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Optical and magneto-optical properties of ZnMnO and ZnMnFeO single crystals and thin films

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Single crystals of oxide diluted magnetic semiconductor $Zn_{1-x}Mn_xO$ have been grown by chemical vapour transport and thin films of $Zn_{1-x}Mn_xO$, $Zn_{1-x-y}Mn_xFe_yO$ have been deposited by pulsed laser ablation and rf magnetron sputtering methods. Optical absorption spectra of the obtained crystals and films have features associated with band-to-band direct type transitions and d–d crystal-field transitions due to presence of Mn^{2+} ions. The observed peculiarities of the Faraday rotation for $Zn_{1-x}Mn_xO$ crystals and films suggest of paramagnetic behaviour. In contrast, $Zn_{1-x-y}Mn_xFe_yO$ film samples exhibit ferromagnetic-like behaviour which is confirmed on typical magnetic field dependence of the Faraday rotation at room temperature.

1 Introduction

At present there is a growing interest to diluted magnetic semiconductors (DMS) containing transition metals or rare earth elements. Special attention is devoted to DMS which can exhibit room temperature ferromagnetism due to their possible applications in spintronic devices. Among many candidates of ferromagnetic semiconductors zinc oxide ZnO doped with transition elements became especially popular for theoretical and experimental studies. First, Dietl et al. [1] theoretically predicted room temperature ferromagnetism in ZnO doped with 5% Mn ions. Wang et al. [2] by using first principle calculations based on the density functional theory and generalized gradient approximation show that the ground state of Mn doped ZnO thin films can change from antiferromagnetic to ferromagnetic when codoped with N. However, experimental results on magnetism in ZnO based DMS are rather controversial. In fact, these results can be divided on two parts. While one part of publications confirms ferromagnetism, in the second part it is not confirmed experimentally. For example, Jung et al. [3] found ferromagnetism in $Zn_{1-x}Mn_xO$ epitaxial films with Curie temperature of 45 K. Sharma et al. [4] revealed ferromagnetism in $Zn_{1-x}Mn_xO$ films with Mn content $x = 0.02$ at room temperature. Confirmation for ferromagnetic behaviour of Mn-doped ZnO was also reported by Kim et al. [5], Diaconu et al. [6], Zhang et al. [7], Mofor et al. [8], Joseph et al. [9], and Liu et al. [10]. On the other hand, Kolesnik et al. [11], Kane et al. [12], and Alaria et al. [13] showed a typical paramagnetic Curie–Weiss behaviour without indication of ferromagnetism. It should be mentioned that high temperature ferromagnetism in ZnO was observed after codoping of Mn with Sn [14, 15]. An important point in understanding of ferromagnetism is to elucidate whether the magnetism is originated from the substitutional dopant on cation sites or from formation of a secondary phase. Obviously for spintronic purposes one needs confirmation for carrier mediated ferromagnetism. In our previous works [16, 17] paramagnetic behaviour of $Zn_{1-x}Mn_xO$ single crystals and thin

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films has been observed. In the present work we include to study new DMS material $Zn_{1-x-y}Mn_xFe_yO$. We report here on ferromagnetism for such DMS films.

2 Experimental details

Bulk $Zn_{1-x}Mn_xO$ crystals with content of Mn $0 < x < 0.1$ were grown by the chemical vapour transport method. One part of the quartz ampoule coated by carbon was filled with mixture of ZnO and Mn_3O_4 powder and kept at temperature of 1050 °C. The opposite side of the ampoule has been kept at 1010 °C. High purity (5N) carbon rods were served as a transport agent. Growth time was about 120 hours. The dimensions of the grown crystals were about 10 mm^3 and their colour varied from yellow to orange.

The deposition of $Zn_{1-x}Mn_xO$ films with $x = 0.1$ was performed by pulsed laser ablation technique. In this method a XeCl excimer laser ($\lambda = 308$ nm, $\tau = 30$ ns) with fluence of (7–10) J/cm^2 was used. The films with a thickness of (500–900) nm were deposited on sapphire substrates at (300–360) °C. The targets in form of ceramic pellets were fabricated by mixing the appropriate amount of ZnO and Mn_3O_4 powders.

For deposition of new quaternary $Zn_{1-x-y}Mn_xFe_yO$ films on glass substrate the method of rf magnetron sputtering has been used. The targets for such kind of deposition were prepared in similar way by mixing ZnO, Mn_3O_4, and Fe_2O_3 oxide powders.

The crystal structure of the grown crystals and films was studied by X-ray diffraction (XRD) measurements using a Cu K_α radiation. Optical transmission, absorption and magneto-optical Faraday rotation were measured on a set-up with a grating monochromator for wavelengths (200–2200) nm, photomultiplier tube and a water-cooled electromagnet which provides magnetic field up to $B = 5$ T.

3 Results and discussion

Structural analysis was realized by XRD spectra which show (002) and (004) peaks of wurtzite structure for the obtained single crystalline and film samples [17]. No Mn or Fe separate phases have been found during structural studies.

Figure 1 shows high photon energy part of the absorption spectra of $Zn_{0.9}Mn_{0.1}O$ thin film at two different temperatures. One can see weakly temperature dependent near band gap absorption edge together with broad absorption band at 3.15 eV, which is absent for undoped ZnO film. In fact, the energy position of this peak for different samples (with different content of Mn) varied from 2.85 to 3.20 eV. This absorption peak is associated with transitions between multiplets of 3d^5 configuration of the Mn^{2+} ions. According to the calculations in framework of the cluster model [18] the ground state of the Mn^{2+} ions is $^6A_1$. The estimated d–d transitions from $^6A_1$ to one of the lowest excited terms $^4A_1$ corresponds to ener-

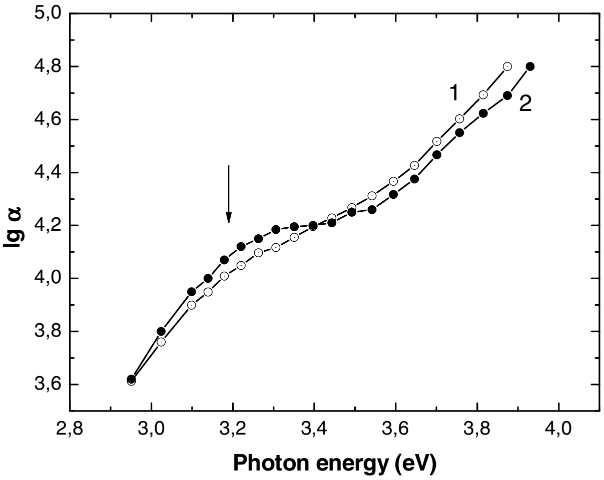

Fig. 1 Absorption spectra of $Zn_{0.9}Mn_{0.1}O$ film at different temperatures (the curves 1 and 2 correspond to 300 and 80 K, respectively).

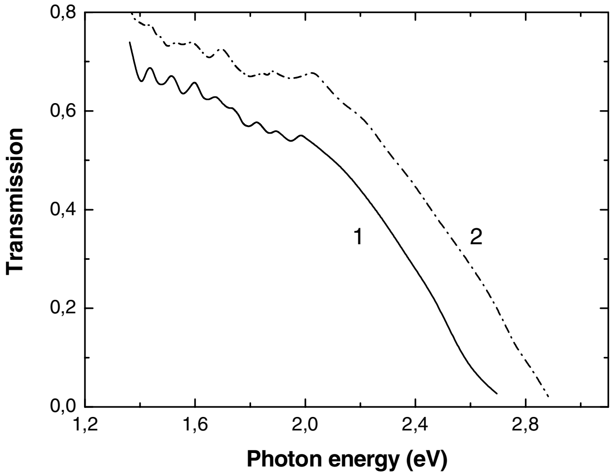

Fig. 2 Transmission spectra of $Zn_{0.98}Mn_{0.02}O$ (curve 1) and $Zn_{0.88}Mn_{0.05}$ $Fe_{0.07}O$ (curve 2) films at room temperature.

gy of 2.99 eV that can be designed to the observed absorption peak. Weak temperature shift of the absorption edge in range of (80–300) K suggests of low value of temperature coefficient of band gap $dE_g/dT = 0.3$ meV/K. The estimated value of this coefficient is in good agreement with value of dE_g/dT reported by Hauschild et al. [19] for undoped ZnO.

Low photon energy part of transmission spectra for samples of $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ films is shown in Fig. 2. The average optical transparency for the studied films is nearly 80%. Fringes seen in both curves are cause by interference effect which suggests of high optical quality of the film surfaces.

Magneto-optical Faraday effect is widely used powerful tool for different bulk DMS materials from point of view to probe magnetisation processes and it is useful for variety of optical applications. To our knowledge in case of oxide DMS the Faraday rotation spectra were measured only in $Zn_{1-x}Co_xO$ films [20]. These experiments demonstrated giant Faraday affect in $Zn_{1-x}Co_xO$ at low temperature as large as in $Cd_{1-x}Mn_xTe$ crystals.

Figure 3 shows the Verdet constant of $Zn_{1-x}Mn_xO$ single crystals as a function of photon energy at $T = 300$ K, $B = 1.5$ T. As seen in Fig. 3 the difference between the presented curves is the change in the sign of the rotation angle θ_F for two different x. In fact, this is typical case for DMS materials type of $Cd_{1-x}Mn_xTe$.

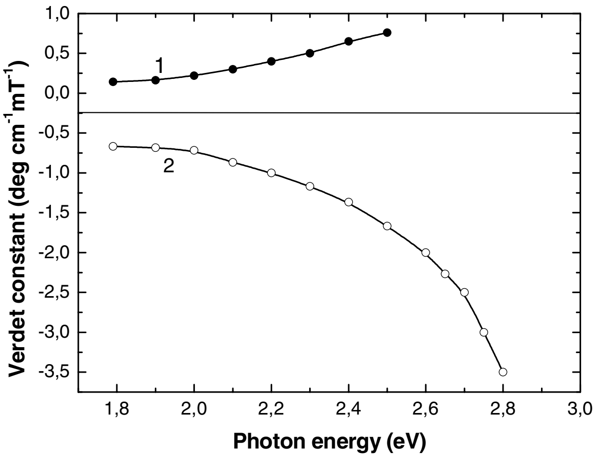

Fig. 3 Spectral dependence of the Verdet constant for $Zn_{0.98}Mn_{0.02}O$ (curve 1) and $Zn_{0.9}Mn_{0.1}O$ (curve 2) single crystals.

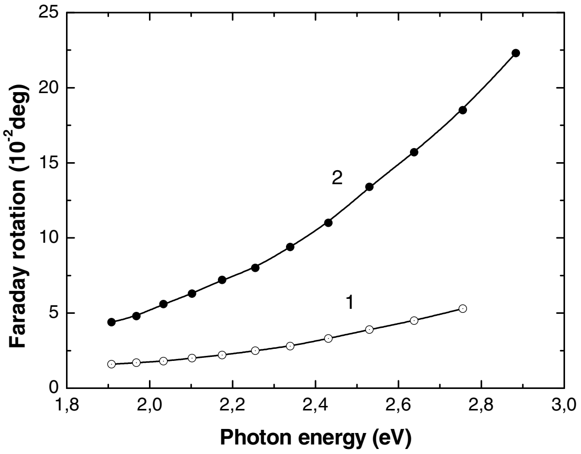

Fig. 4 Spectral dependence of the Faraday rotation for $Zn_{0.9}Mn_{0.1}O$ film on sapphire substrate (curve 1) and $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ film on glass substrate (curve 2) in magnetic field $B = 1.5$ T at room temperature.

The observed reversal of the direction of the Faraday rotation in its spectral dependence is associated with a positive and a negative part due to pure Zeeman and sp–d spin exchange interaction contribution, respectively. According to the microscopic model [21, 22], the Verdet constant $V = \theta_F/B\, d$ can be expressed as

$$V(E) = Z f(X) + C\, Y g(X)\,, \qquad (1)$$

where $X = E/E_g$, E is photon energy and E_g is the band-gap energy, and Z, C, Y are fitting parameters. The $f(X)$ function has a positive sign and $g(X)$ function is negative. Fitting parameters C and Y contain the oscillator strength, exchange integrals and concentration of magnetic ions. Therefore, in available competition between two contributions the second negative term of Eq. (1) is larger than the first one if content of Mn is large enough. However, absolute values of the Verdet constant for $Zn_{0.9}Mn_{0.1}O$ crystal are compared with those for nonmagnetic ZnO because of small value of sp–d exchange integrals $No(\alpha-\beta) \approx 0.1$ eV in oxide DMS [23].

Main problem during magneto-optical studies of semiconductor thin films is that one should take into account the substrate contribution to the observed Faraday rotation angle. In Fig. 4 the Faraday rotation angle is plotted as a function of photon energy for $Zn_{0.9}Mn_{0.1}O$ film on sapphire substrate (thickness $d = 0.5$ mm) and $Zn_{0.88}Mn_{0.05}\,Fe_{0.07}O$ film on glass substrate ($d = 0.2$ mm). Since thicknesses of the used substrates are much larger than typical thickness of the deposited films ($d = 700$ nm) we can see more larger substrate contributions in the resulting Faraday rotation spectra at room temperature. Common picture which illustrates this situation is presented in Fig. 5.

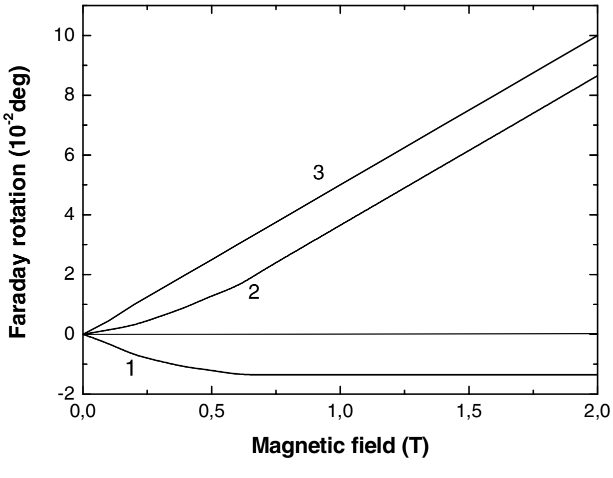

Fig. 5 Magnetic field dependence of the Faraday rotation for separate $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ film (curve 1), the film together with glass substrate (curve 2) and separate glass substrate (stright line 3) at wavelength 600 nm.

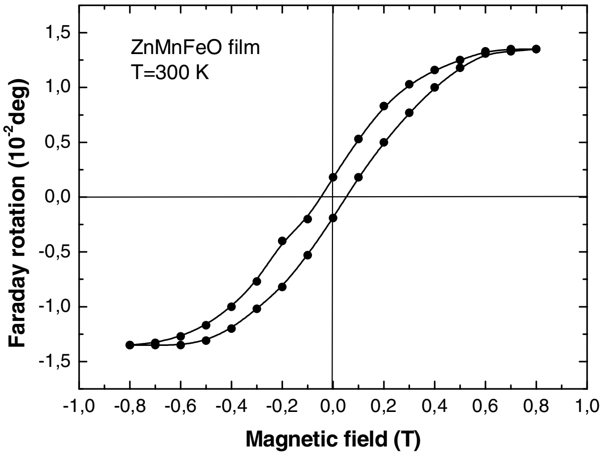

Fig. 6 Room temperature hysteresis loop for $Zn_{0.88}Mn_{0.05}Fe_{0.07}O$ film after subtracting contribution in Faraday rotation from glass substrate at wavelength of 600 nm.

On the base of such kind of consideration we have revealed interesting peculiarities in magnetic field dependence of the corrected Faraday rotation from $Zn_{0.88}Mn_{0.05}$ $Fe_{0.07}O$ film. It was observed clear saturation effect in the $\theta_F(B)$ dependence which starts at 0.75 T. In addition, detailed analysis of many curves of $\theta_F(B)$ allowed us to find the room temperature magnetic hysteretic loop namely for composition of $Zn_{0.88}Mn_{0.05}$ $Fe_{0.07}O$ (Fig. 6). In contrast, the observed linear dependence $\theta_F(B)$ and absence of hysteresis for $Zn_{0.9}Mn_{0.1}O$ film suggests of paramagnetism in this DMS.

The revealed ferromagnetic ordering in ZnMnFeO films is still far from being well understood. However, we suggest that such magnetic behaviour can be explained in terms of Dietl's model [1]. According to this model intrinsic ferromagnetism is mediated by delocalized or weakly localized holes in materials of p-type. In this case magnetic and magneto-optical properties of the oxide DMS are very sensitive to the content of the magnetic ions as well as to presence of other dopants. It should be mentioned the other examples from literature when codoping of ZnO (Mn with N [2] or Mn with Sn [15]) has been stimulated appearance of ferromagnetism.

4 Conclusions

In conclusion, single crystals of $Zn_{1-x}Mn_xO$ were grown by chemical vapour transport and thin films of $Zn_{1-x}Mn_xO$ and $Zn_{1-x-y}Mn_xFe_yO$ were deposited by pulsed laser deposition and rf magnetron sputtering. The observed absorption band near band gap edge is associated with d–d transitions of Mn^{2+} ions. Magneto-optical Faraday rotation measurements confirmed paramagnetism in $Zn_{1-x}Mn_xO$ and ferromagnetic behaviour in $Zn_{1-x-y}Mn_xFe_yO$ film samples at room temperature.

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