Magneto-optic manganese doped ZnO thin films

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Abstract. This investigation deals with the magneto-optical properties of pure and manganese doped ZnO thin films in the spectral region 600 – 1200 nm. The spectra of Verdet constant (V) are determined in the same spectral region for these thin films. The magneto-optic anomaly factor γ has been expressed. The spectral dependence of the spin-spin exchange interaction constant K has been studied. The change in energy splitting due to magnetic field for the investigated doped samples is also presented.

1. Introduction

Transparent oxides thin films have been widely investigated for their interesting structural, optical and electrical performances. Due to the decreasing scale of electronic devices using these oxides raises a growing interest in producing self-assembled micro and nano-structured materials. ZnO has attracted much attention as a promising material in recent years due to its unique properties such as a direct wide band gap on the order of 3.3 eV [1], for short wavelength optoelectronic devices, such as emitting diodes and laser diodes, especially as TCO in solar cells, gas sensors [2–7] and acoustic devices [8–10]. Transition metal doped dilute magnetic semiconductors (DMS), exhibiting room temperature ferromagnetism (RTFM) have attracted wide-spread interest for their promising applications in spintronics. In these materials, the charge and spin state of electrons are accommodated into a single material leading to interesting magnetic, magneto-optical and magneto-electric properties [11,12]. The magnetic properties of II–VI-based DMS have attracted much attention following Dietl’s prediction [13] of RTFM in Mn-doped ZnO as well as its high Curie temperature due to strong p–d hybridization [14].

Therefore, in the present work, ZnO:Mn thin films have been investigated in the magnetic field.

2. Experimental details

ZnO:Mn thin films were deposited on glass substrates at 460°C, using 10⁻² Maqueous solution of zinc acetate di-hydrate (Zn(CH₃COOH)₂·2H₂O). The solution contained a mixture of water and propanol with fraction volumes of 1/4 and ¾ respectively. It was acidified with acetic acid (pH = 5). Magnesium chloride tetrahydrate (MnCl₂·4H₂O) was used as a source of Mn. The Mn-to-zinc molar ratios ([Mn]/[Zn]) were: 0%, 1%, 2% and 3%. Nitrogen was used as the gas carrier (pressure at 0.35 bar) through a 0.5 mm-diameter nozzle. The nozzle to substrate plane distance was fixed at the optimal value of 27 cm [15]. During the deposition process, the precursor mixture flow rate was taken constantly at 4 mL/min throughout the thin films deposition.
3. Results and Discussion

The magneto-optic Faraday effect presents the connection between optics, magnetism and atomic physics. Faraday rotation manifests itself as a rotation of the polarization plane of the light passing through the sample in the presence of a magnetic field, and is characterized by the Verdet constant (V) of the investigated sample. The rotation angle $\phi$ can be expressed by the formula [16]:

$$\phi(\lambda) = \frac{A}{(\lambda^2 - \lambda_0^2)},$$

where $A$ is a constant determined from the matrix elements of the interband transitions, $\lambda$ is the wavelength, and $\lambda_0$ is the wavelength related to the interband transitions and corresponding to the natural frequency $\omega_0 = \frac{2\pi}{\lambda_0}$ of an effective harmonic oscillator. The relationship between the rotation angle and the Verdet constant is $\phi = VBd$, where $B$ is the magnetic induction of the field and $d$ is the sample thickness (figure 1).

The magneto-optic anomaly factor $\gamma$ can be taken as a measure of the degree of covalency that exists in the bonds connecting the ions and atoms [17].

$$\gamma = \frac{\phi}{2mc^2\omega^2},$$

where $\phi$ is the rotation angle in the magnetic field, $e$ is the charge of electron, $\omega$ is the wave length, $m$ is the mass of the electron and $c$ is the velocity of light.

In the paramagnetic materials, the anomaly factors $\gamma$ can vary with the wavelength of the incident light, even if there is only one absorption frequency contributing to dispersion (figure 2). The dispersivity of the investigated crystal can be presented by the following equation:

$$D = \frac{\omega}{c \lambda},$$

$$\gamma = \frac{VB}{2mc^2\omega^2\lambda},$$

where $V$ is the Verdet constant, $B$ is the magnetic induction, $l$ is the thickness of sample and $n$ is the refractive index.

$$m^* = \frac{e\omega}{\omega_0^2 - \omega^2} \frac{Ne_0}{\sqrt{2\pi\varepsilon_0 c^2 \lambda}}$$

where $m^*$ is the effective mass of electrons, $N$ is the number of d shell electrons in Mn$^{2+}$ ions, $\omega_0$ is the natural frequency of an effective harmonic oscillator and $\varepsilon_0$ is the dielectric permittivity in the vacuum.

$$E_d = \frac{13.512}{\varepsilon^2} \left( \frac{m^*}{m} \right),$$

where $Z$ is the serial number of element in the Mendeleyev's table and $\varepsilon$ is the dielectric permittivity.

The magnetic induction is $B = 0.97$ T at the room temperature $T = 300K$ and the paramagnetic sample can be treated has having a linear susceptibility given, to an accurate approximation [18], by

$$\chi = \frac{Ne^2\beta S(S + 1)}{kT} = 2.64 \times 10^{-4} \text{cm}^3/\text{mol},$$
where $N = 5$, $g = 2$, $\beta = 34.21 \times 10^{-5}$ and $S = 5/2$ for Mn$^{2+}$.

The spectral dependence of the spin-spin exchange interaction constant $K$ in the case of pure and manganese doped ZnO thin films is presented in figure 3. It can be calculated by the following formula [19]:

$$K(\lambda) = \frac{V \left[ \left( \frac{1}{\lambda_g^2} \right)^2 - 1 \right]^{1/2}}{\chi \lambda},$$  \hspace{1cm} (8)

where $V$ is the Verdet constant, $\chi$ is the magnetic susceptibility of the sample and $\lambda_g$ represents the wavelength which corresponds with the band gap of the material.

The following formula

$$\Delta E_{ij} = \frac{[\hbar c/(E_d)](\partial E/\partial n)}{\lambda_g}$$  \hspace{1cm} (9)

describes the parameter $\Delta E_{ij}$ [20]. This is the change in energy splitting due to magnetic field for a $d^5$ electron transitions in the Mn$^{2+}$ ion (figure 4).
Figure 2a. The magneto-optic anomaly factor $\gamma$ in the spectral region 600 – 1200 nm for pure ZnO.

Figure 2b. The magneto-optic anomaly factor $\gamma$ in the spectral region 600 – 1200 nm for ZnO:Mn_1%.

Figure 2c. The magneto-optic anomaly factor $\gamma$ in the spectral region 600 – 1200 nm for ZnO:Mn_2%.

Figure 2d. The magneto-optic anomaly factor $\gamma$ in the spectral region 600 – 1200 nm for ZnO:Mn_3%.

Figure 3a. The constant $K(\lambda)$ of spin-spin exchange interaction for ZnO:Mn_1%.

Figure 3b. The constant $K(\lambda)$ of spin-spin exchange interaction for ZnO:Mn_2%.
Figure 3c. The constant $K(\lambda)$ of spin-spin exchange interaction for ZnO:Mn$_{3\%}$.

Figure 4a. The change in energy splitting $\Delta E_{ij}$ for ZnO:Mn$_{1\%}$.

Figure 4b. The change in energy splitting $\Delta E_{ij}$ for ZnO:Mn$_{2\%}$.

Figure 4c. The change in energy splitting $\Delta E_{ij}$ for ZnO:Mn$_{3\%}$. 
The photoluminescence spectra of pure and manganese doped ZnO thin films are presented in [21]. The broad visible bands with the increase of the manganese doping are observed at about 750 nm. This is attributed to the red emissions related to oxygen defects [22]. The values of Verdet constant at about 750 nm decrease when the concentration of Mn content is 1% and 3% and increase when the Mn content is 2% (Figure 1). This means that the effective mass of manganese electrons increases in the first case and decreases when the Mn content is 2% (see eq. 5). When we know the values of $m_{ef}$ at about 750 nm, we can determine the ionization energy $E_d$ of Mn$^{2+}$ ions (see eq. 6). The degree of covalency of bonds between manganese ions at about 750 nm is biggest in the case when the Mn content is 1% (Figure 2). When the Mn content is 3%, the degree of covalency is the same as in the case of pure ZnO thin film. The spin-spin exchange interaction is the smallest, when the Mn content is 3% (Figure 3). This means that the room temperature ferromagnetism of the manganese doped ZnO thin films [21] will be better expressed, when the Mn content is 1 or 2 %. The change in the energy splitting is bigger when the Mn content is 1 or 2 % (Figure 4).

4. Conclusions

The values of Verdet constant are negative. This means that the pure and manganese doped ZnO thin films are paramagnetic. The magnetic anisotropy is proved by calculation of spin-spin exchange interaction constant. All investigations in this work are useful for the application of manganese doped ZnO thin films as the emitting and laser diodes.

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