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Carrier Density Dependence of *sp-d* Exchange in Nanostructured ZnO:Mn Thin Film

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In this work, the nanostructured ZnO:Mn thin films with different Mn concentration (5, 10 and 15 mol%) have been grown on glass substrates at 500°C by the spray pyrolysis technique. The average grain size was estimated about 25 nm using SEM micrographs. The Faraday rotations were determined in applied magnetic fields up to 1.05 T. The highest values of Faraday rotation were observed in the sample with 5 mol% Mn concentration. The carrier density has been calculated from the Faraday rotations and it is observed that the *sp-d* exchange in magnetic semiconductor is strongly affected by carrier parameters.

Keywords: Faraday effect, Carrier density, ZnO, Thin film.

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1. INTRODUCTION

According search for ferromagnetism in diluted magnetic semiconductors (DMS) has denoted that the strong magnetic coupling between localized *d* electrons of the magnetic dopant and *sp* carriers of the semiconductor depends on the carrier density in these materials [1]. The optical excitation of DMS which includes both types of carriers leads to the strong *sp-d* exchange. This magnetic coupling leads to the interesting magneto-optical properties. Huge Faraday rotation observed in $Cd_{1-x}Mn_xTe$ [2], large magneto-optical effect reported in an oxide DMS $Zn_{1-x}Co_xO$ [3] and ferromagnetic state in $Zn_{1-x}Mn_xO$ [4] and $Zn_{1-x}Co_xO$ [5] are the natural result of the *sp-d* exchange interaction. Behan *et al.* [6] showed that the magnetic ordering and magneto-optical properties of materials are affected by the carrier parameters. The carrier properties can be investigated from the Faraday rotation arising from the difference between phase velocities to the of two circularly polarized components [7].

In this work, we present, besides the measurement of the room temperature Faraday rotations observed in ZnO:Mn thin films, calculating the carrier densities of the samples are put forward.

2. THEORY

In this section, we present the formulation to find the carrier density by means of Faraday effect measurements [8]. If the external magnetic field B is assumed to be in the z direction as exactly applied in this work, then the parameters in gyrotropic media relation are defined by:

$$\varepsilon = \varepsilon_0 \left[1 - \frac{\omega_p^2}{\omega^2 - \omega_c^2} \right], \tag{2.1}$$

$$\varepsilon_g = \varepsilon_0 \left[\frac{-\omega_p^2 \times \omega_c}{\omega(\omega^2 - \omega_c^2)} \right], \tag{2.2}$$

where ε, $\omega_c = eB/m^*$ and $\omega_p = (ne^2/\varepsilon_0 \varepsilon m^*)^{1/2}$ are dielectric constant, cyclotron frequency and plasma frequency, respectively. All the parameters used in this section are listed in Table 1. We considered the thin films as the slab of gyrotropic media with the thickness d and the wave propagated parallel to the magnetic field. Upon wave striking the interface, the wave will break up into circularly polarized waves with two different wave numbers, k_+ and k_- given by:

$$k_{\pm} = \omega \sqrt{\mu(\varepsilon \pm \varepsilon_g)}\,, \tag{2.3}$$

Finally, the polarization of the electric field at $z = d$ is linear but rotated by an angle θ_F comparing to the polarization of incident wave will be:

$$\theta_F = \frac{k_+ - k_-}{2} d\,, \tag{2.4}$$

Because of the θ_F dependence on k_+ and k_-, carrier density of the electrons can be measured as discussed above.

Table 1 – List of the all parameters are used in Eqs. (2.1) and (2.2)

ε	Dielectric constant
ε_g	Dielectric constant of vacuum
ω	Incident light frequency
ω_p	Plasma frequency
ω_c	Cyclotron frequency
e	Electron charge
n	Carrier density
m^*	Effective mass

3. EXPERIMENTAL PROCEDURES

In this work, the spray pyrolysis technique was applied to grow nanostructured ZnO thin films with different Mn concentration (5, 10 and 15 mol%) on glass substrates. ZnO:Mn thin films were prepared by depositing a 0.1 M solution comprising of zinc and manganese cations on glass substrates. In order to obtain the clear solution, we dissolved zinc acetate dehydrate and manganese acetate tetrahydrate in a mixture of isopro-

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panol and distilled water at 40°C followed by adding a few droplets of acetic acid. The volume ratio of isopropanol to distilled water was 3 to 1. The system adjusting was determined as follows. The glass substrates were kept at 500°C during deposition. The solution was sprayed at a flow rate about 5 CC/min using compressed air as the carrier gas. The distance of substrates to the nozzle was adjusted at 30 cm. The deposition process of all thin films was identically repeated and only the effects of Mn concentration were studied.

The Faraday rotation was measured using a home designed setup which is including a He-Ne laser (λ = 632.8 nm), an electromagnet, two polarizers and a couple of detectors. The incident light which was polarized by the first polarizer struck the magnetic film and the rotation of polarization plane was then detected. The magnetic field was parallel to the direction of the beam. In order to adjust the setup to achieve highest resolution, the axis of the polarizer and analyzer were set to form the angle of 45° [9]. The two spectra of the Faraday rotation angles, θ_F, were obtained independently for the glass substrate and the substrates with the films at room temperature. In order to approximate the contribution of the film to θ_F, these two spectra were subtracted.

4. RESULTS

Fig. 1 shows the XRD patterns of the ZnO thin film with different manganese concentration grown at 500°C on glass substrates. The major peaks in these patterns are in close agreement with JCPDS data file for ZnO powder corresponding to the reflection peaks of the wurtzite structure which are indexed in this figure. All films exhibit random orientations, because glass substrates allowed the films to crystallize randomly.

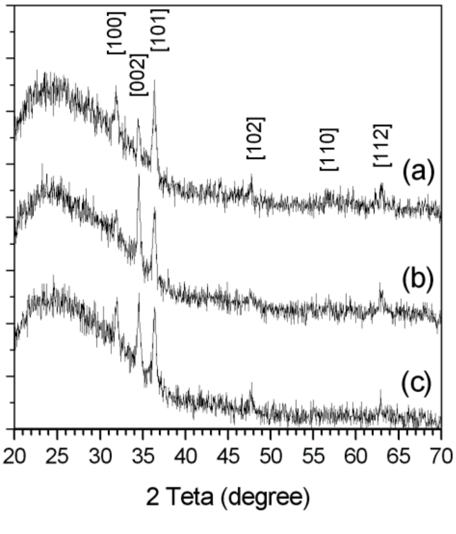

Fig. 1 – XRD patterns of ZnO:Mn thin films with different Mn concentration 5 mol% (a), 10 mol% (b) and 15 mol% (c)

Fig. 2 shows the SEM image of 5 mol% Mn doped ZnO thin film. The average grain size was estimated about 25 nm. This image of ZnO:Mn films show that the grain boundaries are well defined and the grains distribution over the surface is uniform. Fig. 3 shows the measured values for Faraday rotation angles versus applied magnetic field. Faraday rotation originates in anisotropy of refractive index and arises from differences between the phase velocities of two circularly polarized components. The observed Faraday rotation can be attributed to the *sp-d* interaction between the carriers and the localized magnetic moments of Mn ions. As shown in Fig. 3, it is observed that the rotation angles of the thin film with 5 mol% Mn concentration is stronger than the other films with higher Mn content.

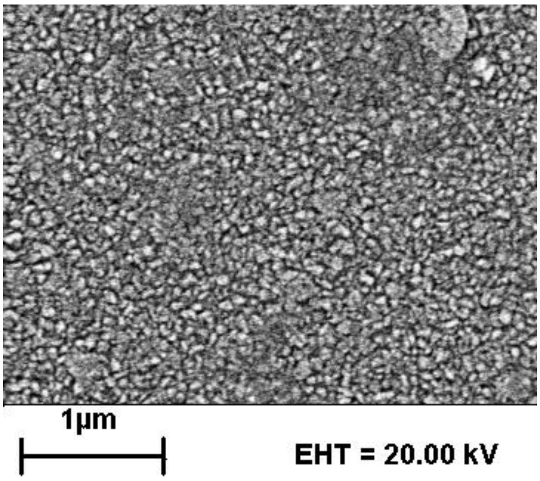

Fig. 2 – SEM image of 5 mol% Mn doped ZnO thin film

According to the carrier-mediated model [1], the magnetic properties of a material are strongly affected by free electron concentration. So, it can be concluded that decreasing the oxygen vacancies in ZnO structure with the increase in Mn content, leads to the reduction in the Faraday rotation angle. Neal *et al.* [10] have been also reported that the carrier density is reduced with the increase in Mn concentration. The validity of this approximation was checked by the calculation of carrier density using Eq. (2.4).

The Faraday rotations were recorded for the magnetic fields from 0 to 1.05 T and the carrier densities can be calculated using the Eq. (2.4). Because the cyclotron frequency is depended on the magnetic field, it may be expected that the carrier density in DMS is also affected by magnetic field. The values of carrier density obtained for all films in two typical magnetic fields (0.3

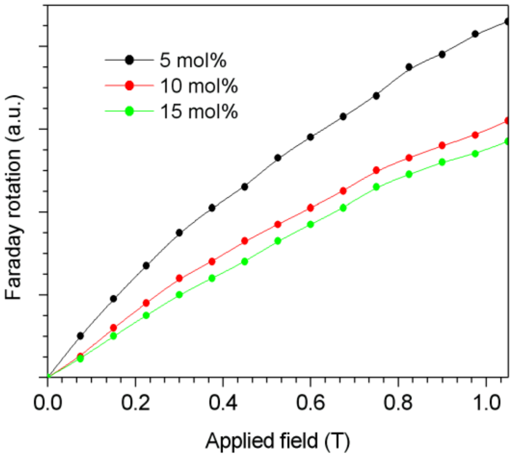

Fig. 3 – Room temperature Faraday rotation spectra versus magnetic field at λ = 632.8 nm

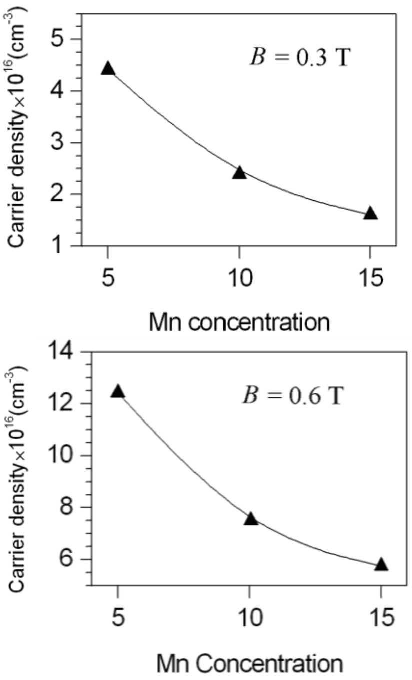

Fig. 4 – Dependence of the carrier density on amount of Mn concentration in the samples

T and 0.6 T) are given in Fig. 4. As shown in this figure, the carrier density decreases with the increase in Mn concentration. Mn atoms tend to accumulate in the grain boundaries and play a significant role in grain boundaries oxidation. So, weakening the magnetic ordering with increase in Mn content originates in decreasing the oxygen deficiencies and hence carrier density in specimens.

Also, the carrier densities increase with the increase in magnetic field from 0.3 T to 0.6 T. As discussed by Ohno [11] and Awschalom *et al.* [12], in magnetic semiconductor quantum structure, the carriers interactions via exchange with magnetic ions (such as Mn in this paper) resulting spin dependent transport and carrier induced ferromagnetism which are in good agreement with our results in Figs. 3 and 4.

5. CONCLUSIONS

In this paper, the transparent thin films of ZnO:Mn were grown by spray pyrolysis. The Faraday effect studies revealed that the rotation angle decreased with the increase in Mn concentration. The similar changes have been also observed between carrier density and Mn content. So, it may be generally accepted that in ZnO based ferromagnetic semiconductors, the carrier density strongly affects the *sp-d* exchange. Also, it is found that the carrier densities increased with increase in magnetic filed which relates to spin dependent transport.

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