

Ferromagnetism and magnetoresistance of Co–ZnO inhomogeneous magnetic semiconductors

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(Received 26 September 2003; accepted 5 February 2004)

Co–ZnO inhomogeneous magnetic semiconductor thin films were synthesized on the subnanometer scale by sputtering. Room temperature ferromagnetism with high magnetization was found. Large negative magnetoresistance of 11% was found at room temperature, and its value increased with a decrease in temperature up to 36% at 4.8 K. The mechanism for large negative magnetoresistance is discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1690881]

Magnetic semiconductors (MS) are attracting considerable attention since they are expected to be key materials in spintronic devices. Recently, stimulated by the success in MS of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ (Ref. 1) and $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ (Ref. 2), ZnO-based MS have been investigated by some groups since they are predicted to be ferromagnetic semiconductors with a high Curie temperature above 300 K and large magnetization.^{3,4} To date, reported experimental results of ZnO-based MS by these groups are different and even contradictory.^{5–14} Near or above room temperature ferromagnetism of ZnO-based MS was found by some groups,^{5–9} while other groups found no ferromagnetism^{10–13} or a very low Curie temperature.¹⁴ Fukumura *et al.*¹¹ and Jin *et al.*¹² observed anomalous magnetoresistance and Ando *et al.* reported a huge magneto-optical effect¹³ in ZnO doped with transition metals, but no ferromagnetism was reported.

However, high magnetization has not yet been achieved at room temperature in ZnO-based MS,^{5–9} and the magnetoresistance becomes negligibly small above 100 K.^{5,10,12,15} In this letter, we report a Co–ZnO inhomogeneous magnetic semiconductor (IMS), which was synthesized on the subnanometer scale and shows high magnetization and large magnetoresistance at room temperature.

The Co–ZnO IMS films were prepared on glass substrates by alternately sputtering very thin Co layers of nominal thickness of 0.6 nm and ZnO layers of nominal thickness of 0.5 nm for 60 periods at room temperature [the nominal structure is (Co 0.6 nm/ZnO 0.5 nm) × 60]. The pressure of Ar gas was stabilized at 3 mTorr during the sputtering pro-

cess. The Co layers were deposited by dc magnetron sputtering at a growth rate of 0.07 nm/s, and the ZnO layers were deposited by rf sputtering at a growth rate of 0.02 nm/s. The preparation of samples is very controllable and reproducible. It also offers some other advantages: The room temperature growth and the very small thickness of Co and ZnO may enable Co and ZnO to become incorporated into each other since the layer thickness, the interface roughness, and the interdiffusion length are comparable. On the other hand, since low temperature growth is a thermal nonequilibrium process, it enables high solubility of Co in ZnO and hence increases the magnetization. Moreover, the low growth temperature and alternating deposition greatly limit crystal grain growth and increase defects such as O vacancies or Zn interstitials, which may increase the conductivity and enhance the s – d exchange interaction and increase the Curie temperature. Furthermore, the structure and the composition of Co–ZnO are uniform on the nanometer scale, but there may be Co-rich and ZnO-rich areas on the subnanometer scale which are introduced by the alternate deposition. Inhomogeneity on the subnanometer scale is also desirable for improving the Curie temperature and magnetoresistance. The preparation for Co–ZnO samples resembles the process for “digital alloys” of the superlattice structure,¹⁶ but it is essentially different in principle in sample design.

The microstructures of the as-grown films were observed by transmission electron microscopy (TEM) in cross section (Fig. 1). The low magnification bright field TEM image [Fig. 1(a)] shows almost even contrast, and the crystallinity of the film is revealed in the high resolution image [Fig. 1(b)]. The film is composed of nanosized particles, with average size of 4–6 nm. No layered structures were observed, although the film was grown by alternately depositing very thin Co and

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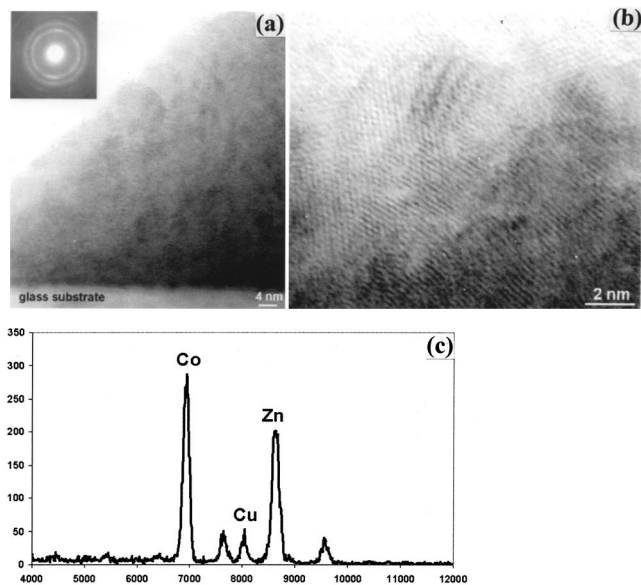


FIG. 1. Low magnification bright field cross-sectional TEM image (a), a high resolution TEM image (b), and an energy dispersive x-ray analysis spectrum (c). The selected area electron diffraction pattern is in the inset of (a).

ZnO layers. The lattice spacings measured vary from 2.51 to 2.30 Å in the high resolution image, indicating compositional inhomogeneity on the subnanometer scale, either due to inhomogeneous diffusion between alternating Co and ZnO layers, or a deficiency of O. A selected area electron diffraction pattern for the film is shown in the inset of Fig. 1(a). The first two rings have the highest intensity with a certain width. Using the externally calibrated camera length, the measured d spacings of the rings midpoint in each ring are 2.61 (ring 1) and 2.01 Å (ring 2). Ring 1 is determined to be a hexagonal ZnO {0002} crystal structure, and the d spacing of ring 2 is close to a hexagonal Co {0002} crystal structure. The composition of an area about 10 nm in diameter across the film was examined by focusing the electron probe, which is the smallest probe achievable in this experiment. The composition obtained by the 10 nm probe is uniform across the film. A typical energy dispersive x-ray (EDX) analysis spectrum is shown in Fig. 1(c). Quantitative analysis gives 47.3% (at. %) Zn, and 52.7% Co. The Cu peak in the EDX spectrum comes from the Cu sample holder. From the above TEM data and taking into account the high solubility of Co in ZnO of more than 40%,¹⁷ it is deduced that the as-grown films may consist of subnanosized Co-rich and ZnO-rich areas (possibly including $Zn_{1-x}Co_xO$, ZnO, and Co). However, we could not directly detect the composition of a single grain and its homogeneity since the grains were too small to be measured by the electron probe.

The magnetic properties were measured by a superconducting quantum interference device (SQUID) from 4.5 K to room temperature. The magnetic field is applied in the sample plane. The magnetization is defined as the magnetic moments divided by the nominal volume of Co metal. The diamagnetic and/or paramagnetic signals of the glass substrate were deducted. Figure 2 shows hysteresis loops measured at 5, 80, and 290 K, respectively. The ferromagnetism is clearly shown by the coercivity, remanence, and relatively low saturation field. At 290 K, the hysteresis (coercivity and

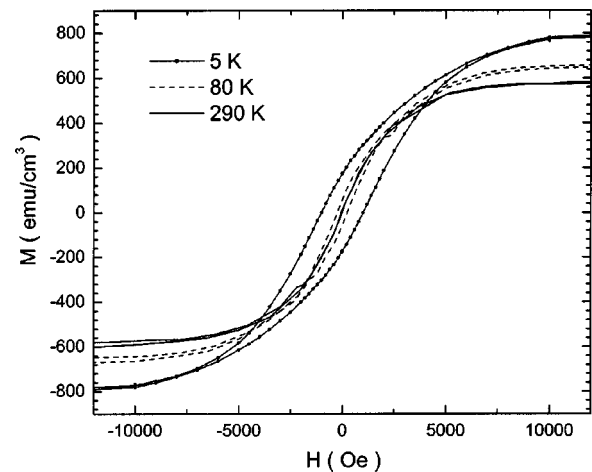


FIG. 2. Hysteresis loops measured at 5, 80, and 290 K, respectively.

remanence) becomes very small which may be due to the intrinsic magnetically soft properties. But the loop still shows the features of ferromagnetism compared with the loops at lower temperature. Since most room temperature MS have small coercivity,⁵ the Curie temperature of our Co-ZnO samples is at least near room temperature. Moreover, compared with the results of other ZnO-based ferromagnetic semiconductors,⁵⁻⁹ the magnetization of our Co-ZnO samples is high, up to 782 emu/cm^3 ($1.05\mu_B/\text{Co}$) at 5 K and 581 emu/cm^3 ($0.78\mu_B/\text{Co}$) at 290 K. We believe that the high magnetization originates from the high concentration of Co and the design structure of the samples.

The electrical transport properties were measured in a van der Pauw configuration from 4.5 K to room temperature. The field applied is perpendicular to the film plane. Figures 3(a) and 3(b) show the dependence of the sheet resistance R and the magnetoresistance (MR) ratio on the magnetic field applied, measured at 4.8 and 293 K, respectively. The MR ratio is defined as $\text{MR} = [R(H_s, T) - R(H, T)] / R(H_s, T)$

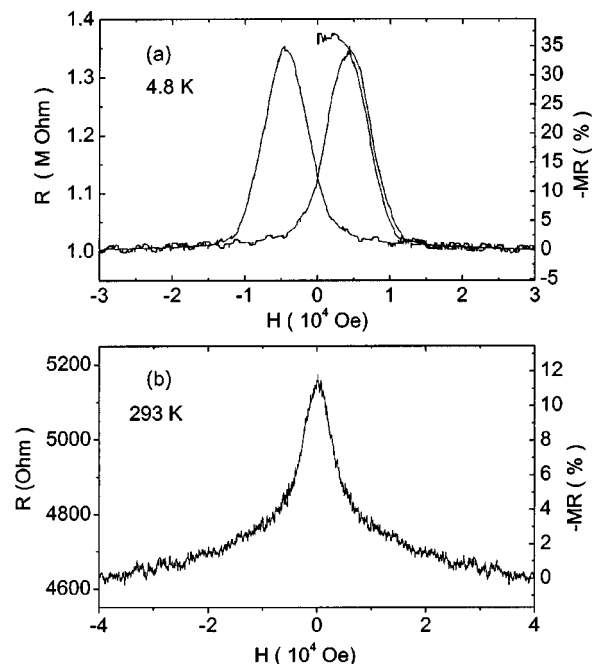


FIG. 3. Dependence of sheet resistance R and the MR ratio on the magnetic field applied measured at 4.8 (a) and 293 K (b), respectively.

$\times 100\%$, where $R(H, T)$ is the resistance at field H and temperature T , and $R(H_s, T)$ is the resistance at maximum H_s field applied ($H_s = 4 \times 10^4$ Oe in our experiments). For all Co–ZnO samples, the current–voltage (I – V) curves (not shown) are linear in the measured range of temperature (4.5–300 K) and voltage (0–10 V). Therefore, the MR ratio has no bias voltage dependence. The Co–ZnO samples show large negative magnetoresistance at relatively small field in the temperature range from 4.5 to 293 K, such as 36% at 4.8 K for the MR peak and 11% at 293 K, as shown in Figs. 3(a) and 3(b). Large negative and/or positive magnetoresistance at very low temperature of a few K was also found in ZnO-based^{5,10,12,15} and TiO₂-based^{2,18} magnetic semiconductors, but it usually becomes negligibly small (much less than 1%) above 100 K. It is interesting to note that the magnetoresistance in the ZnO-based and TiO₂-based ferromagnetic semiconductors quickly disappears even at 100 K while the ferromagnetism can be kept above room temperature.^{2,5,18} However, for our Co–ZnO samples, large magnetoresistance of 11% was observed at 293 K, which is significant for MS for use in spintronic devices.

As for the large negative magnetoresistance observed in the Co–ZnO IMS, it may be related to the spin-dependent hopping^{19,20} and magnetic-field-induced change in the localization length of Anderson localization.^{21,22} Suppose the magnetic field does not modify the energy band structures, then the magnetic field may influence the resistance by the alignment of localized magnetic moments. On the other hand, in our Co–ZnO system, there may be strong exchange interaction between carrier spins and local spins and electron–electron Coulomb interaction. The presence of a magnetic field may cause the redistribution of carriers between spin-up and spin-down states, enhance the energy level of the majority spin carriers, and hence increase the localization length.^{21,22} As a result, large negative magnetoresistance was found.

In summary, Co–ZnO IMS were synthesized on the subnanometer scale. Room temperature ferromagnetism with high magnetization was found. Large negative magnetoresistance of 11% was found at room temperature and it increases with a decrease in temperature up to 36% at 4.8 K. The large negative magnetoresistance may be related to spin-dependent hopping and the magnetic-field-induced change in the localization length.

This work was supported by Project 973 Grant No. 001CB610603 and NSF Grant No. 10234010. One of the authors (Y.X) acknowledges the National High Magnetic Field Laboratory at Florida State University (FSU), part of cooperative Agreement No. DMR-0084173 and a FSU cornerstone PEG grant. A second author (S.-Y.) would like to thank S. von Molnár and X. Peng for useful discussions.

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