J Mater Sci (2010) 45:6174–6178
DOI 10.1007/s10853-010-4710-2

# ZnO:Co diluted magnetic semiconductor or hybrid nanostructure for spintronics?

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Received: 30 September 2009 / Accepted: 11 June 2010 / Published online: 24 June 2010

**Abstract** We have studied the influence of intrinsic and extrinsic defects in the magnetic and electrical transport properties of Co-doped ZnO thin films. X-ray absorption measurements show that Co substitute Zn in the ZnO structure and it is in the 2+ oxidation state. Magnetization (M) measurements show that doped samples are mainly paramagnetic. From M vs. H loops measured at 5 K we found that the values of the orbital $L$ and spin $S$ numbers are between 1 and 1.3 for $L$ and $S = 3/2$, in agreement with the representative values for isolated Co 2+. The obtained negative values of the Curie–Weiss temperatures indicate the existence of antiferromagnetic interactions between transition metal atoms.

## Introduction

Transition metal atoms introduced into the cationic sites of semiconducting host lattices have recently attracted increasing attention because of their potential use in spintronic devices. Since the theoretical prediction of ferromagnetism in Co-doped ZnO, this material is being intensively studied [1]. However, contradicting experimental and theoretical results, concerning magnetic properties, have been reported [2–6]. Some groups observe room temperature ferromagnetism, while others report no ferromagnetism at room temperature or the observed ferromagnetism comes from metallic cobalt clusters. Also, the mechanism of exchange coupling induced by defect states, such as O- and Zn-vacancies, Zn- and N-interstitial or due to an inhomogeneous dopant distribution in the ferromagnetism remains still unclear.

An exchange coupling mechanism has been proposed by Dietl et al. [1] where the wave function of an unpaired electron in the valence band overlap the wave function of the transition metal ion having an opposite spin. The impurity band can interact with local magnetic moments through the formation of bound magnetic polaron (BMP) [1]. The Co ions are often found in the $Co^+$ states in ZnO, and it is necessary to introduce defects with a spin to provide the magnetic state necessary for the exchange coupling [7]. In a recent work, Dietl et al. [8] describe the origin of the ferromagnetic signal in Co-doped ZnO:Al in terms a spinodal decomposition of a Co-rich antiferromagnetic nanocrystals embedded in a Co-poor ZnO:Co host material. The authors describe the ferromagnetism as a consequence of the uncompensated spins at the antiferromagnetic nanocrystals surface. Recently, Coey et al. [9] argument that traditional super-exchange and double-exchange interaction cannot produce long range magnetic

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order at concentration of magnetic cations of a few percent, and they proposed another model for ferromagnetism in DMS materials based on a spin–split donor impurity band. The ferromagnetism exchange in this model is mediated by the defect states that form BMP generating an impurity band which interact with local magnetic moments. To obtain a high Tc, a fraction of polaronic charge must be delocalized (or hybridized). This description of ferromagnetic mechanism opens the possibility to control de magnetic behavior of DMS by injection of carrier using photons or electric field. The latter description suggest us to start a study on electric and magneto-transport mechanisms, and the effect of the interaction between defects and dopants on these mechanisms.

In this work, 10 and 15% Cobalt-doped ZnO films were grown on $SiO_2$/Si and sapphire substrates in $N_2$ or $O_2$ atmospheres by pulsed laser deposition (PLD). In order to understand how the micro or nano-structural inhomogeneity can affect the magnetic and electrical properties of these samples, these properties were investigated by measuring the in-plane magnetization versus magnetic field and also the electrical and electromagnetic transport as a function of temperature between 5 K and room temperature. These results were correlated with structural and compositional studies. All the samples of the series doped with Co showed a paramagnetic behavior. The pure samples were diamagnetic, independently of the growth atmosphere. A giant positive magnetoresistance was estimated using *I*–*V* curves taken at constant temperatures in zero magnetic field and in 10 T. Structural and magnetic characterizations suggest us to consider the system ZnO:Co as an hybrid nanostructure.

## Experimental

Two series of ZnO films of different thickness were prepared by PLD. A Nd:YAG laser beam, operating at 10 Hz, was focused on a rotating target of ZnO:Co with the nominal composition, to yield an energy density of 3.4 J/cm$^2$. In both series, 10 and 15% Cobalt-doped ZnO films were grown on $SiO_2$/Si and c-sapphire substrates in $N_2$ or $O_2$ atmospheres. The substrates were held at a temperature of 673 K. For the first series, a laser wavelength of 266 nm was used and thin films with thicknesses between 50 and 100 nm were deposited, and for the second series thicker films with thicknesses from 800 to 900 nm were deposited using a laser wavelength of 355 nm. X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (EDS) was employed for structural characterizations. In order to determine the local environment of magnetic magnetic impurities, X-ray absorption (XAS) measurements (include EXAFS and XANES) were taken at room temperature in fluorescence mode at the Co K-edge, using a Si (1 1 1) monochromator at the XAFS beamline of LNLS (Campinas, Brasil). Magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer at temperatures from 5 to 300 K. For electrical transport measurements, a symmetric device was fabricated by depositing two coplanar Al disk-shaped contacts (diameter = 0.75 mm) by Ar-sputtering on the top surface of the samples. Leads were soldered on both pair of contacts using In. We employed a two-probe scheme in the setup. In the two-probe method, a fixed voltage was applied across the sample, and the current flow was monitored by measuring the voltage drop across a metal film resistor. This scheme turns out to be more convenient because it allows the stabilization of the dc voltage at sufficiently high level, and that fixed value is not affected by dramatic changes of resistivity at low temperatures. Leakage current values were checked to be always below the current values measured in this work. The *I*–*V* curves were constructed using voltage pulses of increasing amplitude of about 1 s time width, followed by a short time (half a second) without any applied voltage.

## Results

XRD pattern corresponded to the wurtzite structure for all films showing only the (002) and (004) wurtzite reflection. Figure 1a shows an illustration of the patterns corresponding to a 15% Co-doped ZnO thick film of the series growth on sapphire compared with a pure sample growth in identical conditions. The double peaks are observed only in the doped and thicker films. Figure 1b shows a magnification of the double peak at $2\theta \approx 34.08°$. This result could be attributed to a (002) reflection from a composition modulated alloy of two *wurtzite* systems with different lattice parameter. The XRD patterns of thinner films, Fig. 2, all growths on $SiO_2$/Si substrate show a polycrystalline lightly oriented structure. Although no double peaks appear, XRD revealed the segregation of Co particles in some films.

It was already reported the coincidence of the (002) ZnO and w–CoO reflection [10]. Then, considering the possibility of the coexistence of two wurtzite systems in thicker and doped sample, we estimate the c-lattice constants as (5.19 ± 0.01) Å and (5.26 ± 0.01) Å. The c-lattice constant for pure ZnO growth in identical conditions was estimated as (5.24 ± 0.01) Å which suggest us that the lower c-parameter correspond to a probable secondary phase of *wurtzite* CoO. Also the mean sizes of each system were estimated using a best fitting of Gaussian curves and the Scherrer formula, $D = 0.94\lambda/W\cos\theta$. $W$ is the full

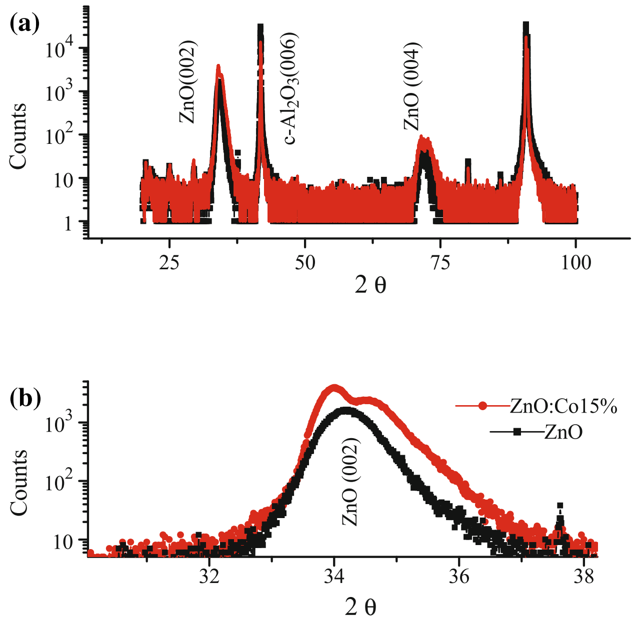

**Fig. 1** XRD spectra of films of ZnO deposited on sapphire prepared by PLD. *Black line* pure ZnO, *red line* $Zn_{0.85}OCo_{0.15}$. **a** Full spectra, **b** zoom of the (002) peaks (Color figure online)

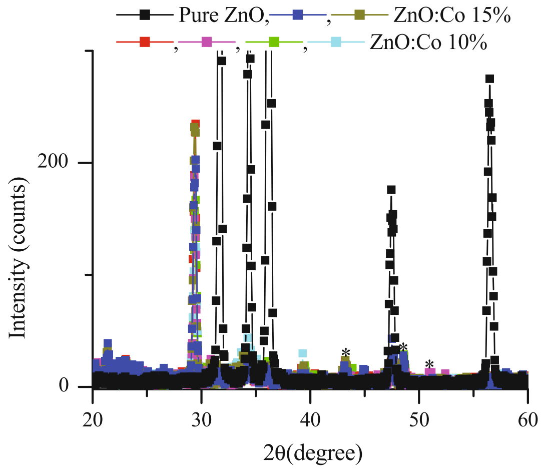

**Fig. 2** XRD spectra of thinner films of ZnO deposited on $SiO_2/Si$, the size of samples are between 50 and 100 nm. *Asterisks* indicate the Co impurity

width at half the maximum (FWHM) of the (002) diffraction peak and $\lambda$ is the X-ray wave length (1.5405 Å). Two particle sizes of 15 and 24 nm were estimated and a relation between the peaks area of 1.6. For the thinner samples the particle sizes range between 30 and 40 nm.

Figure 3a and b shows a scanning electron microscopy with EDS mapping showing the Zn and Co distribution in $Zn_{0.85}OCo_{0.15}$ film grown over sapphire substrates in $N_2$ atmosphere (the same doped film as Fig. 1). Co $K_\alpha$ and Zn *L* X-ray lines were used for the Co and Zn EDS mapping, respectively. Although the Zn distribution seems uniform (similar distribution is obtained for the oxygen, not shown) the segregation observed in the Co EDS mapping seems like a typical spinodal decomposition. Our results suggest us to consider the system ZnO:Co as an hybrid nanostructure.

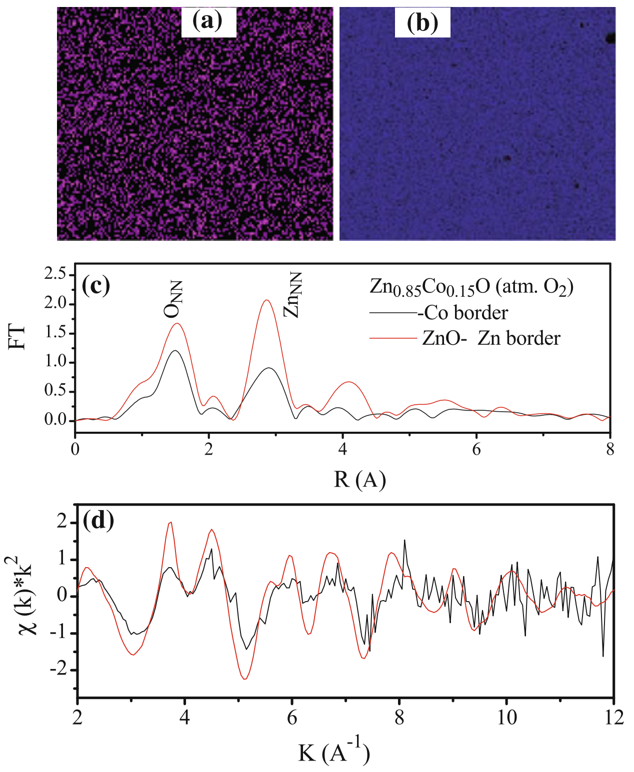

**Fig. 3** Energy dispersive spectroscopy mapping showing the Zn and Co distribution in a same sample using Co $K_\alpha$ in **a** and Zn *L* X-ray lines in **b**. **c**, **d** Fourier transform and EXAFS spectrum of $Zn_{0.85}OCo_{0.15}$ films, respectively

XANES spectra of the doped films (not showed here) have pre-edge and edge onset positions that coincide with Co in CoO. These results indicate that Co in the films is in the 2+ oxidation states. These spectra are also very different from those of the metallic elements, allowing us to rule out the presence of Co metallic precipitates. The Fourier transform of EXAFS spectrum (see Fig. 3c) is qualitatively similar to the corresponding to Zn in ZnO, confirming that Co ions are substituting Zn in the ZnO structure.

*I–V* curves of ZnO thin film doped with 10% Co is shown in Fig. 4. The *I–V* curves were taken at constant temperatures in zero magnetic field and in 10 T. Using these data we can evaluate the magnetoresistance as $MR = (R(H) - R(0))/R(0)$, the results show that the MR is positive and increases when the temperature is decreased. At 50 K the MR reaches 30%. This large positive MR already founded in other DMS [11] and it was explained considering the spin–orbit scattering [12].

Figure 5a shows room temperature SQUID measurements of Co-doped thinner samples. The diamagnetic

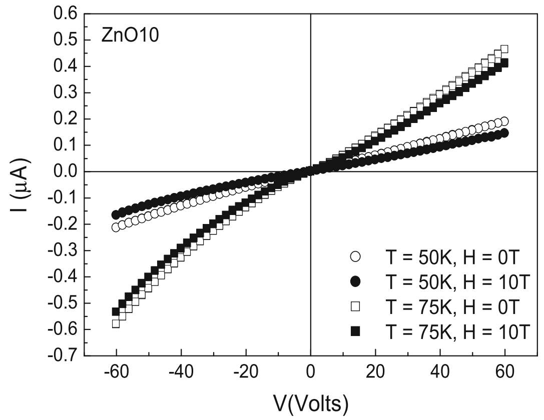

**Fig. 4** *I–V* curves of ZnO thin film doped with 10% Co in zero field and in 10 T

contribution of the substrates has been subtracted. A zoom near the origin is shown in Fig. 5b, we can see that the values of the coercivity are similar for all samples. The thinner samples have similar values of saturation moment with the exception of the 50 nm sample. The *M–H* loop for the non-doped sample is also shown for comparison. In Figure 6, a SQUID loop for representative thicker samples showing the paramagnetic behavior at 5 K for most of them. The magnitude of hysteresis observed in thicker samples is comparable with that measured in thinner samples.

The SQUID data of the thinner and thicker samples was adjusted with a Brillouin function. The only fitting parameter used to normalize the experimental data was the values of the magnetic saturation. The curves fit well for *L* between 1 and 1.3 and for $S = 3/2$ yielding values between $\mu = 4.8\mu_B/\text{Co}$ and $\mu = 5.0\mu_B/\text{Co}$. This result agree with the value expected for Co 2+. However, by taken into account the samples volumes and composition, these results give up a saturation magnetization $\approx 10^{-4}$ emu an order of magnitude larger than the SQUID measurements. The minor values in the measured magnetization could be explained by an antiferromagnetic contribution from grains reach in w–CoO.

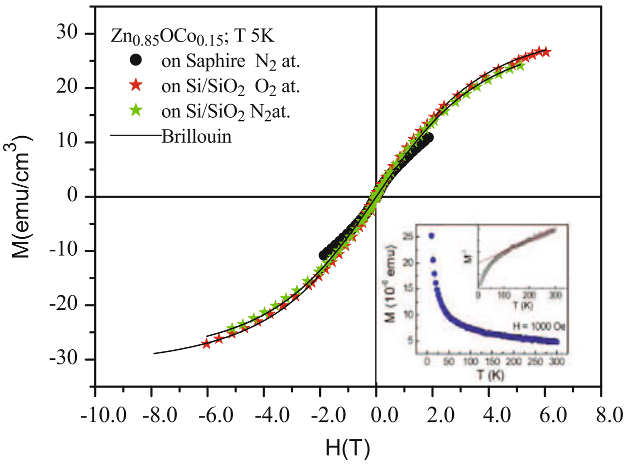

**Fig. 6** *M* vs. *H* loops taken at 5 K for $Zn_{0.85}OCo_{0.15}$ and ZnO films in $O_2$, $N_2$. *Inset M* vs. *T* curve for a $Zn_{0.85}OCo_{0.15}$ film

The negative values of the Curie–Weiss temperature obtained from the extrapolation of the high temperature range of the inverse moment versus temperature, −280K for a thicker film and −166.6 K for a thinner film, indicate the existence of antiferromagnetic interactions, inset of Fig. 6. Considering the XRD results this behavior may be

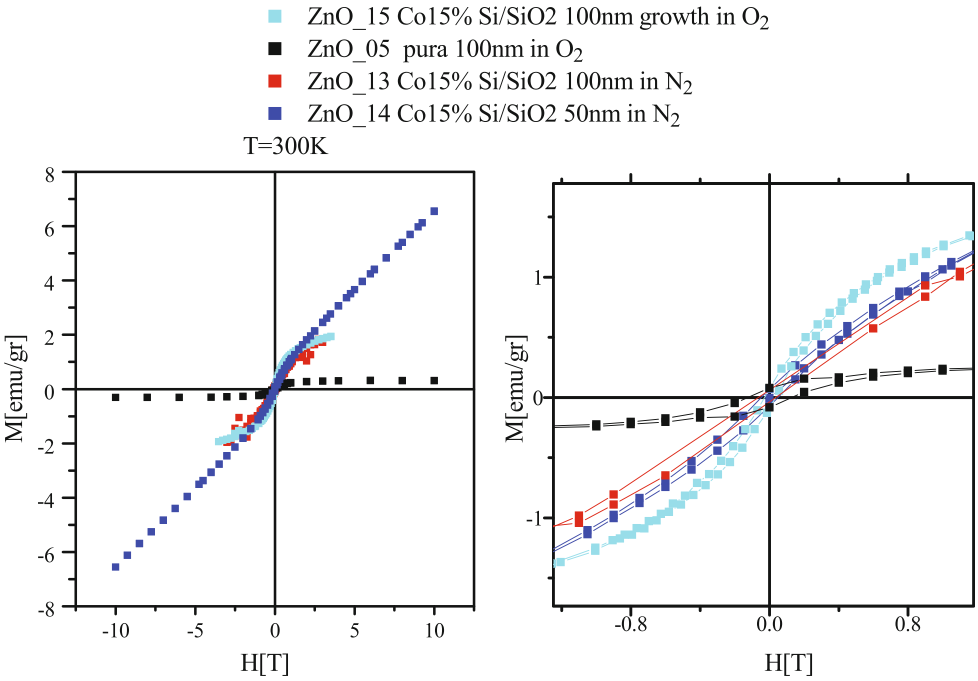

**Fig. 5** *M* vs. *H* loops taken at 300 K for $Zn_{0.85}OCo_{0.15}$ and ZnO films in $O_2$, $N_2$

ascribed to the antiferromagnetism of CoO clusters. On the other side, the possibility of antiferromagnetic exchange of Co clusters in single crystalline ZnO, theoretically and experimentally studied recently by Sati et al. [13], was excluded by the XANES spectroscopy results.

## Conclusion

In this article we suggest an explanation for the origin of the controversial results reported in the literature in polycrystalline Co-doped ZnO films below the limited solubility of Co in ZnO. Structural, magnetic, and magneto-transport measurements reported here suggest that the formation of Co reach clusters, as CoO in its wurzite or cubic structure could be responsible of the interactions in Co:ZnO. We found paramagnetic behavior in all doped samples with a small ferromagnetic contribution in a few samples which origin is difficult to interpret in terms of small amount of impurities or intrinsics defects. This small ferromagnetic signal could be due to the interaction of uncompensated spin at the films surface. The paramagnetic behavior was observed at room temperature down to 5 K. By evaluating our magnetic measurements we reached the conclusion that the Co reach clusters has an antiferromagnetic exchange interaction.

In summary, we present evidence of segregation in Co-doped ZnO and its consequence in magnetic measurements. Considering the system ZnO:Co as an hybrid nanostructure, the possibility to describe the magnetic interaction using the DMS models recently reported [8, 9] is difficult.

**Acknowledgements** This work has been supported by CIUNT under Grants 26/E439, by ANPCyT-PICTR 20770, 35682 and by PROALAR-DAAD DA0805.

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