Enhancement of ferromagnetic properties in Zn$_{1-x}$Co$_x$O by additional Cu doping

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The high-temperature ferromagnetism in Co-doped ZnO samples fabricated by the standard solid-state reaction method is reported. Additional Cu doping into bulk Zn$_{0.98}$Co$_{0.02}$O is essential to achieve room-temperature ferromagnetism. Structure and composition analyses revealed that cobalt is incorporated into the lattice structure, forming a solid solution instead of precipitates. In the case of Zn$_{0.97}$Cu$_{0.01}$Co$_{0.02}$O, the coercive field measured by a vibrating sample magnetometer at room temperature is 60 Oe. The implication of the effect of Cu doping in bulk Zn$_{0.98}$Co$_{0.02}$O is also discussed. © 2004 American Institute of Physics.

Diluted magnetic semiconductors (DMSs) have attracted much interest in recent years because of the possibility involving charge and spin degrees of freedom in a single substance. It is expected to establish semiconductor spin electronics (spintronics) as a practical technology based on such functional materials. Therefore, there has been strong encouragement to synthesize a ferromagnetic DMS whose Curie temperature ($T_C$) is much higher than room temperature.

Diel et al. suggested, by a mean field theory, ZnO and GaN as candidates having a high $T_C$ and a large magnetization. Some experimental results were reported. Sato et al. predicted that 3d transition metal atoms of Mn, Fe, Co, and Ni show ferromagnetic ordering in ZnO.

From the viewpoint of industrial application, ZnO has many attractive aspects such as its low cost, abundance, and being environmentally friendly. It also attracts considerable attention as an optoelectronic material because of its wide band-gap energy of 3.3 eV and high excitation binding energy of 60 meV. Therefore, further investigation on the feasibility of ZnO-based DMSs is of great interest.

Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O polycrystalline samples were fabricated by the standard solid-state reaction method. ZnO (99.9+%), CoO (99.9+%), and CuO (99.9+%) powders were mixed and ground for 24 h. Then, the mixture samples were put in a quartz tube filled with Ar gas and calcined at 1173 K for 24 h. The crystal structures of the Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O samples were characterized using 2θ–θ x-ray diffraction (XRD) and transmission electron microscopy (TEM). Magnetic measurements were performed by using either a superconducting quantum interference device (SQUID) magnetometer or a vibrating sample magnetometer (VSM). The composition distributions were also characterized by an energy dispersive x-ray spectrometer (EDX) mapping. To investigate the optical properties, we measured photoluminescence (PL) spectra in the ultraviolet–visible range at room temperature, carried out using a He–Cd laser ($\lambda = 325$ nm) as the excitation light source.

Figure 1 shows a typical powder XRD patterns of Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O with $x=0$–0.04. The subsequent XRD showed that the doping does not change the wurzite structure of ZnO (■) for Cu doping concentration below $x=0.01$ and we could not find any Co or Cu clusters in the XRD measurements. Upon further doping Cu above $x=0.02$, the diffraction pattern reveals an undesired peak (●), which corresponds to the peak of CuO. The results of the XRD patterns without CuO peaks do not mean that it is absent of Co or Cu clusters. We did not exclude the possibility of the formation of clusters small enough or too few in content not detectable in XRD. In order to explore the detailed microstructure in the samples, we used high-resolution TEM (HRTEM) to investigate the polycrystalline samples.

Magnetic properties of Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O samples were measured using VSM and SQUID. Figure 2 shows the mag-
netization ($M$) versus magnetic field ($H$) behavior at 300 K for Cu-doped ZnCoO samples. A small amount of additional Cu doping, however, brought drastic changes in $M$ as illustrated in Fig. 2. The magnetization is greatly enhanced with a small amount of Cu doping ($x \sim 0.01$). Upon further doping Cu above $x=0.02$, Fig. 2 shows the abrupt decrease in magnetization. The saturation magnetization ($M_s$) of the Zn$_{0.97}$Cu$_{0.01}$Co$_{0.02}$O sample is estimated to be $4 \times 10^{-4}$ electromagnetic units per gram (emu/g) from the $M-H$ curve.

The saturation field is about 1000 Oe, and the coercive field is about 60 Oe. A typical magnetization ($M$) versus temperature ($T$) curve was measured in an applied field of 2000 Oe for bulk Zn$_{0.97}$Cu$_{0.01}$Co$_{0.02}$O sample as shown in Fig. 2(b). The trend is similar to paramagnetic behavior, but the ferromagnetic hysteresis loop was observed between 10 and 300 K as show in Fig. 2(c). The increment of temperature seems to decrease the paramagnetic behavior and the ferromagnetic behavior is more manifest.

ZnO is a well-known optoelectronic material, however, the luminescence properties of Cu-doped ZnCoO have rarely been studied. The room-temperature PL of the Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O samples are shown in Fig. 3. The spectrum of a pure ZnO substrate is also shown as reference. The 386 nm peak is assigned to the ZnO near-band edge transition. The broad and intense green emission around 518 nm appears more and more as the incorporation of Co or Cu into ZnO material increases. The green emission is ascribed to arise from the defects in the ZnO material. Therefore, Fig. 3 shows the defects that increase with increasing Cu/Co doping concentration. Unfortunately, the UV emission peak dis-

![FIG. 4. HRTEM image of the bulk Zn$_{0.97}$Cu$_{0.01}$Co$_{0.02}$O. The inset shows the corresponding selected-area electron diffraction pattern.](image)

![FIG. 3. PL spectrum of the bulk Zn$_{0.98-x}$Cu$_x$Co$_{0.02}$O samples at room temperature.](image)
the lattice image of the bulk Zn_{0.97}Cu_{0.01}Co_{0.02}O. The sample was further examined by HRTEM. Figure 4 shows elemental homogeneity of the Zn_{0.97}Cu_{0.01}Co_{0.02}O sample rated uniformly into the entire ZnO material. In addition, the This strongly suggests that Co and Cu atoms were incorporated uniformly into the entire ZnO material. In addition, the elemental homogeneity of the Zn_{0.97}Cu_{0.01}Co_{0.02}O sample was further examined by HRTEM. Figure 4 shows the corresponding electron image of the bulk Zn_{0.97}Cu_{0.01}Co_{0.02}O. The corresponding electron diffraction pattern is shown in the inset, the Zn_{0.97}Cu_{0.01}Co_{0.02}O does not show additional reflections. This strongly suggests that Co and Cu atoms were incorporated uniformly into the entire ZnO material. In addition, the elemental homogeneity of the Zn_{0.97}Cu_{0.01}Co_{0.02}O sample was further examined by EDX mapping. The image to the top left of Fig. 5 is a regular TEM image. The others represent EDX mapping of Zn, Co, and O elements, respectively. The arbitrary gray scale is proportional to the element’s concentration. On this particular sample, the recorded images also indicate a homogeneous distribution of the Co element. Thus, we would like to emphasize that magnetic properties reported in this work are not a result from the secondary magnetic phases, but rather due to solid solution Zn_{0.97}Cu_{0.01}Co_{0.02}O structure.

The possibility of ferromagnetic ordering in ZnO-based semiconductors was predicted by Dietl et al.\textsuperscript{2} They considered the influence of the delocalized or weak localized carriers on the interaction between magnetic ions. The theoretical treatment predicted that carrier densities could be achieved sufficiently high to drive a ferromagnetic phase in bulk II–VI DMSs. The method has been employed by Story \textit{et al.},\textsuperscript{9} and Munekata \textit{et al.}\textsuperscript{10} In our research, we consider the Ruderman–Kittel–Kasuya–Yosida (RKKY) model, which provides the energy $J_{ij}$ of the exchange coupling. If we exclude the structure defects in the bulk Zn_{0.98−x}Cu_{x}Co_{0.02}O, the Fermi momentum $k_F$ and the distance between two Co atoms are $1.6 \times 10^9$ m$^{-1}$ and 12 Å, respectively. The product value $2k_Fr \sim 3.8$ exactly corresponds to the first ferromagnetic zone in the RKKY model ($2k_Fr \leq 4.5$). By the way, structure defects will decrease the Fermi momentum $k_F$ and enhance the ferromagnetic behavior. We suppose the small amount of additional Cu doping ($x \sim 0.01$) will create the appropriate amount of carriers. Therefore, the magnetization will be greatly enhanced. On the other hand, the extra doping of Cu will create the secondary phase (CuO) and accompany the decrease of the carrier concentration and the abrupt decrease in magnetization.

We did try to measure the Hall effect. However due to the large bulk resistance to create measurable Hall voltage, the carrier concentration was not obtained.

In conclusion, we have synthesized the DMS Zn_{1−x}Cu_{x}O by a standard solid-state reaction method. The bulk Zn_{1−x}Co_{x}O exhibits obvious ferromagnetic ordering above room temperature with additional particular amount of Cu doping. From the results of x-ray and EDX mapping, no secondary phases were observed and the Co is homogeneous distribution in the Zn_{0.97}Cu_{0.01}Co_{0.02}O phase.

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