Co atoms could distribute more uniform in ZnO matrix, reducing the short-range magnetic interaction between Co atoms, which may be reason for the decrease of RTFM.

Subsequently, the sintering temperature is fixed as 800 °C in order to investigate the effects of annealing atmosphere on RTFM for the Zn_{0.95}Co_{0.05}O bulks. Fig. 1 presents the
magnetization versus magnetic field at room temperature for the Zn$_{0.95}$Co$_{0.05}$O bulks. It is clear that the saturation magnetization $M_s$ and coercivity $H_c$ vary strikingly for different annealing atmosphere with the value of 0.03, 0.26 and 0.73 $\mu_B$/Co and 154.3, 181.0, 233.8 Oe for the air-annealed, vacuum-annealed and Ar/H$_2$-annealed bulks respectively. Compared with as-sintered bulk, air-annealing has no remarkable effects on the $M_s$ and $H_c$, but the $M_s$ and $H_c$ have a drastically increase for the vacuum-annealed and Ar/H$_2$-annealed bulks, indicating that RTFM is enhanced when annealed in vacuum and Ar/H$_2$. Fig. 2 presents the XRD patterns for the Zn$_{0.95}$Co$_{0.05}$O bulks. As can be seen, ZnO wurtzite single phase can be obtained when the bulk sintered at 800 °C, and the annealing atmosphere has no effects on the structure, indicating that the ferromagnetism is not origin from secondary magnetic phase.

Fig. 1. Magnetization versus magnetic field at room temperature for the Zn$_{0.95}$Co$_{0.05}$O bulks.

Fig. 2. XRD patterns: (a) as-sintered, (b) air-annealed, (c) vacuum-annealed, and (d) Ar/H$_2$-annealed Zn$_{0.95}$Co$_{0.05}$O bulks.

Oxygen vacancies ($V_o$) play a significant role for the ferromagnetic origin in oxide DMSs $^{[9]}$. We expect that the Co$^{2+}$-$V_o$-Co$^{2+}$ groups would be common in Co-doped ZnO. An electron locally trapped in $V_o$ occupies an orbital, overlapping the $d$ shells of Co$^{2+}$ neighbors, which has an important function on the spin orientations of neighboring Co$^{2+}$. Based on Hund’s rule and Pauli exclusion principle, spin orientations of trapped electrons and neighboring Co$^{2+}$ are parallel in the same direction, thus ferromagnetism is achieved. More oxygen vacancies lead to more Co$^{2+}$-$V_o$-Co$^{2+}$ groups, which increase the chance of creating more Co$^{2+}$ into the ferromagnetic state and enhanced ferromagnetism is observed. In our experiment, the oxygen vacancy density ($D_{V_o}$) was not detected, but it could be correlated with annealing atmosphere. When annealed in air, O elements could fill up the oxygen vacancies, thus the $D_{V_o}$ reduces. While more O elements could be carried off by Ar/H$_2$ annealing, resulting in high $D_{V_o}$. So, it can be considered that $D_{V_o, \text{air-anneal}} < D_{V_o, \text{vacuum-sintered}} < D_{V_o, \text{Ar/H}_2\text{-annealed}}$ for the Zn$_{0.95}$Co$_{0.05}$O bulks. According to this oxygen vacancies-mediated ferromagnetic exchange coupling mechanism in the oxide DMSs, the enhancement of RTFM for the vacuum-annealed and Ar/H$_2$-annealed Zn$_{0.95}$Co$_{0.05}$O bulks can be well explained.

Fig. 3. Magnetization versus magnetic field at room temperature for the Ar/H$_2$ annealed Zn$_{0.95}$Co$_{0.05}$O bulks annealed at 500 °C.

Fig. 4. XRD patterns for the Zn$_{0.95}$Co$_{0.05}$O bulks annealed at (a) 500 °C, (b) 600 °C, and (c) 700 °C in Ar/H$_2$, respectively.

The effects of Ar/H$_2$ annealing temperature on the room temperature ferromagnetic behavior for the Zn$_{0.95}$Co$_{0.05}$O bulks were investigated due to its remarkable contribution to the enhancement of ferromagnetism. Fig. 3 presents the magnetization versus magnetic field at room temperature for the Ar/H$_2$ annealed Zn$_{0.95}$Co$_{0.05}$O bulks, and the insert is the
dependence of $M_s$ and $H_c$ on annealing temperature. It is obviously that the $M_s$ and $H_c$ vary slightly with the value from 0.54 to 0.73 $\mu_B$/Co and from 234.0 to 233.8 Oe when annealing temperature increases from 500 °C to 600 °C. However, the $M_s$ and $H_c$ sharply change to 1.51 $\mu_B$/Co and 164.1 Oe with annealing temperature further increasing to 700 °C. Fig. 4 presents the XRD patterns for the Ar/H$_2$ annealed Zn$_{0.95}$Co$_{0.05}$O bulks. It is found that when annealing temperature varies from 500 °C to 600 °C, the bulks are of typical ZnO wurtzite structure and no secondary phase formation is detected. But the bulks cannot keep pure single phase with further increasing annealing temperature. The peak of Co (111) and Co (200) yields when annealing temperature reaches 700 °C. The present of Co phase could be reason for the abnormal high $M_s$ and low $H_c$.

4. Conclusions

In summary, the pure single phase Co-doped ZnO ferromagnetic semiconductors are successfully prepared, which promises new spintronic devices in the future. It is found that the origin of room temperature ferromagnetism in Co-doped ZnO bulks is correlated with the oxygen vacancies-mediated ferromagnetic exchange coupling interaction. High oxygen vacancies density controlled by the annealing atmosphere can give rise to enhanced room temperature ferromagnetic behavior.

References


