

Spin manipulation in Co-doped ZnO

Heidemarie Schmidt^{1,a}

¹Forschungszentrum Dresden-Rossendorf e.V., Bautzner Landstrasse 400, 01328 Dresden, Germany

^aHeidemarie.Schmidt@fzd.de

Keywords: magnetic ZnO, n-type conducting, s-d exchange coupling, spin-splitting conduction band, magnetotransport

Abstract. The magnetoresistance of n-type conducting, paramagnetic Co-doped ZnO films prepared by pulsed laser deposition on sapphire substrates has been studied experimentally and theoretically. Positive magnetoresistance (MR) of 124% has been observed in the film with the lowest electron concentration of $8.3 \cdot 10^{17} \text{ cm}^{-3}$, while only a negative MR of -1.9% was observed in the film with an electron concentration of $9.9 \cdot 10^{19} \text{ cm}^{-3}$ at 5 K. The positive MR is attributed to the quantum correction on the conductivity due to the *s-d* exchange interaction induced spin splitting of the conduction band. The negative MR is attributed to the magnetic field suppressed weak localization [1]. Voltage control of the electron concentration in Schottky diodes revealed a drastic change of the magnetoresistance and demonstrated the electrically controllable magnetotransport behavior in Co-doped ZnO [2]. The magnetically controllable spin polarization in Co-doped ZnO has been demonstrated at 5 K in magnetic tunnel junctions with Co-doped ZnO as a bottom electrode and Co as a top electrode [3]. There spin-polarized electrons were injected from Co-doped ZnO to a crystallized Al_2O_3 layer and tunnelled through an amorphous Al_2O_3 barrier. Our studies demonstrate the spin polarization and manipulation in Co-doped ZnO.

Introduction. Spintronics is related to the manipulation of spins. It mainly consists of three processes, spin generation, spin transportation, and spin detection. Diluted magnetic ZnO can be realized by epitaxial growth on transparent substrates using pulsed laser deposition (PLD). A ferromagnetic coupling of the magnetic moments localized at cation lattice sites has been theoretically predicted for p-type conducting ZnO doped with magnetic ions [4]. However, typically 1 μm thick magnetic ZnO films are intrinsically n-type conducting or insulating and contain up to 10 at.% magnetic ions being isovalently incorporated on cation lattice sites. The magnetic properties of ZnO depend on the hybridization between the magnetic ions or intrinsic defects and the charge carriers at the Fermi edge, thus they depend on the thin film growth conditions. Weak ferromagnetism has been probed in insulating Mn-doped ZnO thin films, in n-type conducting, partially compensated Mn-doped ZnO thin films and in n-type conducting, partially compensated ZnO thin films without magnetic ions. Space charge spectroscopy has been used to reveal acceptor-like defects in the n-type conducting, partially compensated, ferromagnetic thin films, i.e. acceptor-like defects mediate the weak ferromagnetism probed in Mn-doped ZnO. The capture cross section of deep traps for charge carriers is smaller in magnetic films compared to unmagnetic ones. Energetically deep lying defects in ZnO follow the Meyer-Neldel rule, which describes the entropy change during charging of deep electron defects, with the isokinetic temperature amounting to 226 K [5]. X-ray magnetic circular dichroism measurements at 30 K confirmed the paramagnetic properties of Co-doped ZnO films [6]. Magnetoresistance changes in n-type conducting, magnetic ZnO films with different magnetic species and concentrations of free charge carriers have been systematically investigated as a function of an external magnetic field with regard to future applications in magnetoresistive ZnO-based spintronics devices. Especially, at the metal-insulator transition, which has been determined to lie at $n_c = 4.9 \times 10^{19} \text{ cm}^{-3}$ in ZnO thin films [7], the magnetoresistance can be sensitively controlled. Modelling the positive magnetoresistance in ZnO:Co thin films being superimposed by a weak negative magnetoresistance was possible for the

strong ($n < n_c$) and weak ($n > n_c$) localization regime [1]. In this paper we will focus on the spin-splitting of the conduction band due to sd-exchange interaction between free charge carriers and localized magnetic moments, the electrically controllable magnetoresistance and magnetically controllable spin polarization in Co-doped ZnO thin films, Schottky diodes and magnetic tunnel junctions, respectively.

Experimental Results and Discussion. Magnetotransport measurements in the classical van-der-Pauw geometry represent a fast and precise method for investigating conducting, magnetic thin films. In n- or p-conducting ZnO the s-(3d,4f) or p-(3d,4f) exchange interaction, respectively, leads to spin polarization and may cause positive magnetoresistance. We modeled the corresponding spin polarization from the magnetotransport data. However, because of different mechanisms influencing the magnetotransport properties, superimposed positive and negative magnetoresistance may be observed in dependence on temperature and magnetic field strength. An advanced magnetotransport modelling approach should combine different mechanisms for example magnetic polarons and electron localization causing negative magnetoresistance and s-d and s-f induced spin splitting of the conduction band causing positive magnetoresistance in magnetic, n-type conducting ZnO films.

Spin-splitting of the Conduction Band. We modeled the spin polarization in ZnO:Co and ZnO:Mn from the decrease of positive magnetoresistance with the free electron concentration [8]. Positive magnetoresistance has been interpreted in terms of the influence of the sd-exchange interaction on the disorder-modified electron-electron interactions [9, 10] and may be attributed to magnetic scattering of spin polarized free electrons. The electron concentration of spin up \uparrow or spin down \downarrow electrons can be calculated by:

$$\int_{E_c}^{\infty} \frac{2\pi}{h^3} (2m^*)^{\frac{3}{2}} E^{\frac{1}{2}} (1 + \exp((E - E_f)/k_B T))^{-1} dE, \quad (1)$$

where m^* is the effective mass of electrons, E_f the Fermi energy, E_c is the bottom of the spin up \uparrow or spin down \downarrow conduction band, respectively, and k_B the Boltzmann constant. Due to the splitting of the conduction band, there is an energy gap δ between the spin-up and spin-down polarized conduction band (Fig. 1a). The position of the Fermi level E_f was adjusted to obtain the electron concentration n , which equals $n_{\uparrow} + n_{\downarrow}$.

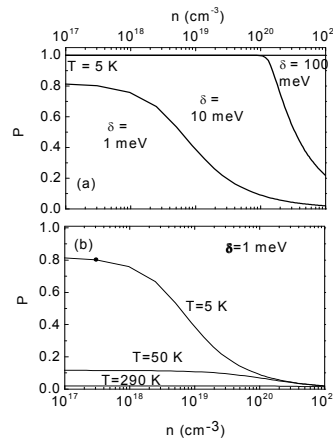


Fig. 1 (a) Simulated spin polarization P in dependence on the electron concentration n at 5 K for different conduction band splittings δ and (b) at different temperatures for $\delta = 1 \text{ meV}$. We use $m^* = 0.24 m_0$ as the effective electron mass in ZnO. The modelling has been performed under the assumption that the free electron model is valid for n ranging from 10^{17} to 10^{20} cm^{-3} [8].

There exists no experimentally determined value for the conduction band splitting δ in magnetic ZnO and we use 1, 10, and 100 meV as initial values for modelling the spin polarization P (Fig. 1(a)). P is defined by $(n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$. For $\delta = 100$ meV, P is nearly independent on n . For $\delta = 10$ meV, P keeps 1 for $n < 10^{20} \text{ cm}^{-3}$ and drops with n increasing above 10^{20} cm^{-3} . For $\delta = 1$ meV, P continuously decreases with increasing n and almost drops to zero for $n > 10^{20} \text{ cm}^{-3}$. By comparing the dependence of the simulated spin polarization P and of the measured positive magnetoresistance on temperature and electron concentration, we determined a splitting of the conduction band E_c in ZnO:Co and ZnO:Mn below 10 meV [8].

Electrically Controllable Magnetoresistance. Diluted magnetic semiconductors provide the capability of controlling the charge and spin of the charge carriers simultaneously. The clear understanding of the magnetotransport properties of DMS in an external magnetic and electric field is important for future spintronics applications. A $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ film with low electron concentration (about $1.5 \times 10^{17} \text{ cm}^{-3}$ at 21 K) on a highly conducting $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ layer has been deposited on an *a*-plane sapphire substrate by PLD [2]. To study the magnetoresistance of depleted, highly insulating Co-doped ZnO an Au ohmic contact and a Pd Schottky contact were deposited on the $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ and $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ layer, respectively. Positive magnetoresistance of 30 % with a current of 10^{-6} A was observed at 5 K (Fig. 2). The positive MR decreases drastically at 5 K and changes to negative MR at 50 K with increasing current, which is considered to be due to the bias voltage control of the electron concentration in the $\text{Zn}_{0.96}\text{Co}_{0.04}\text{O}$ layer. The concentration of free electrons in the undepleted Co-doped ZnO has been measured by capacitance-voltage measurements and amounts to $1.5 \times 10^{17} \text{ cm}^{-3}$ at 21 K. The concentration of remaining free electrons in the depleted Co-doped ZnO has been estimated to be about $3 \times 10^{13} \text{ cm}^{-3}$ from the correspondingly measured resistivity (about $90 \text{ } \Omega \cdot \text{m}$ measured at 5 K with $1 \text{ } \mu\text{A}$) and using the electron mobility in Co-doped ZnO [7].

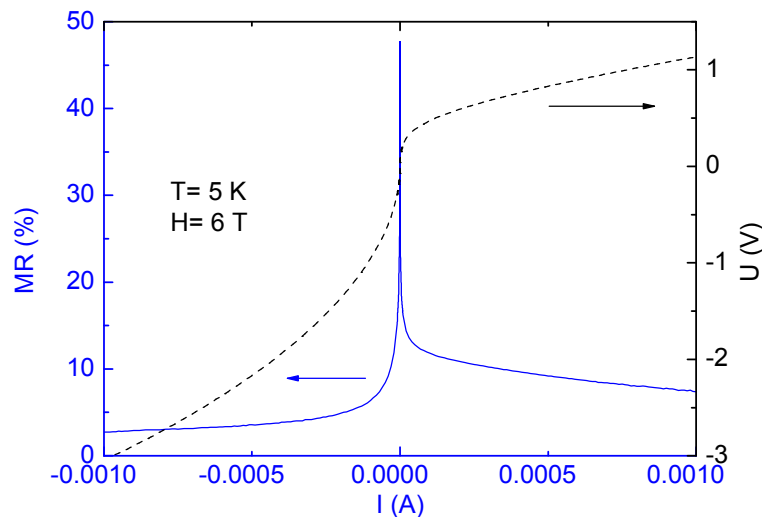


Fig. 2 The current dependent MR (solid line) and the IV characteristics (dashed line) measured at 5 K and 6 T.

This work demonstrates the electrically controllable magnetotransport behavior in Co-doped ZnO Schottky diodes due to the electrically controllable electron concentration n and the dependence of the magnetoresistance in Co-doped ZnO on n [2].

Magnetically Controllable Magnetoresistance. Future developments will also tackle the exploitation of magnetic oxides in magnetic random access memory (MRAM) devices based on

tunnel magnetoresistance (TMR) structures where the magnetization can be switched by an external magnetic field. The magnetically controllable spin polarization in Co-doped ZnO has been demonstrated at 5 K in magnetic tunnel junctions with Co-doped ZnO as a bottom electrode and Co as a top electrode on a nonconducting substrate [3]. Before depositing the Co-doped ZnO bottom electrode, we deposited an Al-doped ZnO layer as a buffer layer on the sapphire substrate. At low field the small negative magnetoresistance (MR) of the bottom electrode (not shown here) might originate from the Al-doped ZnO [9]. However, the deposition parameters of Co-doped ZnO were chosen to prepare the highly conductive film, which will also lead to the low field negative MR [7]. The positive MR at intermediate field and negative MR at high fields originate from the Co-doped ZnO [7]. In our junction structure, the current will then go perpendicular to the film through the Al_2O_3 barrier layer to the Co top electrode. The mainly interesting phenomenon is the low field butterfly positive MR behaviour, as shown in Fig. 3. Contradicted to the normally observed TMR effect, double peaks have been observed in each swept curve which are located at both sides of 0 T. As one can see, with increasing applying current, the MR effect becomes weaker, which is typical TMR effect [11]. With applying 1 μA , the butterfly positive MR disappears, and the junction was broken, and no butterfly positive MR at low field can be observed as shown in Fig. 2(d). After the application of 1 μA , no butterfly positive MR at low field can be observed with smaller current. As an example the first ZnO-based TMR structure revealing magnetic field switching is shown in Fig. 3.

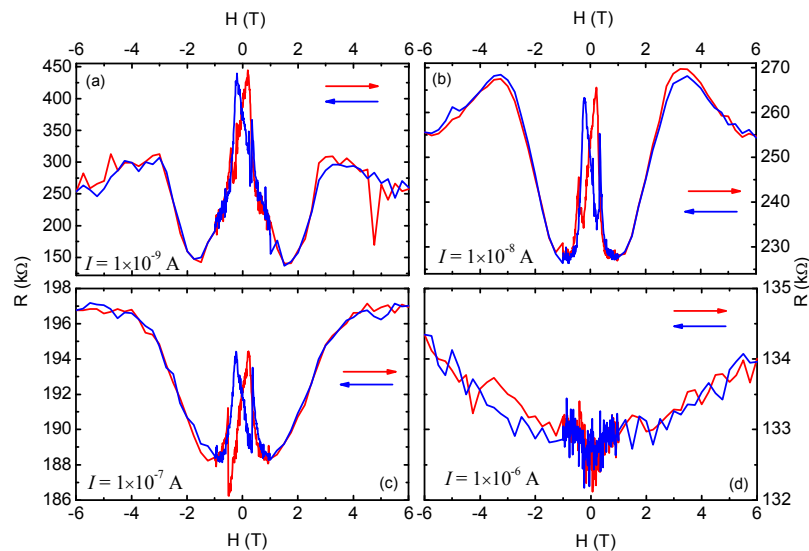


Fig. 3 Field dependent resistance of the TMR sample (ZnCoO bottom electrode, crystalline/amorphous Al_2O_3 barrier, Co top electrode) measured at 5 K with field applied in the film plane with the higher voltage applied on the Co top electrode and lower voltage on the ZnO bottom electrode for different constant currents. The applied constant current is (a) 1×10^{-9} A, (b) 1×10^{-8} A, (c) 1×10^{-7} A, (d) 1×10^{-6} A. The arrows show the field sweep direction, from -6 T to 6 T (red) and from 6 T to -6 T (blue) [3].

The MR curves at high field ($H > 1$ T) are very similar to the MR curves probed on ZnCoO thin films. The low field butterfly positive MR behavior reveals double peaks located at both sides of 0 T with the lower peak at the starting field and the higher peak at the end field for each sweep direction. When applying a current of 1 μA the junction was destroyed and the butterfly positive MR disappears [3]. Note that novel MRAM devices based on TMR structures reveal current-induced switching of magnetization.

Summary and outlook. Insulating and n-type conducting, diluted magnetic ZnO films have been prepared by pulsed laser deposition and the electric and magnetic controllability of magnetoresistance has been demonstrated. The magnetotransport properties of magnetic ZnO depend on the species and concentration of magnetic ions, the concentration of free charge carriers and the film thickness. The large positive magnetoresistance in n-type conducting ZnCoO is attributed to the quantum correction on the conductivity due to the sd-exchange interaction induced spin-splitting of the conduction band. The sd-exchange induced splitting of the conduction band being proportional to the exchange coupling constant α is less than 10 meV. By comparing the exchange coupling constants α and β in II-VI compound semiconductors it is expected that the pd-exchange interaction induced splitting of the valence band being proportional to the exchange coupling constant β is larger than 30 meV, thus producing a finite spin polarization in p-type conducting, magnetic ZnO even above room temperature. Room temperature ferromagnetism in diluted magnetic ZnO could pave the way to exploit the spin in addition to charge in future ZnO-based spinelectronics devices. Because Co ions are isovalent dopants in ZnO, additional acceptor dopants have to be added, e.g. by implantation, and electrically activated by pulsed laser annealing under oxygen overpressure, otherwise oxygen tends to evaporate from the ZnO surface. Therefore, the incorporation of acceptor dopants above their solubility limit is the main challenge for the fabrication of ferromagnetic ZnO. Because Co and Mn shows a very low diffusivity in ZnO over the entire temperature range, from a thermodynamical point of view p-type conducting Co- and Mn-doped ZnO spintronics devices will be stable enough for room temperature applications [12]. The thermodynamic stability of laser annealed p-type conducting magnetic semiconductors has already been proven by the hysteretic magnetotransport of spin-polarized holes in accordance with magnetization below the Curie temperature in Mn-doped Ge [13] and in Mn-doped GaAs [14].

References

- [1] Q. Xu, L. Hartmann, H. Schmidt, H. Hochmuth, M. Lorenz, D. Spemann and M. Grundmann, Phys. Rev. B 76 (2007), p. 134417
- [2] Q. Xu, S. Zhou, D. Bürger, H. Hochmuth, M. Lorenz, M. Grundmann and H. Schmidt, Jpn. J. of Appl. Phys. 49 (2010), p. 043002
- [3] Q. Xu, L. Hartmann, S. Zhou, A. Mücklich, M. Helm, G. Biehne, H. Hochmuth, M. Lorenz, M. Grundmann and H. Schmidt, Phys. Rev. Lett. 101 (2008), p. 076601
- [4] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Science 287 (2000), p. 1019
- [5] H. Schmidt, M. Wiebe, B. Dittes, M. Grundmann, Appl. Phys. Lett. 91 (2007), p. 232110
- [6] Q. Xu, S. Zhou, D. Marko, K. Potzger J. Fassbender, M. Vinnichenko, M. Helm, H. Hochmuth, M. Lorenz, M. Grundmann, H. Schmidt, J. of Phys. D: Appl. Phys. 42 (2009), p. 085001
- [7] Q. Xu, L. Hartmann, H. Schmidt, H. Hochmuth, M. Lorenz, R. Schmidt-Grund, C. Sturm, D. Spemann, M. Grundmann, Phys. Rev. B 73 (2006), p. 205342
- [8] Q. Xu, L. Hartmann, H. Schmidt, H. Hochmuth, M. Lorenz, R. Schmidt-Grund, C. Sturm, D. Spemann, M. Grundmann, Y. Liu, J. Appl. Phys. 101 (2007), p. 063918
- [9] T. Fukumura, Zhengwu Jin, A. Ohtomo, H. Koinuma, M. Kawasaki, Appl. Phys. Lett. 75 (1999), p. 3366

-
- [10] T. Andrearczyk, J. Jaroszyński, G. Grabecki, T. Dietl, T. Fukumura, M. Kawasaki, Phys. Rev. B 72 (2005), p. 121309(R)
- [11] J. S. Moodera, Lisa R. Kinder, Terrilyn M. Wong, R. Meservey, Phys. Rev. Lett. 74 (1995) p. 3273
- [12] D. Bürger, M. Seeger, S. Zhou, I. Skorupa, M. Helm, H. Schmidt, *submitted*.
- [13] S. Zhou, D. Bürger, C. Baumgart, W. Skorupa, C. Timm, P. Oesterlin, M. Helm, H. Schmidt, Phys. Rev. B 81 (2010), p. 165204
- [14] D. Bürger, S. Zhou, M. Pandey, C.S. Viswanadham, J. Grenzer, O. Roshchupkina, W. Anwand, H. Reuther, V. Gottschalch, M. Helm, H. Schmidt, Phys. Rev. B 81 (2010), p. 115202