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X-Ray Spectroscopic Investigations of $Zn_{0.94}Co_{0.06}O$ Thin Films

Gillian Mayer[1], Mikhail Fonin[1], Sönke Voss[1], Ulrich Rüdiger[1], and Eberhard Goering[2]

[1]Fachbereich Physik, Universität Konstanz, Konstanz 78457, Germany
[2]Max Planck Institut für Metallforschung, Stuttgart 70569, Germany

We investigated $Zn_{0.94}Co_{0.06}O$ thin films on sapphire (0001) substrates with respect to their structural and magnetic properties. X-ray diffraction shows a c axis oriented growth and no secondary phases within its resolution. A clear improvement of the crystalline quality was obtained by post annealing under vacuum conditions. Further information about the local electronic structure is obtained by X-ray absorption spectroscopy at the Co $L_{2,3}$ and the O K edge. Magnetic properties were investigated with a superconducting quantum interference device (SQUID) and by X-ray magnetic circular dichroism at the Co $L_{2,3}$ edge. Both techniques yield mainly paramagnetic behavior of the samples. For low temperatures, an additional small ferromagnetic contribution was observed in SQUID measurements. Several possible origins of this ferromagnetic contribution are discussed.

Index Terms—**Co-doped ZnO, diluted magnetic semiconductors, XAS, XMCD, ZnO.**

I. Introduction

DURING the last years, diluted magnetic semiconductors attracted considerable attention due to their possible application in spintronic devices, using both spin and charge degrees of freedom of the same material. Especially zinc oxide (ZnO), which has a predicted Curie temperature above room temperature [1], has been studied with a wide range of transition metal dopants, such as Co or Fe. Early results by Ueda *et al.* [2] who observed room temperature (RT) ferromagnetism in Co-doped ZnO films grown by pulsed laser deposition, stimulated further investigations. Nevertheless, the origin of ferromagnetism is still under debate. There are several theoretical models based on different sorts of coupling mechanisms like Zener exchange [1], bound magnetic polarons [3]–[5], and double exchange [6], [7], as well as density functional calculations [8], [9]. However, there are still experimental results that cannot be explained by these works. The interpretation is complicated due to spreading results, as not only ferromagnetism, but also paramagnetism [10], [11] and antiferromagnetism [12] were found. The reports on ferromagnetic behavior range from strong RT ferromagnetism [13]–[15] to weak ferromagnetism only at low temperatures [16], [17]. Several groups even found ferromagnetic behavior with a superconducting quantum interference device (SQUID), while X-ray magnetic circular dichroism (XMCD) showed paramagnetic behavior of the Co atoms [18], [19]. Calculations showing carrier mediated ferromagnetism stimulated experimental work with additional co-doping [20]. Annealing in Zn vapor was found to enhance ferromagnetism dramatically, whereas ferromagnetism vanished with additional annealing in oxygen [21]–[23]. Also, H annealing has a strong influence on the ferromagnetism [24]–[26]. An enhancement of ferromagnetism could also be found in preparation methods with reduced oxygen partial pressure or thermal annealing under vacuum conditions [27], [28]. These controversial results indicate that ferromagnetism in Co-doped ZnO is sensitive to the preparation method and preparation conditions. Even samples prepared by the same deposition technique and the same Co concentration show a lack of reproducibility. In this work, we report the preparation and investigation of structural and magnetic properties of $Zn_{0.94}Co_{0.06}O$ thin films. Mainly paramagnetic behavior of the samples was observed by magnetic measurements with a SQUID magnetometer, as well as by XMCD at the Co $L_{2,3}$ absorption edge at RT. For low temperatures, an additional small ferromagnetic contribution was observed in SQUID measurements. Several possible origins of this ferromagnetic contribution are discussed.

II. Experimental

$Zn_{0.94}Co_{0.06}O$ thin films of 100–200 nm were prepared by radio frequency magnetron sputtering from a composite oxidized ZnCo target (90:10 wt.%). $Al_2O_3(0001)$ single crystals were used as substrates. The sputtering was performed with pure Ar and residual O_2 as sputtering gases at a working pressure of around $3 \cdot 10^{-3}$ mbar. The substrate temperature was kept at 500°C during the deposition. Post annealing was performed under vacuum conditions (10^{-9} mbar) at temperatures ranging from 700 °C to 850 °C to enhance the crystalline quality and to introduce oxygen vacancies, which are expected to enhance ferromagnetism [3]. X-ray diffraction (XRD) was carried out with a Siemens D5000 diffractometer and Cu K_α radiation. $\theta/2\theta$-scans were used to identify the crystal structure, whereas rocking curves around the (002) reflex of $Zn_{0.94}Co_{0.06}O$ gave information about the crystalline quality. The composition of the samples was analyzed with energy dispersive X-ray analysis (EDX), which yields a total Co concentration of 3 at.% in the samples studied. This is less than expected from the target composition. The main reason can be found in the magnetic properties of Co which impede the rf magnetron sputtering process of this element. SQUID measurements were performed using a Quantum Design MPMS XL5 magnetometer. All X-ray absorption (XAS) and XMCD spectra were recorded at the bending magnet beamline PM3 at BESSY II (Berlin) in the surface sensitive total electron yield mode (TEY) with a typical energy resolution of $E/\Delta E = 5000$ and a photon flux at normal incidence geometry. A fast switching superconducting magnet system was used to flip the external magnetic field at each energy data point

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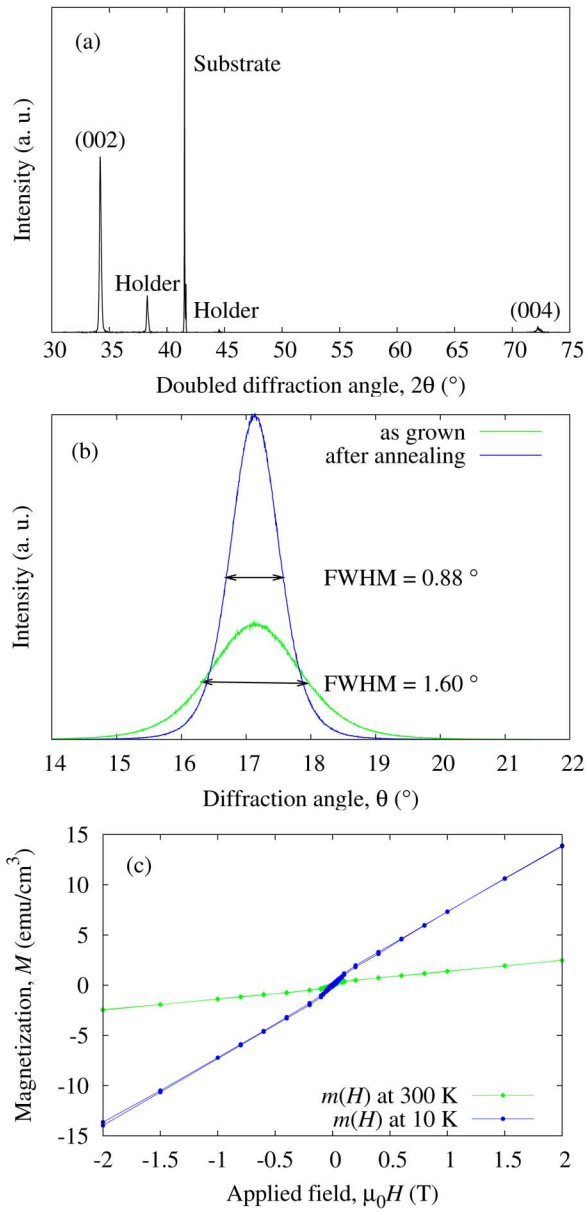

Fig. 1. (a) XRD scan of $Zn_{0.94}Co_{0.06}O$ after annealing under vacuum conditions. Beside the (002) and (004) reflexes of c axis oriented $Zn_{0.94}Co_{0.06}O$, reflexes of the substrate and the sample holder (Al) can be observed. (b) Rocking curve around the (002) reflex of $Zn_{0.94}Co_{0.06}O$ before (green) and after (blue) annealing under vacuum conditions. A clear improvement of the crystalline quality can be seen. (c) SQUID measurement of $Zn_{0.94}Co_{0.06}O$ at 300 K (green) and 10 K (blue). The contribution is mainly paramagnetic with a small ferromagnetic superposition at low temperature.

within 6 s to obtain a very high signal-to-noise XMCD level, which allows the investigation of paramagnetic and diluted transition metal ions. The maximum external field that could be applied was ± 2 T.

III. Results

Fig. 1(a) shows an XRD $\theta/2\theta$-scan of $Zn_{0.94}Co_{0.06}O$ on $Al_2O_3(0001)$ after annealing under vacuum conditions for 2 h at 700 °C and further 30 min at 850 °C. Besides the $Zn_{0.94}Co_{0.06}O$ reflexes at $2\theta = 34.0°(002)$ and $2\theta = 71.9°(004)$, two reflexes of the Al sample holder and one reflex of the substrate can be seen. The ZnO reflexes are typical for c axis oriented growth in the wurtzite structure. Annealing clearly improved the crystalline quality, as shown in Fig. 1(b). Comparing a rocking curve at 34° of the as grown sample (green) with the annealed sample of Fig. 1(a) (blue), the intensity rises remarkably and the full width at half maximum (FWHM) is reduced from 1.60° to 0.88°. Within the resolution of XRD, no secondary phases can be found.

Fig. 1(c) shows SQUID measurements of $Zn_{0.94}Co_{0.06}O$ at 300 K (green) and 10 K (blue). The sample was annealed for 3 h at 750 °C under vacuum conditions, not only to improve the crystalline quality but also to introduce oxygen vacancies which are expected to mediate ferrromagnetic coupling between the Co atoms [3]. Nevertheless, the SQUID measurements show mainly paramagnetic behavior, which means linear dependence of the applied field, especially at 300 K. At low temperature, the paramagnetic signal is superimposed by a small ferromagnetic contribution (nonlinearity in the paramagnetic behavior). A significant opening of a hysteresis cannot be observed. The ferromagnetic contribution can have several origins besides the possibility of a diluted magnetic semicondutor, which is discussed below.

In our earlier investigations, strong ferromagnetic behavior of the $Al_2O_3(0001)$ single crystals after annealing under vacuum conditions was found [29]. In order to minimize the substrate contribution to the ferromagnetic signal of the sample, one reference substrate was treated in the same way as the samples, but without the sputter deposition of $Zn_{0.94}Co_{0.06}O$, and measured by SQUID magnetometry. A clear ferromagnetic signal was found (not shown). This measurement was subtracted from the sample measurement. The resulting data is shown in Fig. 1(c). The pure substrate and the sample substrate are not absolutely identical and also systematic errors can occur in SQUID measurements. So, although the influence of the substrate was minimized by the reference measurements, it cannot be excluded completely, that the observed small ferromagnetic contribution is not due to the influence of the substrate. However, the ferromagnetic contribution can also result from intrinsic properties of the film. Besides the state of a diluted magnetic semiconductor (Co diluted in ZnO and coupling ferromagnetically), a surface effect as found by Martín-Gonzáles *et al.* [30] might be possible and has still to be investigated. Even oxygen vacancies as source of the ferromagnetism [31] and not as mediators of the coupling between the Co atoms [3] are conceivable. Mixed valence states of Co or Co clusters in the surface region can be ruled out, as we find only Co^{2+} in the $3d^7$ high spin state tetrahedrally coordinated by oxygen atoms in surface sensitive XAS measurements in TEY mode [32] (see below).

Fig. 2(a) shows XAS measurements of $Zn_{0.94}Co_{0.06}O$ at the Co $L_{2,3}$ edge at RT in an external field of ± 2 T. The sample equals that of the SQUID measurements in Fig. 1(c) and, thus, was also annealed for 3 h under vacuum conditions at 750 °C. The XAS measurements were taken for parallel (SOUTH) and antiparallel (NORTH) alignment between the sample magnetization and the photon beam direction, to be able to evaluate the XMCD signal, resulting from a subtraction of the two spectra (NORTH–SOUTH). The shape of the TEY XAS spectra is quite

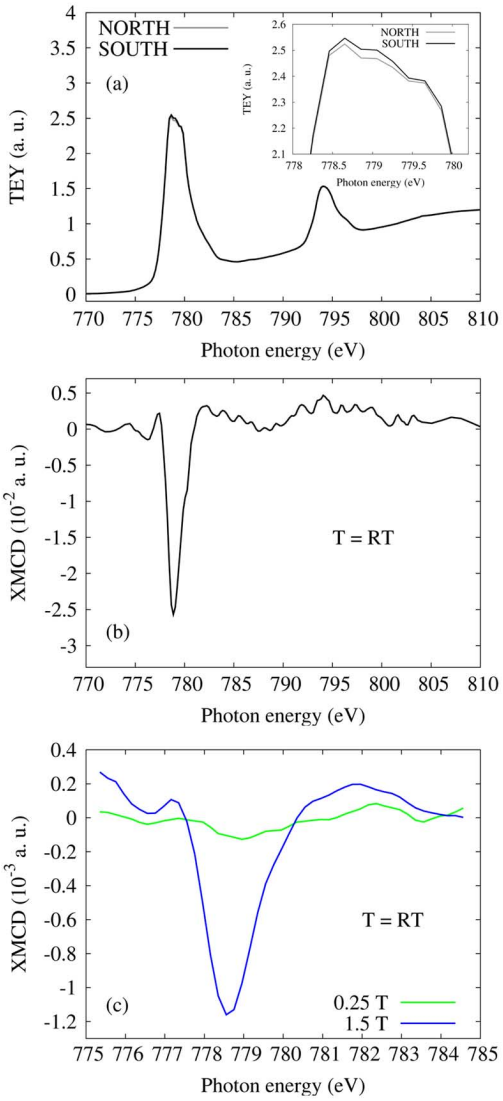

Fig. 2. (a) XAS spectra of $Zn_{0.94}Co_{0.06}O$ at the Co $L_{2,3}$ edge at RT for two opposite magnetic field directions (NORTH and SOUTH). The resulting spectra fit well with those of [32] showing the incorporation of Co as Co^{2+}, substituting Zn at its lattice sites. (b) XMCD spectrum at RT resulting from (a). A clear dichroic signal at the Co L_3 edge can be seen. (c) XMCD spectra at the Co L_3 edge for external fields of 0.25 T (green) and 1.5 T (blue) at RT, showing that the XMCD spectra rises with rising external field.

different from those of pure Co and, thus, Co clusters in the surface region can be excluded as the origin of the small ferromagnetic contribution. However, to prove that Co clusters are also absent in deeper sample regions total fluoresence measurements are needed. The XAS spectra show a fine structure at the Co L_3 edge at 779 eV, typical for Co incorporated as Co^{2+} [32] substituting Zn at its lattice sites and, thus, being present in the $3d^7$ high spin configuration. This fine structure and the difference in the both spectra can better be seen in the inset of Fig. 2(a), which shows an enlargement of the Co L_3 edge. The signal obtained for NORTH magnetic field orientation is slightly smaller than that for SOUTH. The dichroic signal becomes obvious in Fig. 2(b), where the difference between NORTH and SOUTH direction is plotted. A clear negative signal can be seen at the Co L_3 edge at 779 eV and a slight positive signal can be observed

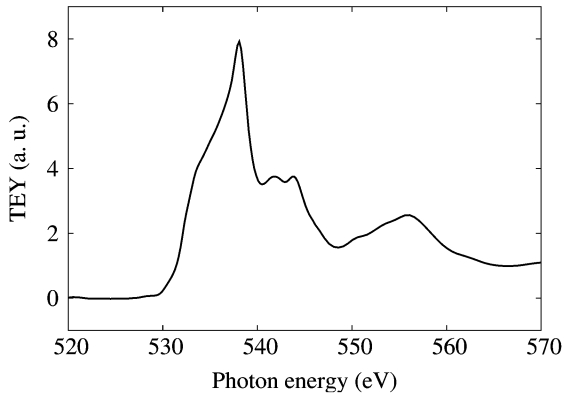

Fig. 3. XAS spectrum of $Zn_{0.94}Co_{0.06}O$ at the O K edge at RT. The spectrum agrees well with those from undoped ZnO [33].

at the Co L_2 edge at 794 eV. The high-frequency modulation of the XMCD signal is due to charging. Fig. 2(c) shows XMCD spectra of the same $Zn_{0.94}Co_{0.06}O$ sample at the Co L_3 edge at RT for two different magnetic fields strengths. The spectrum at 1.5 T (blue) looks similar to 2 T spectrum, a clear dichroic signal is visible at 779 eV. In contrast, the spectrum at 0.25 T (green) is nearly flat and no XMCD signal can be found. Hence, Co atoms contribute only paramagnetically to the magnetism of the sample. In case of ferromagnetic behavior a dichroic signal should be observable even at low magnetic fields. A similar behavior was found by Gacic *et al.* [18] and Barla *et al.* [19] with the only difference that those samples showed stronger ferromagnetic behavior in the SQUID measurements.

Fig. 3 shows an XAS spectrum of $Zn_{0.94}Co_{0.06}O$ at the O K edge at RT. This sample was also annealed at 750°C for 3 h under vacuum conditions. The spectrum agrees well with those from Krishnamurthy *et al.* [33] and Chang *et al.* [34] measured at undoped ZnO. No visible change of the spectral features between 530 and 544 eV due to the presence of oxygen vacancies [16], [33], [34] can be observed, which leads to the conclusion that an effective introduction of oxygen vacancies has not been achieved. XMCD measurements by Tietze *et al.* [31] also showed that oxygen itself is not the origin of ferromagnetism in Co-doped ZnO.

IV. Conclusion

In conclusion, we prepared $Zn_{0.94}Co_{0.06}O$ by radio frequency magnetron sputtering. XRD measurements showed a c axis oriented growth and an improvement of the crystalline quality by postannealing under vacuum conditions. Magnetization measurements at 300 K as well as at 10 K revealed a mainly paramagnetic behavior of the samples. Only for low temperature a small ferromagnetic contribution was observed. XAS measurements at the Co $L_{2,3}$ edge show that Co is incorporated as Co^{2+} in the $3d^7$ high spin state, substituting Zn at its lattice sites. XMCD measurements at the same absorption edge show the presence of only paramagnetic Co. XAS spectra at the O K edge are close to those of undoped ZnO. Thus, we suggest that a small number of oxygen vacancies, which do not show up in XAS measurements, or the Al_2O_3 substrate are possible sources of the ferromagnetic contribution measured by SQUID.

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Manuscript received March 03, 2008. Current version published December 17, 2008. Corresponding author: G. Mayer (e-mail: gillian.mayer@uni-konstanz.de).