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Growth and characterization of ZnMnO thin films

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Abstract

Zn_{1-x}Mn_xO ($0 \leq x \leq 0.1$) thin films were grown on sapphire substrates by pulsed laser deposition and rf magnetron sputtering methods. As a target source ceramic pellets prepared by mixing ZnO and Mn₃O₄ powders were used. The shift of the absorption edge due to increase the energy band gap with increasing Mn content was observed in optical absorption spectra of the Zn_{1-x}Mn_xO thin films. Magnetic susceptibility and magneto-optical Faraday rotation experiments show paramagnetic behavior and absence of ferromagnetic ordering in the studied films.

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1. Introduction

Semimagnetic semiconductors or diluted magnetic semiconductors are attractive materials because of exhibition of the sp–d exchange interaction between the localized magnetic moments and the spins of the band carriers. The unique spin-dependent phenomena in these semiconductors can introduce new functionality to spintronic devices. Recently the family of semimagnetic semiconductors was increased by addition of the semiconducting oxides [1,2]. Initially interest in oxide-based semimagnetic

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semiconductors was stimulated by the theoretical prediction of Dietl et al. [3] that ZnO would exhibit ferromagnetism at room temperature after doping with 5% Mn ions. Ferromagnetism in ZnO doped with magnetic ions was theoretically studied by ab initio calculations based on the local density approximation [4]. Wang et al. [5] 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 film changes from antiferromagnetic to ferromagnetic when codoped with N.

Until now several research groups attempted to obtain experimental evidence for such ferromagnetism in powder, bulk and thin film forms of ZnO doped with transition metals.

So far studied thin films of ZnO-based semimagnetic semiconductors were grown by the spin coating method [6], sol–gel method [7,8], metallorganic chemical vapour deposition [9], radio frequency magnetron sputtering [10] and pulsed laser deposition technique [11–16]. It should be noted that in most of the studies the obtained material was the n-type. Fukumora et al. [11] have shown that the Mn content in $Zn_{1-x}Mn_xO$ can reach $x = 0.35$ whereas the equilibrium solubility limit is only $x = 0.13$. For these films large magnetoresistance has been revealed but no evidence for ferromagnetism. On the other hand, recently Jung et al. [17] found ferromagnetism in $Zn_{1-x}Mn_xO$ epitaxial films with a Curie temperature of 45 K. Sharma et al. [16] reported ferromagnetism at room temperature for $Zn_{1-x}Mn_xO$ films with small content of Mn $x = 0.02$. Thus, as one can see, the results have been rather controversial. It is obvious that the magnetic properties for oxide films are extremely sensitive to the sample preparation conditions.

In our previous work different methods for growth of the single crystals and $Zn_{1-x}Mn_xO$ thin films were presented [18]. In the present work, we focus on the preparation and characterization of $Zn_{1-x}Mn_xO$ thin films.

2. Experimental

The depositions of the $Zn_{1-x}Mn_xO$ ($0 \leq x \leq 0.1$) thin films were performed in a stainless-steel chamber under vacuum of 10^{-5} Pa. A XeCl pulsed excimer laser ($\lambda = 308$ nm, $\tau = 30$ ns) with a fluence of (7–10) J/cm² has been applied. The number of pulses was set at 30 000 for each deposition. The ablated material was collected on a substrate located in a plane parallel to the target surface and 30 mm apart from it. The films with a thickness of several hundred nanometers were deposited on sapphire(0001) substrates at 360 °C. The $Zn_{1-x}Mn_xO$ targets were fabricated by mixing the appropriate amount of ZnO and Mn₃O₄ powders and preparing of ceramic pellets. For this purpose the mixture of ZnO and Mn₃O₄ powders was first calcined at 450 °C for 7 h, then the pressed pellet was sintered at 920 °C for 10 h in flowing oxygen. Similar targets were applied also in the technique of radio frequency (rf) magnetron sputtering. The sputtering was performed under a mixture of Ar and O₂ gases in order to compensate oxygen vacancies in the obtained films.

The crystal structure of the deposited films was studied by X-ray diffraction (XRD) measurements using a Cu-K α radiation. The magnetic susceptibility was measured by the Faraday method using an electronic balance at temperatures of 80–300 K and magnetic fields up to 1.0 T. Optical absorption and Faraday rotation spectra were measured on a

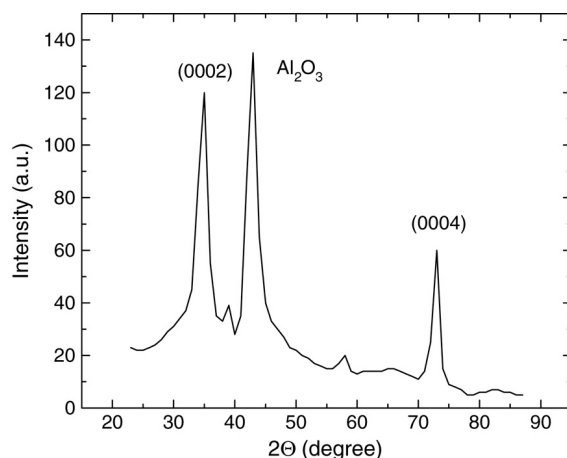


Fig. 1. XRD patterns of c -oriented $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films.

set-up with a grating monochromator for wavelengths (200–2200) nm and a water-cooled electromagnet with maximal magnetic field of 5 T, and temperatures of 5–300 K.

3. Results and discussion

As shown in Fig. 1, the grown films showed (002) and (004) peaks of wurtzite structure in X-ray diffraction spectra, indicating that the films are c -axis oriented.

Fig. 2 shows the absorption spectrum which was extracted from the transmission spectra for $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ crystalline samples of different thickness. The observed absorption band at 2.8 eV is due to the presence of Mn ions because it is absent for undoped ZnO. This structure is interpreted by d - d crystal-field transitions between multiplets of $3d^5$ configuration of the Mn^{2+} ions. According to the calculations using the cluster model [21] the ground state of the Mn^{2+} ions is ${}^6\text{A}_1$. The d - d transitions from ${}^6\text{A}_1$ to the lowest excited terms ${}^4\text{T}_1$, ${}^4\text{T}_2$, ${}^4\text{E}$, and ${}^4\text{A}_1$ give energies 2.55, 2.85, 2.97, and 2.99 eV, respectively. Since the intensity of ${}^4\text{T}_1$ is weak compared to those of ${}^4\text{T}_2$, ${}^4\text{E}$, and ${}^4\text{A}_1$ we can assign the broad absorption band around 2.8 eV to the transitions from ${}^6\text{A}_1$ to ${}^4\text{T}_2$, ${}^4\text{E}$, and ${}^4\text{A}_1$.

Investigation of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films allows us to study absorption spectra in the region of higher absorption coefficients and at shorter wavelengths. The observed shift of the absorption edge to the high photon energy side is due to the increase of the energy band gap E_g with x . In order to determine the energy band gap E_g the data for the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films with different values of x are plotted in dependence on the square of the absorption coefficient α^2 versus photon energy, as shown in Fig. 3. In this case the value of E_g can be estimated from the intersection of the extrapolated lines with the horizontal axis. The estimated values for the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ E_g are 3.26, 3.35, and 3.40 eV for $x = 0.0$, $x = 0.06$, and $x = 0.1$, respectively. The obtained variation with Mn content is in good agreement with the expression $E_g = 3.273 + 1.32x$ (eV) from [11].

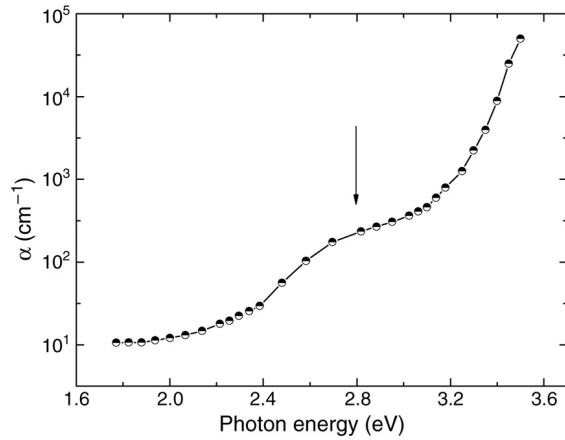


Fig. 2. Absorption spectrum of $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ extracted from transmission data of single crystal samples with different thickness.

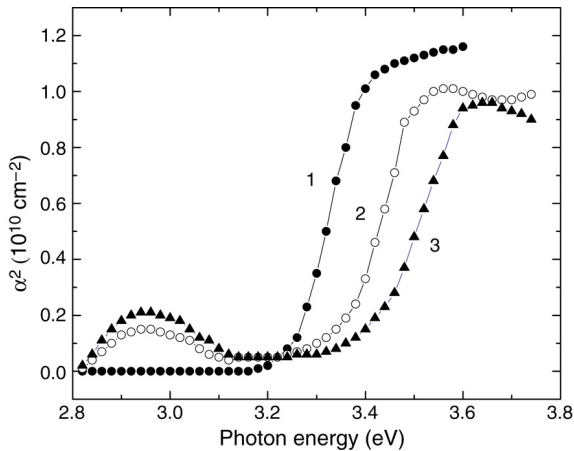


Fig. 3. Absorption spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ films with different Mn content (the curves 1, 2 and 3 correspond to $x = 0.0$, $x = 0.06$, $x = 0.1$, respectively).

The temperature dependence of magnetic susceptibility χ shown in Fig. 4 clearly demonstrates paramagnetism of the studied material. The diamagnetic contribution of pure ZnO is equal to $\chi_d = -0.38 \times 10^{-6}$ emu/g. Magnetic susceptibility data fits well to an expression of $\chi = C_M(T - \theta_p)^{-1}$, where C_M is the molar Curie constant and θ_p is the Curie–Weiss temperature. The negative sign of θ_p indicates on antiferromagnetic interaction between Mn^{2+} ions in the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.

The study of the Faraday effect in semimagnetic semiconductors is useful from the point of view of a probe into the microscopic magnetic properties of these materials and

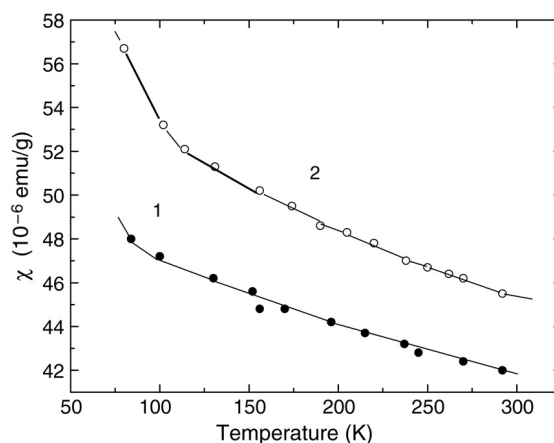


Fig. 4. Temperature dependence of the magnetic susceptibility for $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ (the curves 1 and 2 correspond to $x = 0.06$ and $x = 0.1$, respectively).

can thus give additional data to improve their understanding [19,20]. For instance, by using the Faraday rotation one can estimate exchange interaction between the Mn^{2+} ions and the band electrons. In addition, information about type of magnetism can be extracted from the magnetic field dependence of the Faraday rotation. In Fig. 5 the spectral dependence of the Verdet constant is shown for a $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ single crystal sample. The main feature is the change in the sign of the rotation from positive to negative when we go from pure ZnO to semimagnetic oxide. This is a typical situation for semimagnetic semiconductors which is attributed to the domination of the sp–d spin exchange contribution to the Faraday effect. An advantage of using thin films to investigate the Faraday rotation lies in the possibility to measure the oscillatory behaviour shown in Fig. 6. The oscillatory behaviour can be described by a simple dielectric model which takes into account the fact that light circularly polarized as σ_+ and σ_- propagates through a material with velocities corresponding to refractive indices n_+ and n_- , respectively. For semimagnetic semiconductors the difference in refractive indices ($n_- - n_+$) which gives its main contribution to the Faraday rotation angle is much larger than in nonmagnetic materials. The corresponding large difference between the refractive indices n_+ and n_- is due to large excitonic spin splitting (giant Zeeman effect) which is enhanced in semimagnetic semiconductors by the sp–d spin-exchange interaction. According to the recent calculations [21] the magnitude of the p–d exchange constant in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ is much larger than that in other II–VI- and III–V-based semimagnetic semiconductors.

4. Conclusion

In conclusion, thin films of oxide semimagnetic semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x \leq 0.1$) were fabricated by pulsed laser deposition and rf magnetron sputtering. From optical absorption spectra the energy band gap was found to increase with Mn content and

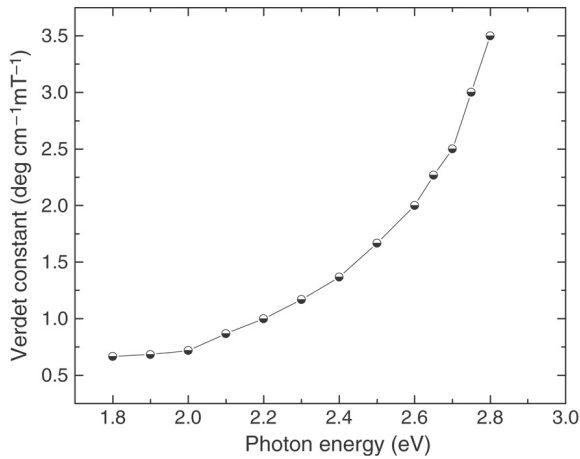


Fig. 5. Spectral dependence of the Verdet constant for $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ single crystals.

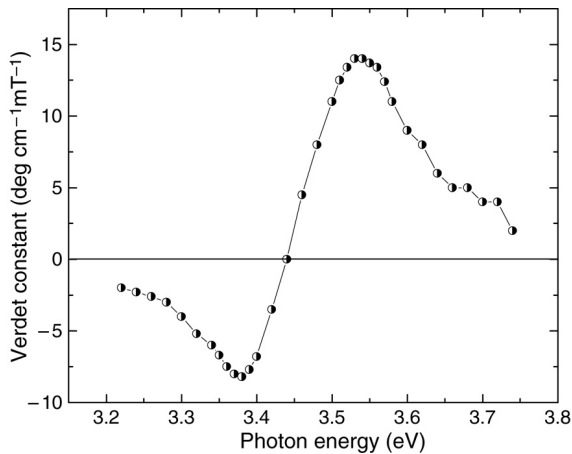


Fig. 6. Spectral dependence of the Verdet constant for $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ films.

the absorption band is interpreted in the framework of d–d transitions. The temperature dependence of the magnetic susceptibility suggests paramagnetic behaviour for the studied material. The magneto-optical Faraday effect of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ thin films demonstrates features which are typical for II–VI-based semimagnetic semiconductors.

Acknowledgments

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References

- [1] S.J. Pearton, W.H. Heo, M. Ivill, D.P. Norton, T. Steiner, *Semicond. Sci. Technol.* 19 (2004) R59.
- [2] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Prog. Mater. Sci.* 50 (2005) 293.
- [3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* 287 (2000) 1019.
- [4] K. Sato, H. Katayama-Yoshida, *Japan. J. Appl. Phys.* 39 (2000) 255.
- [5] Q. Wang, Q. Sun, P. Jena, Y. Kawazoe, *Phys. Rev. B* 70 (2004) 052408.
- [6] A. Shwartz, N.S. Norberg, O.P. Nguen, J.M. Parker, D.R. Gamelin, *J. Am. Chem. Soc.* 125 (2003) 13205.
- [7] H.J. Lee, S.Y. Jeong, C.R. Cho, C.H. Park, *Appl. Phys. Lett.* 81 (2002) 4020.
- [8] Y.M. Kim, M. Yoon, I.-W. Park, J.H. Lyoo, *Solid State Commun.* 129 (2004) 175.
- [9] A.C. Tuan, J.D. Bryan, A.B. Pakhomov, V. Shutthanandan, S. Thevuthasan, D.E. McCready, D. Gaspar, M.H. Engelhard, J.W. Rogers Jr., K. Krishnan, D.R. Gamelin, S.A. Chambers, *Phys. Rev. B* 70 (2004) 054424.
- [10] K.J. Kim, Y.R. Park, *J. Appl. Phys.* 96 (2004) 4150.
- [11] T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, M. Kawasaki, *Appl. Phys. Lett.* 75 (1999) 3366.
- [12] K. Ando, H. Saito, Z. Jin, T. Fukumura, M. Kawasaki, Y. Matsumoto, H. Koinuma, *Appl. Phys. Lett.* 78 (2001) 2700.
- [13] Z. Jin, K. Hasegawa, T. Fukumura, Y.Z. Yoo, T. Hasegawa, H. Koinuma, M. Kawasaki, *Physica E* 10 (2001) 256.
- [14] A. Tiwari, C. Jin, A. Kvit, D. Kumar, J.F. Muth, J. Narayan, *Solid State Commun.* 121 (2002) 371.
- [15] E. DePosada, G. Tobin, E. McGlynn, J.G. Lunney, *Appl. Surf. Sci.* 208–209 (2003) 589.
- [16] P. Sharma, A. Gupta, F.J. Owens, A. Inoue, K.V. Rao, *J. Magn. Magn. Mater.* 282 (2004) 115.
- [17] S.W. Jung, S.-J. An, G.-C. Yi, C.U. Jung, S.-I. Lee, S. Cho, *Appl. Phys. Lett.* 80 (2002) 4561.
- [18] A.I. Savchuk, P.N. Gorley, V.V. Khomyak, K.S. Ulyanytsky, S.V. Bilichuk, A. Perrone, P.I. Nikitin, *Mater. Sci. Eng. B* 109 (2004) 196.
- [19] P.I. Nikitin, A.I. Savchuk, *Sov. Phys. Usp.* 33 (1990) 974.
- [20] E. Oh, D.U. Bartholomew, A.K. Ramdas, J.K. Furdyna, U. Debska, *Phys. Rev. B* 42 (1990) 5201.
- [21] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, M. Kawasaki, *Phys. Rev. B* 65 (2002) 85209.