Cu⁺-codoping inducing the room-temperature magnetism and p-type conductivity of ZnCoO diluted magnetic semiconductor

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1. Introduction

Much attention has been devoted to diluted magnetic semiconductors (DMSs) due to their potential application in what is now called “spintronics” devices. An essential task in realization of the potential is to find a DMS with the Curie point above room temperature. A theoretical prediction by Dietl et al. [1] suggested that room-temperature ferromagnetism should exist in heavily p-type doped alloys of ZnO. As Co is highly soluble in ZnO, Co-doped ZnO has been studied widely. But experimental results on FM properties of ZnCoO were complicated. There have been several reports about the ferromagnetic properties of ZnCoO thin films above room temperature [2,3], while a recent result showed FM at room temperature in pure Zn₁₋ₓCoₓO was not found with x value up to 0.1 [4]. The microstructure of ZnCoO nanostructure, fabricated by different growth conditions, was another point to affect the room-temperature FM [5]. So origin of room-temperature ferromagnetism of ZnCoO is very complex.

A computational study by Spaldin [6] predicted that ferromagnetism would only be found in Co-doped ZnO in the presence of p-type carriers. As Cu⁺ can be used as an additional p-type dopant into naturally n-type ZnO samples, it is suggested that the Cu-codoped to the ZnCoO is a way to attain room-temperature ferromagnetism. Until now, the room-temperature FM of Cu-codoped ZnCoO films containing both Cu⁺ and Cu²⁺ has been reported, however, no more information can be observed for Cu⁺ as the acceptors to induce the p-type carriers [7]. In the letter, we have attained the room-temperature ferromagnetism by adding Cu ions to the Co-doped ZnO films by sol–gel method. Meanwhile, we found that the Cu is univalent in the films, which indicate that Cu behave completely as acceptors in the films.

2. Experimental

The films were grown by the sol–gel method. The sol was composed of Zn(NO₃)₂·6H₂O, Cu(CH₃COO)₂·H₂O, Co(NO₃)₂·6H₂O and polyvinyl pyrrolidone (PVP) in an ethanol solution. The total concentration of metal ions was controlled at 0.1 mol/l. The concentration of Cu ions was adjusted to 0 mol/l, 0.001 mol/l and 0.002 mol/l and the concentration of Co²⁺ was maintained at 0.001 mol/l. The films were spin-coated on Si (1 0 0) and quartz substrates at 2000 r/min. After the deposition, the substrates were first heated to 100 °C in air for 10 min to evaporate the solvent, then at 350 °C in O₂ for half-an-hour to eliminate the organic
component in the film. This process may be repeated many times to reach the desired thickness. Then thermal annealing was performed for 1 h in an O$_2$ environment at 700 °C in order to crystallize the film. The thicknesses of the samples were all near 150 nm.

X-ray diffraction (XRD) measurement was taken on a Siemens D500 diffractometer using Cu K$_{\alpha}$ radiation of 1.5418 Å. Magnetic characteristics are studied using a vibrating sample magnetometer (VSM) (Lake Shore Company) at room temperature. The electrical properties and Hall data are measured using four probes with Van der Pauw geometry. The chemical nature of surfaces was analyzed by X-ray photoelectron spectroscopy (VG ESCALAB MK II XPS, VG Co., East Grinstead, UK). The binding energies were calibrated by centring the aliphatic carbon peak at 284.6 eV.

3. Results and discussion

X-ray photoelectron spectroscopy (XPS) was done to investigate the bonding characteristics and the oxidation state of the transition metal dopants in the codoped ZnO films. Typical Co 2p core level XP spectrum is presented in Fig. 1. The Co 2p$_{3/2}$ peak occurs at 780.3 eV, while the Co 2p$_{1/2}$ peak is located at 795.8 eV, showing large chemical shifts compared to that of pure Co metal [8]. The difference between Co 2p$_{3/2}$ and Co 2p$_{1/2}$ is 15.5 eV, which is different from 15.05 eV of pure Co metal [8]. These results indicate that Co ions have a valance of 2+. Satellite peaks appeared at about 785.1 eV and 802.3 eV, respectively. The very intense satellite structure results from the charge-transfer band structure characteristic of the late 3d transition metal monoxides [9]. These results may prove that Co ions are surrounded by oxygen atoms and have a chemical valence of 2+.

From Fig. 2, it can be seen that the copper 2p peaks shows a Cu 2p$_{3/2}$ peak at 932.1 eV and a Cu 2p$_{1/2}$ peak at 952.3 eV, which indicates that the valence state of Cu in the films is Cu$^+$, rather than Cu$^{2+}$ [7,10]. Thus, Cu ions play the role of acceptors. The relative quantitative analysis of each element is completed using the XPS peak area data of different elements and their own elemental sensitivity factor. From the former results, we conclude that the content ratio of Co is 0.5%. That is, only 0.5% content of Co entered the ZnO lattice and the rest was lost. The content ratio of Cu is 0%, 0.5% and 1.1%, which was labeled sample A, sample B and sample C, respectively.

X-ray diffraction patterns of Zn$_{0.995-x}$Co$_{0.005}Cu_x$O are shown in Fig. 3. The diffraction pattern can be identified as the wurtzite structure, which indicates that the Co- and Cu-codoping cannot disturb the structure of ZnO. No additional peaks (such as Co, CoO, Cu, Cu$_2$O) can be observed in the Zn$_{0.995-x}$Co$_{0.005}Cu_x$O, which indicates no impurity exists in the films. Furthermore, it should be noticed that with increasing the doping concentration of Cu ions all the diffraction peaks in the XRD patterns shift to the lower angle side gradually, due to ionic radius of Cu$^+$ (0.95 Å) is larger than that of Zn$^{2+}$ (0.60 Å). Meanwhile, the peak intensity decreases when the Cu concentration is increased, which means that the crystalline quality degrades with Cu ions doping. The XRD result indicates that Cu ions are doped into ZnCoO crystal lattice successfully with substituting positions of Zn ions.

The Cu$^+$ states indicate that the Cu-doped ZnCoO films should be as the acceptors. In order to confirm the carrier type, the electrical transport properties of the samples are summarized in Table 1. Based on the hall-effect measurement, the sample A is n-
type conductivity. After the Cu doping, the Hall coefficient is inverted to positive, which indicates a hole-dominant transport effect and the film converts to the $p$-type conductivity. The hole concentrations increase with the increasing Cu doping concentration from $2.83 \times 10^{16}$ cm$^{-3}$ to $4.40 \times 10^{17}$ cm$^{-3}$. The mobility is the 1.35 cm$^2$/V s and 2.69 cm$^2$/V s, respectively. And the resistivity of the samples decreases while increasing Cu doping concentration. Due to the Cu doping, the Cu$^+$ as the acceptors to compensate donors arising from the oxygen vacancies, so the density of acceptor will be dominant, leading to the ZnO inverted from $n$-type to $p$-type.

Fig. 4 shows the hysteresis behavior of the samples measured at the room temperature with the magnetic field perpendicular to the film surface. For the pure ZnCoO sample paramagnetism was detected. But the two Cu-codoped samples are ferromagnetic at room temperature. It is noted the ferromagnetic moment and $M_s$ increase with increasing concentration of Cu$^+$. Based on the above experiments, the ferromagnetic behavior of the samples could not originate from Co nanoclusters. Because all the samples were grown under the same condition, and ZnCoO film is paramagnetism. This result is well agreement with the XRD patterns. Therefore, the $p$-type carriers generated by Cu doping is considered a main factor to induce the ferromagnetic phenomenon [11].

Since the theoretical prediction by Dietl et al. [1] suggested that room-temperature ferromagnetism should exist in heavily $p$-type doped alloys of ZnO. Spaldin [6] also suggested that robust ferromagnetism will only be obtained in transition-metal-doped ZnO if $p$-type carriers are also included. In our letter, according to the hall-effect measurement, it is obtained that the Cu-codoped samples are all $p$-type. Meanwhile, the XPS measurements also showed that the valence state of Cu in the samples is Cu$^+$. Thus, Cu ions play the role of acceptors to compensate donors, which lead to the ZnO inverted from $n$-type to $p$-type. As the as-grown samples are only electron conductivity, we consider the above phenomenon could be explained by the hole-mediated exchange interactions [1]. Under this theory, a bound magnetic polarons (BMPs) could be formed with the introduction of $p$-type dopants. Magnetic exchange interactions between defect-bound valence band holes and Co$^{2+}$ ions occupying the same space are proposed to align Co$^{2+}$ spins with respect to one another, forming a BMP [12]. The hole induced FM in ZnCoO has already been observed by Li doping [4]. And the author also theoretically argued that Co has the best potential as a Zn substitutional dopant in ZnO for producing DMS when combined with a hole dopant [4]. So based on the BMP model, the $p$-type doping from the Cu will induce ferromagnetic interactions between the Co ions, resulting in the room-temperature ferromagnetism were observed in the Cu ions codoped samples.

4. Conclusions

In conclusion, room-temperature ferromagnetism were obtained in the Cu-codoped ZnCoO films. Here, the $p$-type carriers generated by Cu-codoping is considered a main factor to induce the ferromagnetic phenomenon. According to the XPS and Hall-effect measurement, it is concluded that the Cu ions are univalent in the films, which indicate that Cu completely as acceptors in the films.

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