Magnetoresistance of Co-doped ZnO thin films

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Longitudinal, transverse, and perpendicular magnetoresistances were investigated at temperatures $1.2 < T < 300$ K in fields of up to 20 T for four ZnO films: one undoped, two with 4% Co (one paramagnetic, the other exhibiting anhysteretic ferromagnetism at room temperature), and one with 25% Co which exhibits hysteretic ferromagnetism, butterfly magnetoresistance, and presence of Co clusters. The magnetoresistance becomes negligibly small above 50–100 K, and magnetic terms are only evident below 20 K, where the mobility is sufficiently high. Quantum oscillations observed below 2 K in the paramagnetic sample with 4% Co give two different extremal Fermi surface cross sections. The data for dilute ferromagnetic samples are consistent with coherent spin transport in a ferromagnetic matrix; data for the $x=25\%$ films suggest that spin-polarized electrons can tunnel coherently between well-separated cobalt clusters. © 2006 American Institute of Physics.

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Much interest has been sparked by the discovery of ferromagnetism in a range of transparent oxides doped with a few percent of transition metal cations.¹ The ferromagnetism in these compounds is not an intrinsic bulk property.² Ferromagnetism appears only in thin films and nanocrystalline samples prepared in conditions promoting extended solid solubility.³ In some cases, transition metal clustering has been identified as the origin of ferromagnetic behavior.⁴ Homogeneous dopant distributions in bulk samples and in some thin film samples give rise to paramagnetism.¹

The low temperature magnetoresistance of $\text{Zn}_{1-x}\text{Co}_x\text{O}:\text{Al}$ ($x < 0.05$) has been studied by Jin *et al.*^{5,6} and subdivided into a negative contribution close to zero field, attributed to weak electron localization effects, a positive contribution due to a field dependence of the Thomas-Fermi radius, and a negative term due to the decrease of spin disorder at higher fields. Negative and predominantly isotropic magnetoresistance is often reported in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x < 0.3$), combined with a “Kondo-like” minimum in the resistivity and absence of anomalous Hall effect.⁷ A model has been advanced and illustrated for the case of $\text{Zn}_{1-x}\text{Mn}_x\text{O}:\text{Al}$ ($x = 0.03$ and $x = 0.07$), based on the $\mathbf{k} \cdot \mathbf{p}$ approach including spin-orbit coupling and s - d exchange interactions.⁸ Ferromagnetism or superparamagnetism found in inhomogeneous Co–ZnO magnetic semiconductor multilayers^{9,10} is accompanied by “butterflylike” magnetoresistance curves at low temperatures, attributed to spin-dependent hopping.

Here we report the magnetoresistance of Co-doped ZnO, including data up to 20 T. Four samples have been studied, one with $x=0$, two with $x=0.04$ prepared in different conditions, and one with $x=0.25$. All samples were prepared by pulsed laser deposition on sapphire substrates maintained at 450 or 600 °C. We find that there is a narrow process win-

dow of substrate temperature around 450 °C where films on c -cut Al_2O_3 exhibit ferromagnetism. They all show 001 texture with $a=0.316$ nm and $c=0.524$ nm. The film thickness is 80–100 nm. The films with $x=0.25$ and one of the two with $x=0.04$ are ferromagnetic with Curie temperatures well above room temperature and moments of $0.5\mu_B/\text{Co}$ and $0.1\mu_B/\text{Co}$, respectively. The other film with $x=0.04$ is paramagnetic. Co metal clusters were detected by x-ray diffraction (XRD) in the sample with $x=0.25$, with an average size of 18 ± 1 nm, while clusters were not resolved in the films with $x=0.04$ prepared and measured in the same conditions. Four times thicker films, analogous to the ones used in the present study, but with $x=0.05$, were found to contain a detectable by XRD concentration of Co metal clusters with an average size of 7 ± 1 nm. Therefore, no perfect substitution is expected for the Co ions, even in the films with $x=0.04$. Judging from recent experimental data,¹¹ the blocking temperature can be expected to be above room temperature, already for Co clusters with an average size of 3.5 nm. The oxidation state of Co in films with $x < 0.05$, analogous to the ones used in the present study, was found to be 2+.¹² The samples were measured either in the van der Pauw geometry or as patterned by wet-etching Hall bars. Contacts were made by thermal evaporation of Al/Au bilayer.

Resistivity curves for undoped and Co-doped ZnO films are shown in the insert of Fig. 1(b). The samples are near-degenerate semiconductors with a small temperature-dependent activation energy. Only below about 20 K is there much sign of carrier freeze-out. Hall effect measurements give a carrier density $> 10^{26} \text{ m}^{-3}$.

Magnetoresistance curves for the $x=25\%$ film show a butterfly curve (Fig. 1), which corresponds to the 200 mT hysteresis observed in the magnetization curve at the same temperature. A set of magnetoresistance for undoped, oxygen-deficient ZnO are shown as a function of tempera-

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FIG. 1. (Color online) (a) Butterfly magnetoresistance of a $(\text{Zn}_{0.75}\text{Co}_{0.25})\text{O}$ sample measured at 4.2 K. The electrical hysteresis corresponds to the ferromagnetic hysteresis loop. The insert shows the temperature dependence of the resistivity of this and the other ZnO thin films.

ture in Fig. 2 for fields of up to 5 T. A small, negative magnetoresistance is apparent below 20 K. A complete set of data on the ferromagnetic sample with $x=0.04$ is shown in Fig. 3.

In order to make sense of these data, we consider the known sources of magnetoresistance in semiconductors as follows.

(i) A classical positive magnetoresistance which arises in a two-band model from the action of the Lorentz force on the mobile carriers. For carriers in closed orbits, this term is of the form $\Delta\rho_{\text{CO}}/\rho_0 = aH^2/(b^2 + cH^2)$, where a, b , and c are parameters dependent on the carrier partial conductivities $\sigma_{1,2}$ and signed mobilities $\beta_{1,2}$ such as $a = \sigma_1\sigma_2(\beta_1 - \beta_2)^2$, $b = \sigma_1 + \sigma_2$, and $c = (\beta_1\sigma_1 + \beta_2\sigma_2)^2$. It is quadratic in low fields, and it saturates in high fields.

(ii) The corresponding term for open orbits, for which the magnetoresistance is quadratic and nonsaturating: $\Delta\rho_{\text{OO}}/\rho_0 = dH^2$.

(iii) A negative term due to spin-flip scattering from singly occupied localized states with $s=1/2$. The term $\Delta\rho_{\text{LS}}/\rho_0 = \cosh(H/f)^{-1} - 1$, where $f = k_B T / g\mu_B$ is quadratic in low fields.¹³

(iv) A negative term due to scattering from a paramagnetic or ferromagnetic moment, which varies as M^2 such as $\Delta\rho_{\text{MS}}/\rho_0 = hM(H)^2$, where h is the dimensionless coefficient

FIG. 2. (Color online) Magnetoresistance of an undoped, substoichiometric ZnO sample at different temperatures. The magnetoresistance is predominantly due to scattering from localized states with $s=1/2$.

FIG. 3. (Color online) Perpendicular (a), longitudinal (b), and transverse magnetoresistances (c) of a ferromagnetic $(\text{Zn}_{0.96}\text{Co}_{0.04})\text{O}$ film as a function of temperature (from top to bottom: 1.8, 2.5, 3.5, 5.0, 7.0, 10, 14, and 20 K). The solid lines in panel (a) are fits to the data using the contributions (i)–(iv) described in the text. The contributions (i) and (iii) are the dominant ones.

that depends on the strength of the s - d scattering in the system. The magnetoresistance due to magnetic inclusions is expected to have similar magnetization dependence.

Apart from the four terms contributing to the magnetoresistance, already discussed, there are two other effects worth mentioning. One is the anisotropic magnetoresistance (AMR) effect, commonly associated with the presence of substantial d -band splitting and spin-orbit coupling in transition metals and alloys (see, for example, Ref. 14). In this case the magnetoresistance ratio is a function of the angle θ , between the current and the magnetization of the sample (measured in the film plane for thin films), and for polycrystalline samples has the form $\Delta\rho_{\text{AMR}}/\rho_0 = A \cos^2 \theta$, where A is a constant dependent on the density of d -like states at the Fermi level, sample quality, temperature, etc. Anisotropic magnetoresistance coefficients A larger than 0.1 were observed in the sample with $x=0.04$ at low temperature (below 20 K), which can be a sign of the significant presence of d -like states at the Fermi level in this system.

Another possible magnetoresistance term is associated

with the weak localization phenomenon commonly observed in thin disordered metal films (see, for example, Ref. 15). The maximal theoretical correction to the resistivity is of the order of $(1/2)(\hbar/e^2)(2\pi)^2 L_m$ for the three dimensional (3D) case or $(1/2)(\hbar/e^2)(2\pi)t$ for the two dimensional (2D) case, where $L_m = \sqrt{e/\hbar B}$ is the magnetic length and t is the film thickness. Both expressions yield resistivity change of about $10^{-3} \Omega \text{ m}$ for film thickness of 80 nm or magnetic field of 1 T, which is of the order of the magnetoresistive changes observed in the present study. Details in the low-field (below about 3 T) magnetoresistance and AMR can give information about the spin-spin and spin-orbit characteristic scattering times, but are the subject of a separate publication.

Data on the paramagnetic 4% sample are shown in Fig. 4(a) (top). These extend to 20 T, and a good fit of the 3.5 K curve is obtained with the four terms. The main contributions are (i) and (iii). From the fit to the expression for the scattering from singly occupied localized states, we find $\mu_0 f = 4.5 \text{ T}$, which corresponds to a moment of $1.1 \pm 0.1 \mu_B$, as expected. This confirms the origin of the negative magnetoresistance mechanism in the paramagnetic samples.

On lowering the temperature to 1.2 K, Shubnikov-de Haas oscillations appear in the magnetoresistance. Two series can be resolved, with periods in $1/B$ of 0.30 T^{-1} and 0.05 T^{-1} . The corresponding extremal areas of the Fermi surface are 3.2×10^{16} and $1.9 \times 10^{17} \text{ m}^{-2}$.

The ferromagnetic sample with $x=0.04$ is of poorer crystalline quality, and no quantum oscillations were observed at low temperatures. Data obtained for $x=0.25$ at 2 K are included in Fig. 4(b) (bottom).

The data for dilute ferromagnetic samples are consistent with coherent spin transport in a ferromagnetic matrix. The anhysteretic magnetic sample with $x=0.04$ shows signs of magnetic scattering (small negative magnetoresistance contribution) in low fields [Fig. 3(b)]. The ferromagnetism here may be of the “wandering axis” or “random anisotropy” variety, with a short spin coherence length in zero applied field. Data for the $x=25\%$ films suggest that spin-polarized electrons can tunnel coherently between well-separated cobalt clusters, which account for some of the cobalt in these materials.

The mobility in all the present ferromagnetic samples is rather small (of order $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and it decreases rapidly with increasing temperature. As a result, the magnetic term (iv) in the magnetoresistance is small, and the anomalous Hall effect is practically unmeasurable. In other words, s - d scattering is not dominant in this system.

In conclusion, our results suggest that codoping with Al will not improve the magnetoresistance. Co doping that creates deep traps will only exacerbate the scattering. This might be done by controlling the defects entailed by oxygen substoichiometry to give small, but highly mobile carrier concentrations. If these defects are responsible in some essential way for the ferromagnetism, prospects for useful magnetoresistive functionality may be dim.

FIG. 4. (Color online) (a) (Top) High-field magnetoresistance of paramagnetic and ferromagnetic $(\text{Zn}_{0.96}\text{Co}_{0.04})\text{O}$ films at 3.4 K [the line is a fit to the data using (i)–(iv)]. (b) (Top) Angular dependence for the same sample. (a) (Bottom) The magnetoresistance of the paramagnetic film at 1.3 K, showing Shubnikov-de Haas oscillations of the resistance. (b) (Bottom) Magnetoresistance for the $(\text{Zn}_{0.75}\text{Co}_{0.25})\text{O}$ film.

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