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Magnetotransport properties of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ films

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Abstract

$Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ films have been prepared on a-plane sapphire substrates by pulsed laser deposition. Paramagnetism mainly caused by Mn^{2+} ions was observed in the films from room temperature down to 2 K. Magnetotransport properties (magnetoresistance (MR) and Hall effect) were studied from 5 K to 290 K up to a field of 6 T. Negative MR was observed at temperature above 100 K. Low field positive MR and high field negative MR was observed at 5 K. Clear anomalous Hall effect with a kink at low field was observed below 20 K, indicating that there exist two different scattering mechanisms for the Mn^{2+} and Cu^{2+} ions.

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Keywords: Diluted magnetic semiconductor; Magnetoresistance; Anomalous Hall effect; ZnO

1. Introduction

Diluted magnetic semiconductors (DMS) have attracted much research attention for their potential applications in spintronics by combining the ferromagnetic and semiconducting properties in a hybrid material. Till now the main obstacle for the application of DMS is the realization of room temperature ferromagnetism. Room temperature ferromagnetism has been theoretically predicted for p-type conducting Mn-doped ZnO [1]. However, till now the realization of p-type conducting ZnO is still a challenge. Most works focus on 3d transition metal (TM) doped, n-type conducting ZnO. Cu dopants may be used as additional acceptor impurities in intrinsically n-type conducting ZnO. For example, Cu seems to mediate room temperature ferromagnetism in Fe-doped ZnO:Cu [2]. In this paper, we study the magnetization and magnetotransport in Mn and Cu codoped ZnO, paramagnetism and anomalous Hall effect (AHE) were observed.

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2. Experimental details

Mn and Cu codoped ZnO films have been grown on 10×10 mm^2 a-plane sapphire substrates from a $Zn_{94.5}Mn_5Al_{0.25}Cu_{0.25}O_{100}$ target by pulsed laser deposition (PLD) using a KrF excimer laser [3]. The Al was added to the target to make the film conductive for the magnetotransport measurement. The temperature of the substrate holder was about 720 °C. The distance between the PLD target and substrate was 10 cm, and the oxygen partial pressure during the deposition was 0.01 Pa. The film thickness was controlled by the number of the laser pulses with an energy density on the target of 2 J cm^{-2} and afterwards measured by spectroscopic ellipsometry in the energy range of 1–4 eV [4]. The depth distribution of each element was studied by the secondary neutral mass spectroscopy (SNMS). The exact composition was $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ as determined by combined Rutherford Backscattering Spectrometry and Particle Induced X-ray Emission measurements. Due to the influence of the underlying Al_2O_3 substrate, the Al content could not be accurately determined. The crystal structure of the films was characterized by X-ray diffraction (XRD) with θ–2θ scans using Cu K_α radiation. A superconducting quantum interference device (SQUID) was used to measure the sample magnetization. The magnetoresistance

(MR) and Hall effect were measured with the magnetic field applied parallel to the c-axis of the films (perpendicular to film surface) in the van der Pauw configuration. Fields up to 6 T were applied over the temperature range from 5 K to 290 K.

3. Results and discussions

Fig. 1 shows the θ–2θ XRD pattern of a $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film of 594 nm thick. The weak (002) ZnO K_β peak at about 31° arises from the not complete filtering of the primary X-ray in the used diffractometer (Cu K_β). No additional peaks related to the impurity phase within the detection limit of the used Philips X'Pert diffractometer were observed, indicating that the Mn and Cu ions substitute for Zn on Zn sites without changing the wurtzite structure. Only (002) and (004) peaks of wurtzite ZnO were observed, indicating that the films are highly c oriented. The (110) peak of the a-plane sapphire substrate was used as an internal standard. The c lattice constant of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ amounts to 5.226 Å, which is larger than that of undoped ZnO amounting to 5.209 Å. The c-axis lattice constant of Mn-doped ZnO increases monotonously with increasing Mn content [5]. However, the c lattice constant of Cu-doped ZnO decreases monotonously with increasing Cu content [6]. The larger Mn content compared to the Cu content causes the slight increase of the c lattice constant of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$.

The magnetic properties of the $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film were studied by SQUID measurements from 2 K to 300 K with the magnetic field applied parallel to the film plane. Since the sapphire substrate might be weak ferromagnetic [7], the substrate magnetization was measured separately. Ar^+ sputtering was used to remove the deposited film. The magnetization of the film was obtained by subtracting the substrate magnetization from the SQUID data obtained with the film. Fig. 2 shows the depth dependent distribution profile of Zn, Mn, Cu, and Al by SNMS taken simultaneously during the Ar^+ sputtering. It can be seen that the depth resolved Cu distribution is significantly nonuniform. Cu tends to accumulate at the film surface. The depth profile of Mn distribution is similar to that of Zn, indicating that Mn ions were uniformly distributed in the film. The M–H curves at 5, 10 and 20 K are shown in Fig. 3(a) The M–H curves without hysteresis indicate paramagnetic behaviour of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$. Fig. 3(b) shows the M–T curve with the temperature ranging from 2 K to 300 K in a field of 0.1 T. The inset of Fig. 3(b) shows the magnetic susceptibility χ vs. $1/T$. Here χ is defined as M divided by a field of 0.1 T. The linear relationship between χ and $1/T$ indicates that the magnetization of the sample follows Curie's law, which further demonstrates the paramagnetic properties of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$.

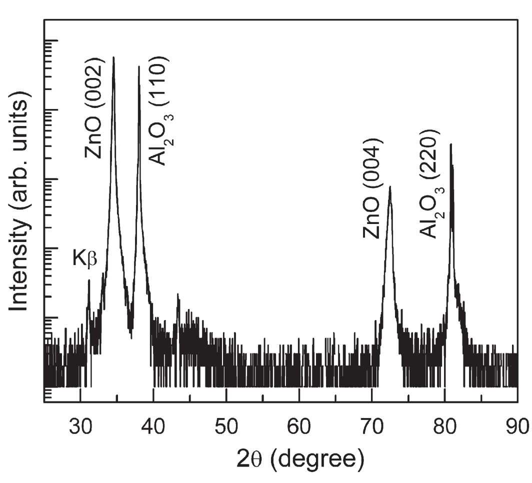

Fig. 1. XRD patterns of a $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film with a thickness of 594 nm. The intensity is shown on a logarithmic scale. At about 31° the weak K_β peak is ZnO (002) peak arising from the not complete filtering of the primary X-ray in the used diffractometer (Cu K_β).

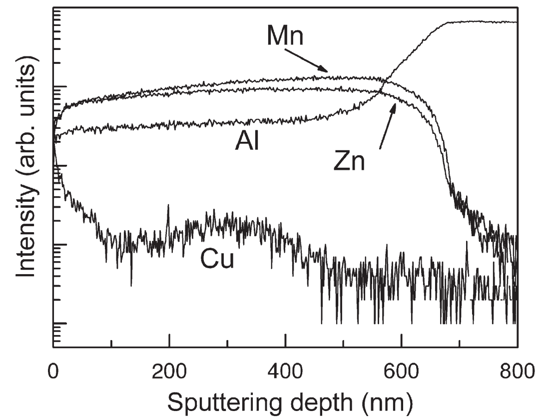

Fig. 2. SNMS depth profile of the isotope intensities of the $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ thin film on sapphire substrate, assuming a constant sputtering rate.

For paramagnetic materials, the field dependence of magnetization will follow the Brillouin function $B_j(\alpha)$ with j being the angular momentum and α defined by $\alpha = g\mu_B H/k_B T$ in the case one has single, independent multiplets, each one with equally spaced energy levels. Mn^{2+} has 5d electrons, thus $j=5/2$, and Cu^{2+} has 9d electrons, thus $j=1/2$. To understand the contribution of Mn^{2+} and Cu^{2+} to the magnetization of the film, the simulated magnetization curve at 5 K, 10 K and 20 K by considering appropriate amounts of either Mn^{2+} or Cu^{2+}, and the fitting curves are shown in Fig. 3(c). All the simulated results are normalized by the respective temperature dependent experimental magnetization at 6 T. It can be clearly seen that the calculated data from Mn^{2+} fits the experimental magnetization data very well, while the calculated magnetization from Cu^{2+} deviates from the experimental data. The calculation indicates that the magnetization of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ is mainly due to Mn^{2+}.

MR was measured at different temperatures and determined using $MR=[R(H)-R(0)]\times 100/R(0)$. Fig. 4(a) shows isothermal MR data of a $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film. At 5 K, positive MR at low field (<2 T) and negative MR at higher field (>2 T) were observed. At 20 K, only positive MR was observed below 6 T. At 50 K, the MR changed to negative at low field. With increasing temperature above 100 K, only a small negative MR was observed. The positive MR in 3d TM doped ZnO is attributed to disorder-modified electron interaction influenced by the spin-splitting of the conduction band by the s–d exchange interaction [8–10]. For Cu-doped ZnO, only negative

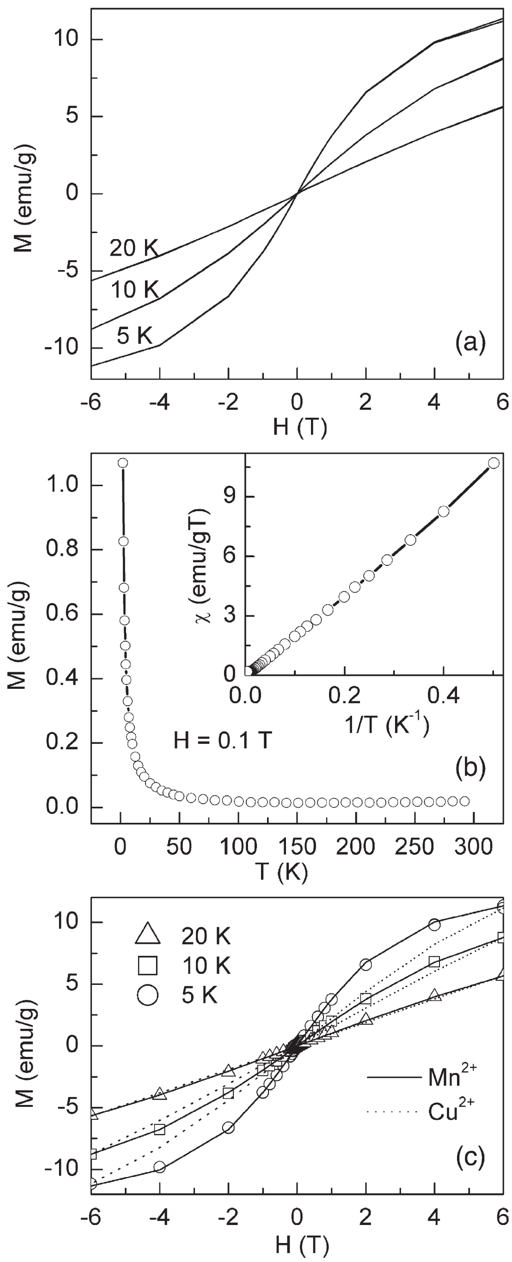

Fig. 3. (a) The magnetization vs. field curves for the $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film from Fig. 1 measured at 5 K, 10 K, and 20 K. (b) The magnetization vs. temperature curve for the $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film from Fig. 1 measured in field of 0.1 T. The inset shows the susceptibility χ vs. $1/T$ curve, here $\chi = M/0.1$ T. (c) The experimental magnetization of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ at 5 K (open circle), 10 K (open square) and 20 K (open triangle). The solid and dashed lines are the magnetization calculated by the corresponding Brillouin function for Mn^{2+} and Cu^{2+} at 5 K, 10 K and 20 K, respectively. The simulated results are normalized to the experimental magnetization at 6 T at each temperature.

MR has been observed even at 5 K [11]. The MR behaviour of $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ is similar to Mn-doped ZnO films [12], indicating that the Mn^{2+} ions mainly determine the magneto-transport behaviour. The high field negative MR may come from the magnetic scattering of conduction electrons by isolated Mn ions, and Cu ions [13].

We probed the Hall voltage at different temperatures. Hall resistivity is the sum of the ordinary and anomalous Hall term being proportional to magnetic induction B and magnetization M, respectively. The anomalous Hall resistivity ρ_{xy} can be obtained by subtracting the ordinary Hall term from the Hall resistivity [14]. AHE has been observed in ferromagnetic [15] and superparamagnetic [16] materials. The ordinary Hall term shows that the film is n-type conducting, which is due to the PLD target containing 0.25 at.% Al and to the growth in oxygen atmosphere. The field dependence of ρ_{xy} is shown in Fig. 4(b). The data were obtained by calculating $\rho_{xy} = [\rho_{xy}(H) - \rho_{xy}(-H)]/2$ in order to eliminate any magnetic field effects which are an even function of field H, i. e., MR. In first approximation we expect a proportionality between the AHE and the magnetization of the sample, thus the shape of the AHE curve should mirror the magnetization curve. However, for $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ with Brillouin function like magnetization (Fig. 3(a)), the AHE curve has a positive slope at low field and negative slope at higher fields at temperatures below 20 K. Thus below 20 K the magnetization probed by AHE (Fig. 4(b)) differs from the magnetization probed by SQUID (Fig. 3(a)). The anomalous Hall term is conventionally attributed to asymmetric scattering processes involving a spin-orbit interaction between the conduction electrons and the magnetic moments in the material [14]. Though the film is paramagnetic (Fig. 3), the d spins of the Mn^{2+} and Cu^{2+} scatter the conducting electrons, leading to the observed AHE. We attribute this AHE behaviour to the different temperature dependent

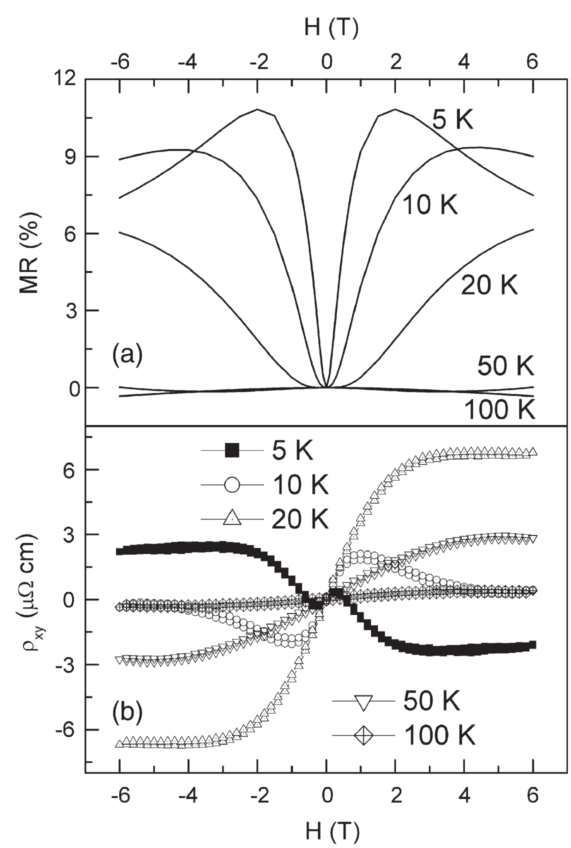

Fig. 4. (a) The field dependent MR curves for $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film measured at 5 K, 10 K, 20 K, 50 K, and 100 K. (b) The field dependent anomalous Hall resistivity curves for $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ film after the subtraction of the ordinary Hall term measured at 5 K, 10 K, 20 K, 50 K, and 100 K.

scattering of the conducting electrons by Mn^{2+} and Cu^{2+}. The component of the AHE with negative slope decreases with increasing temperature much faster than that with positive slope. Above 20 K, only the component with positive slope remains and the conventional s-shape AHE curve is observed, vanishing above 100 K. We have studied the Hall effect in n-type conducting Mn-doped ZnO film prepared under oxygen atmosphere, and no AHE was observed in the whole measuring temperature range from 5 K to 290 K. This indicates that the codoped Cu^{2+} plays a role in the asymmetric scattering processes. More experimental and theoretical work is needed to clarify the interaction between Mn^{2+} and Cu^{2+}, which may help the realization of ferromagnetism in 3d TM doped ZnO.

4. Summary

In summary, $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$ films have been prepared on a-plane sapphire substrates by PLD. Down to 2 K only paramagnetism was observed in $Zn_{90}Mn_{7.5}Cu_{2.5}O_{100}$. Low field positive MR and high field negative MR was observed at 5 K, and only negative MR was observed for temperatures above 100 K. An anomalous Hall effect with a kink at low field indicates that the scattering of conducting electrons by Mn^{2+} and Cu^{2+} is separate. The interaction between Mn^{2+} and Cu^{2+} ions needs further study, which may help the realization of ferromagnetism in 3d TM doped ZnO.

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