

# Defect induced ferromagnetism in Co-doped ZnO thin films

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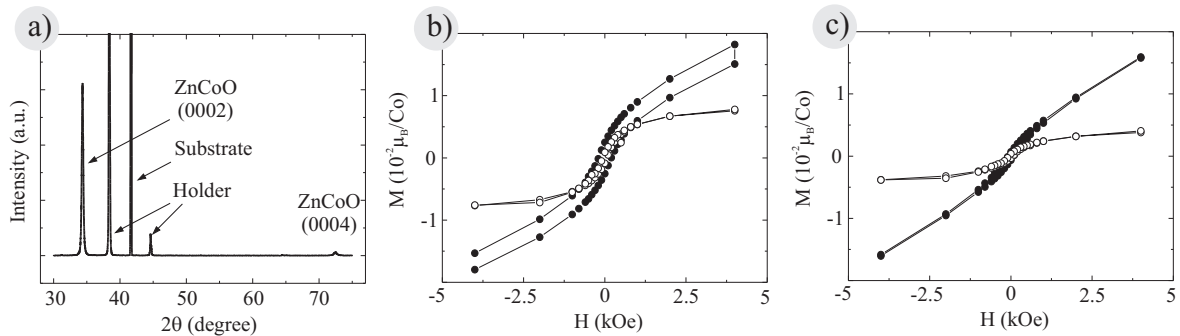
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**Abstract.** We present a study on the structural, magnetic, and optical properties, as well as the electronic structure of Co-doped ZnO films prepared by magnetron sputtering. Magnetization measurements performed at different temperatures indicate ferromagnetic and paramagnetic behavior for the samples prepared at oxygen-poor conditions whereas the samples prepared at oxygen-rich conditions show only paramagnetic behavior corroborating that the presence of oxygen-related defects is essential for ferromagnetism in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ . X-ray absorption spectroscopy (XAS) at the Co  $L_{2,3}$  edge together with optical transmittance measurements show that Co ions are present in the high-spin  $\text{Co}^{2+}$  ( $d^7$ ) state under tetrahedral symmetry indicating a proper incorporation in the ZnO host lattice. Comparison of the O  $K$  edge XAS spectra of the samples prepared at different conditions show substantial changes in the spectral line shape which are attributed to the presence of lattice defects such as oxygen vacancies in the ferromagnetic oxygen-poor Co-doped ZnO samples. Our findings indicate that the ferromagnetic properties of Co-doped ZnO samples are strongly correlated with the presence of oxygen vacancies in the ZnO lattice supporting the spin-split impurity band model.

Diluted magnetic semiconductors (DMS) have become recently the subject of an intensive research because of the potential application in spintronics. Investigations on the DMSs were originally inspired by the discovery of spontaneous low temperature ferromagnetism in Mn-doped GaAs exhibiting a Curie temperature ( $T_C$ ) of about 110 K [1]. Theoretical studies on the basis of Zener's model showed that transition-metal-doped wide-gap semiconductors, among them Mn-doped ZnO, are promising candidates for room temperature (RT) ferromagnetism [2]. This has stimulated numerous experimental works on the preparation of RT ferromagnetic transition-metal-doped ZnO [3]. Ferromagnetism at RT has been found in transition metal doped n-type ZnO [4, 5] while other studies showed only very low magnetic ordering temperatures in  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  [6, 7] or even the absence of ferromagnetism in the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  samples prepared by different techniques [8, 9]. These controversial experimental results give an indication that ferromagnetism in DMS is very sensitive to the preparation method and preparation conditions. Moreover, even magnetic properties of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  samples prepared by the same deposition technique with the same cobalt concentration show a lack of reproducibility.

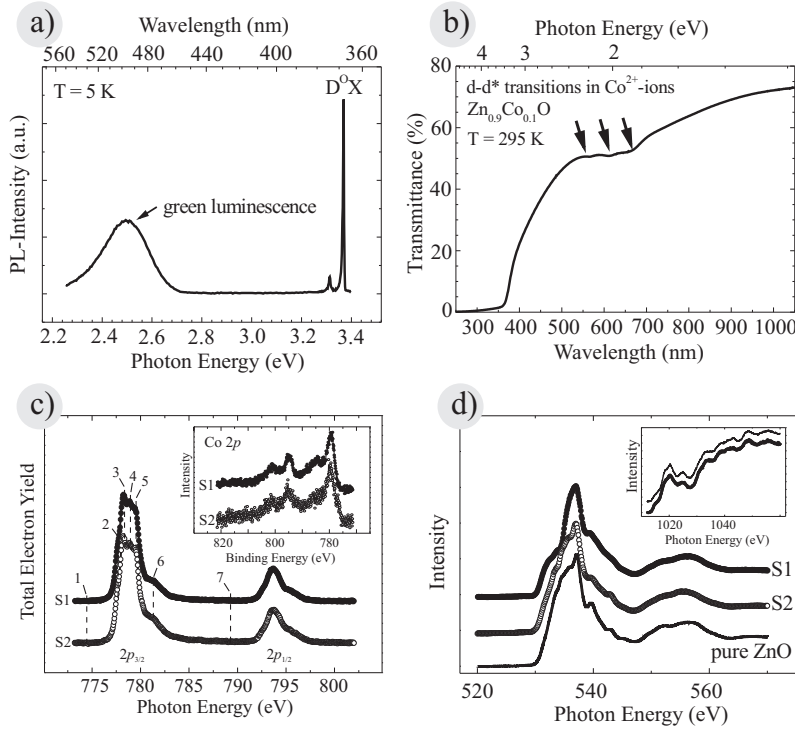
In this study, we report on the investigation of structural, magnetic, optical, and electronic properties of Co-doped ZnO films which indicate that ferromagnetic properties of the samples are strongly correlated with the presence of oxygen defects.  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  ( $x = 0.05$  and  $0.1$ ) thin



**Figure 1.** (a) A typical XRD pattern of a  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  thin film. (b) Magnetization loop of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample *S1* grown in oxygen-poor conditions measured at 5 K (solid circles) and 300 K (open circles). (c) Magnetization loop of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample *S2* grown in oxygen-rich conditions measured at 5 K (solid circles) and 300 K (open circles).

films were prepared by radio-frequency reactive magnetron sputtering of  $[\text{ZnO}(20 \text{ \AA})/\text{Co}(d \text{ \AA})]_{50}$  ( $d = 2$  and  $d = 5$ ) multilayers on  $\text{Al}_2\text{O}_3(0001)$  substrates. Oxygen-poor samples further referred to as *S1* and oxygen-rich samples further referred to as *S2* were prepared by sputtering in a pure Ar atmosphere as well as in an Ar/ $\text{O}_2$  mixture with a ratio of 5:2 at the same deposition pressure of  $3 \times 10^{-3}$  mbar, respectively. The substrate temperature was maintained at  $480^\circ$  during the growth as well as within 2 hours after the growth. Oxygen-rich samples have been additionally heated *ex situ* in oxygen atmosphere at  $600^\circ\text{C}$  and 1 bar for 2 hours. Figure 1 (a) shows a typical XRD pattern of a 120 nm-thick  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  film prepared on  $\text{Al}_2\text{O}_3(0001)$ . Two diffraction peaks were observed at about  $34.4^\circ$  and  $72.4^\circ$  which correspond to the (0002) and (0004) reflections of the hexagonal ZnO wurtzite structure showing the excellent quality of the ZnO films with *c*-axis orientation. Magnetization measurements of two sample sets, *S1* (oxygen-poor) and *S2* (oxygen-rich), were performed as a function of magnetic field  $[M(H)]$ . Fig. 1 (b) shows  $M(H)$  curves of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  film grown in oxygen-poor conditions. A clear hysteresis loop with a coercive field of about 200 Oe can be observed at 5 K. Figure 1 (c) shows the  $M(H)$  curves of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample *S2* grown in oxygen-rich conditions followed by subsequential annealing in  $\text{O}_2$  showing that ferromagnetism in these samples is strongly suppressed or even absent. Thus, a controlled variation of the magnetic behavior of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  samples can be achieved by varying of the oxygen content in preparation conditions.

Photoluminescence (PL) together with the optical transmittance measurements have been performed at the Co-doped ZnO samples in order to investigate the optical properties of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  samples. Fig. 2 (a) shows a photoluminescence spectrum of a  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  sample measured at 5 K. The most intensive luminescence is visible near the band gap region of ZnO at 3.37 eV in agreement with Reynolds *et al.* [10], and is attributed to the neutral-donor-bound-exciton  $\text{D}^0\text{X}$  recombination. A second smaller peak is observed at lower energies, which is possibly due to the donator-acceptor transitions (D,A) [11]. At lower energies, a broad PL band is visible around 2.5 eV. The appearance of the green luminescence can be ascribed to the transitions involving deep-levels within the band gap associated with oxygen vacancies [12, 13, 14]. Fig. 2 (b) shows the optical transmittance spectrum of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample performed at RT. The transmittance increases drastically at the band gap energy around 368 nm corresponding to 3.37 eV. Furthermore, optical absorption lines are visible from 550 to 700 nm, which are attributed to the  $\text{Co}^{2+}$  absorption bands, because the  $3d$  levels are split in



**Figure 2.** Typical photoluminescence (a) and optical transmittance (b) spectra of a  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  sample. (c)  $\text{Co } L_{2,3}$  XAS spectra of the  $S1$  and  $S2$   $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  samples. Inset shows the core-level PES spectra of both samples where  $\text{Co } 2p_{1/2}$  and  $2p_{3/2}$  peaks are visible. (d)  $\text{O } K$  edge XAS spectra of an undoped reference  $\text{ZnO}$  sample (black line), the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample  $S1$  (solid circles), and the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample  $S2$  (open circles). The inset shows a comparison of the  $\text{Zn } L_{2,3}$  edge XAS spectra of pure  $\text{ZnO}$  (black line) and the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample  $S1$  (solid circles).

the crystal field of  $\text{ZnO}$ . These absorption bands correspond to intraionic  $d-d^*$  transitions [15] in tetrahedrally coordinated high-spin  $\text{Co}^{2+}$  ions substituting  $\text{Zn}^{2+}$  sites in the  $\text{ZnO}$  host lattice.

The electronic structure of the  $\text{Co}$ -doped  $\text{ZnO}$  thin films was investigated in detail by means of XAS and PES. Fig. 2 (c) shows XAS spectra of the  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  samples  $S1$  and  $S2$  measured at  $\text{Co } L_{2,3}$  absorption edge. The line shape of XAS spectra from samples  $S1$  and  $S2$  are clearly different from that of the  $\text{Co}$  metal showing the absence of any  $\text{Co}$  clustering which could be expected due to the multilayer growth. Thus these data rules out phase segregation as the source of ferromagnetism in  $\text{Co}$ -doped  $\text{ZnO}$  and point to an intrinsic origin. The observed line shape is similar to that of the previously reported spectra from both ferromagnetic [16] and nonmagnetic [17]  $\text{Co}$ -doped  $\text{ZnO}$  as well as to several atomic multiplet configuration interaction calculations [16, 17] confirming that cobalt ions are present in the high-spin  $\text{Co}^{2+}$  state under tetrahedral coordination indicating a proper incorporation into the  $\text{ZnO}$  host lattice. The inset of Fig. 2 (c) shows  $\text{Co } 2p$  core level PES spectra of both  $S1$  and  $S2$   $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  samples taken at  $h\nu=1000$  eV. The  $\text{Co } 2p$  spectra of both samples are similar to that of  $\text{CoO}$  supporting the presence of  $\text{Co}^{2+}$  ions in the samples.

Additionally we used  $\text{O } K$  edge XAS measurements on both sets of samples ( $S1$  and  $S2$ ) to probe the local structure of  $\text{Co}$ -doped  $\text{ZnO}$  and especially the oxygen-related defects in the  $\text{ZnO}$  host lattice. Figure 2 (d) shows the comparison of  $\text{O } K$  edge XAS spectra from the undoped reference  $\text{ZnO}$  sample, the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample  $S1$ , and the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  sample  $S2$ . The spectral line shape of the  $\text{O } K$  edge agrees well with the XAS spectra obtained from  $\text{ZnO}$  powder [18], PLD grown  $\text{Co}$ -doped  $\text{ZnO}$  [19], and CVD prepared samples [20]. The region between 530 and 538 eV can be attributed to the hybridization between  $\text{O } 2p$  and  $\text{Zn } 4s$  states followed by the region between 539 and 550 eV which is due to the hybridization between  $\text{O } 2p$  and  $\text{Zn } 4p$  states. Above 550 eV the spectrum can be assigned to the hybridization between  $\text{O } 2p$  and  $\text{Zn } 4d$  states. The broadening of the spectral features observed in the  $S1$  sample in comparison with the sample  $S2$  as well as to the undoped reference  $\text{ZnO}$  sample at 537, 540

and 543 eV were recently assigned to the presence of the oxygen vacancies [19] showing that the oxygen-related defect concentration in the sample *S1* is higher than in sample *S2*. Zn  $L_{2,3}$  XAS spectra shown in the inset of Fig. 2 (d) are in agreement with the XAS measurements at ZnO nanorods [21] and crystalline ZnO [22] corroborating that no significant Zn defect related features such as Zn interstitials are present in the samples. The spectroscopic measurements show that oxygen vacancies or oxygen related defects rather dominate than Zn interstitials. In particular, the oxygen vacancies concentration in *S1* samples is higher than in the *S2* samples as well as in the ZnO reference sample confirming that in the presented samples a specific variation of oxygen vacancies was achieved. Moreover, magnetic and spectroscopic data presented here imply that the oxygen vacancies concentration in Co-doped ZnO is strongly correlated with the observed ferromagnetism confirming the central hypothesis of the spin-split impurity band model proposed by Coey *et al.* [3], namely that ferromagnetism depends strongly on the oxygen vacancy constituted bound magnetic polarons.

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