Ferromagnetism in Nanocrystalline ZnO Thin Films

Manju Arora, Sachin Bhardwaj and R.P. Pant

***Abstract*—EPR spectroscopy has been used to investigate ferromagnetism and oxygen vacancies in nanocrystalline ZnO thin films derived from different zinc acetate sol concentrations on quartz substrate by sol-gel process. In low sol concentration ZnO thin film, a broad ferromagnetic EPR resonance signal of g-value about 2.000 is observed due to zinc vacancies. While on increasing sol-concentration, a narrow EPR resonance signal superimposed on broad line and only narrow line signal of g-value 1.9264 appears due to the formation of oxygen vacancies in films during synthesis.**

***Index Terms*—Nanocrystalline, Zinc oxide, Thin Film, Ferromagnetism**

I. Introduction

THE Synthesis and characterization of thin films of ZnO is an active area of research for nearly half a century. ZnO is a semiconductor with a wide band gap of 3.37 eV and large exciton binding energy of 60 meV. Besides applications in photonics, thin films of ZnO find application in various sensing devices as well due to the piezoelectric nature of the material. The combination of piezoelectric and semiconducting behavior makes ZnO as unique and strategic material for a variety of technological applications [1]-[5]. MEMS based sensors involve zinc oxide films for a number of applications in pressure transducers, accelerometers, acousto-optic devices, bulk and surface acoustic wave devices. It is an excellent material for various photonic applications in energy storage and conversion devices when doped with suitable dopant. Therefore, variety of techniques are utilized for thin film deposition of ZnO. Sol-gel, wet chemical route, chemical methods [6-9] are inexpensive and are preferred over other techniques such as MBE, MOCVD which are expensive. Thus, a large number of candidate materials can be prepared for exploratory studies using sol-gel techniques. Characterization of such films becomes important in deciding their device worthiness before integrating them in the device for the cost effectiveness, consistency and reliability of the sensor.

Recently, the research of diluted magnetic semiconductor is a subject of current interest due to the possibility to control spin and charge simultaneously for future spintronics. Mn-doped GaAs is a successful diluted magnetic semiconductor (DMS), however, the highest Curie temperature Tc is only 173 K, far below room temperature. Magnetic doped ZnO was intensively studied after the theoretical predication of room temperature ferromagnetism in Mn-doped, *p*-type conducting ZnO. Because of good solubility into ZnO, most of the magnetic doping were 3*d* transition metals, such as Mn, Co, Fe, Ni, etc. However, ZnO is intrinsically *n*-type conducting. Diverse magnetic properties were observed, for example, ferromagnetism, paramagnetism, antiferromagnetism, etc. The observed ferromagnetism in magnetic doped ZnO is very weak and, therefore, an extrinsic origin due to magnetic impurities could not be excluded. The magnetic properties in cobalt doped ZnO consist of two parts, strong temperature dependent paramagnetism which follows the Brillouin function and temperature independent ferromagnetism, while x-ray magnetic circular dichroism measurements only revealed a paramagnetic behavior of the active Co-dopant atoms in contrast to similar measurements on similar samples reported earlier. These results indicate that a specific parameter is not yet well controlled.

The origin of the ferromagnetism in pure ZnO was attributed to oxygen vacancies or to defects on Zn sites. Recent theoretical calculations indicate that the ferromagnetism in ZnO might originate from Zn vacancies and not from oxygen vacancies [10]-[15].

We have reported ferromagnetic properties in nanocrystalline ZnO thin films derived by sol-gel process using different concentrations of sol. Zinc actetate was used as precursor material for these films deposition on quartz substrate. These results indicate that the observed ferromagnetism in ZnO originate from the vacancies in the crystal lattice and not from the magnetically active dopant ions. The ferromagnetic resonance signal arose from defects was observed in the electron paramagnetic resonance (EPR) spectroscopy studies. The importance of defects in triggering magnetic order in otherwise diamagnetic materials appears to be a key issue of ferromagnetism.

II. Synthesis & Experimental Measurements

Nanocrystalline ZnO thin films on transition metal ion free quartz substrate by sol gel method. Zinc acetate dihydrate [$Zn(CH_3COO)_2$. $2H_2O$] was used as precursor for 5%, 15% and 25% concentration sol preparation and the turbidity of sol solution was removed by adding few drops of diethanolamine. Quartz plate of dimensions 1cm x 1cm x 0.5 cm were placed on the sample holder of sol-gel system with drop of sol was allowed to spin at the rate of 3000 – 4000 rpm. Followed by drying the coated wafer at 100 ^oC and subsequent annealing at 450^o C for one hour. Multiple coatings were done to obtain the workable thickness of the film. The ellipsometric data

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show that for ten coatings, the film thickness was only of the order of 2000-2500 Å.

These ZnO films were characterized by Bruker AXS D8 Advance diffractometer which has in built Diffrac^{plus} software using CuKα radiation for structural details, LEO - 440 SEM with EDS attachment for surface morphology and Varian make E-line Centuary E-112 X-band CW EPR spectrometer for paramagnetic defect analysis. DPPH was used as a standard reference for g-value calculations.

III. Results & Discussion

Zinc oxide crystallizes in the form of a wurtzite structure with alternating planes composed of tetrahedrally coordinated Zn^{2+} and O^{2-} stacked alternately along c-axis of hexagonal unit cell with a_0 = 0.3250 nm and c_0 = 0.5207 nm as shown in Fig. 1.

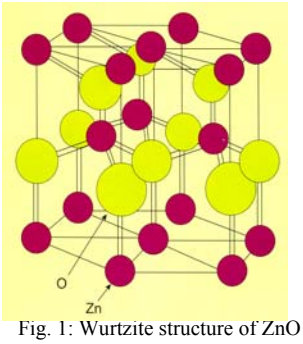

Fig. 1: Wurtzite structure of ZnO

XRD pattern of sol gel deposited nanocrystalline ZnO thin film derived from 5%, 15% and 25% sol concentrations are presented in Fig. 2(a,b, c).

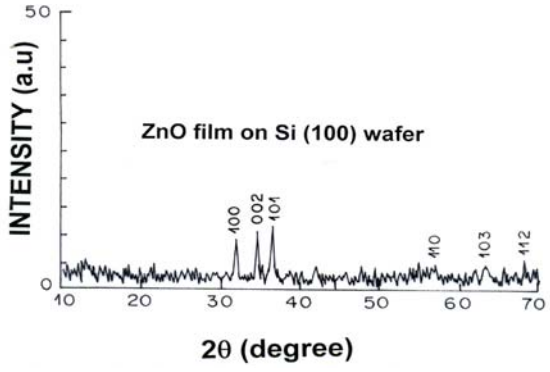

Fig. 2(a): XRD diffraction pattern of nc-ZnO thin film derived from 5% sol concentration

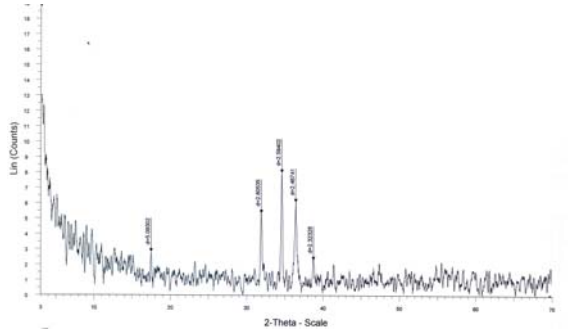

Fig. 2(b): XRD diffraction pattern of nc-ZnO thin film derived from 15% sol concentration

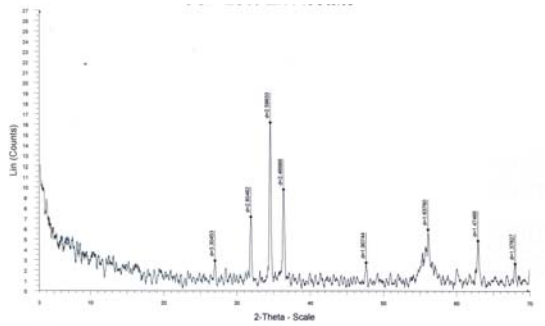

Fig. 2 (c): XRD diffraction pattern of nc-ZnO thin film derived from 25% sol concentration

XRD pdiffraction pattern shows diffraction peaks at 2θ (in degrees) 31.680, 34.340, 36.180, 56.540, 62.780 and 68.260 of [100], [002], [101], [110], [103] and [112] planes respectively in all the spectra. This confirms the polycrystalline nature of the deposited film. In 5% sol derived ZnO thin film, there is a very little preferential orientation along [101] plane while on increasing sol concentration the preferential orientation along [002] direction improves because ZnO is a polar crystal and have Zn^{2+} positively terminated and O^{2-} negatively terminated polar surfaces, which develops a net dipole moment along the *c* axis. The surface energies of the polar planes are higher than nonpolar planes. So preferential growth along the *c* axis direction is energetically favorable. It means that ZnO nuclei will grow faster along c-axis and the similar results are obtained from XRD. The crystallite size of ZnO thin film was measured by using Sherrer formula:

$D = k\lambda/\beta\cos\theta$

Where D is crystallite size, k proportionality constant (= 0.9), λ is wavelength of X-ray radiation used (CuKα in the present case), β is the FWHM of diffraction peak in radians, θ is the Bragg angle. In this sol gel grown ZnO thin film particle size is 20 -30 nm along c-axis direction.

SEM micrographs recorded on LEO SEM 440 instrument with EDS attachment. SEM micrograph of 5%, 15% and 25% sol derived nanocrystalline ZnO thin show the irregular spindle shaped, bundles of nanowires arranged in a random manner and fine nanowires respectively.

Electron Paramagnetic resonance is a very powerful sophisticated technique for the characterization of magnetic properties and spin dynamics in solids. EPR spectra are generally recorded by scanning the magnetic induction (β) at constsnt microwave frequency (i.e. 9.36 GHz in X-band EPR spectrometer). The position of EPR line depends upon the ratio of β to ν and the effective gyrometric factor (g-value). The linewidth and shape of resonant signal gives information about the magnetic and electronic state.

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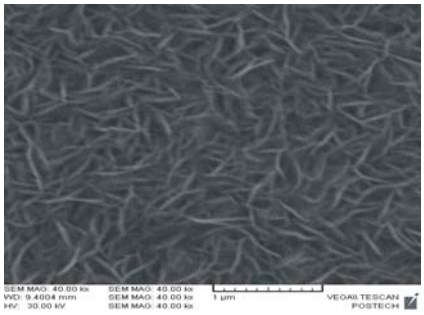
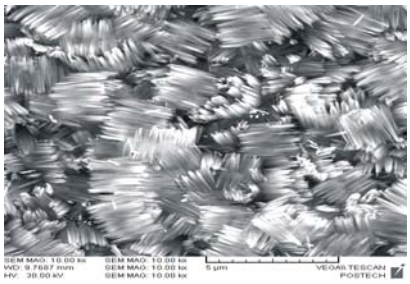


(a)



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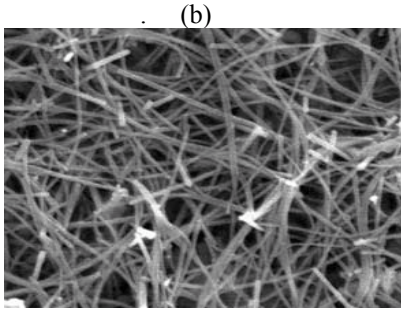

(c)

Fig. 3: EPR spectrum of nc-ZnO thin film derived from (a) 5%, (b) 15% and (c) 25%sol concentration

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Earlier, EPR spectroscopy has been used to characterize oxygen vacancies in nanocrystalline ZnO thin films. Magnetic dipole interactions among nanoparticles and superexchange interactions between the magnetic ions through oxygen ions are the two predominant factors which determine the EPR parameters g-value and resonance linewidth (ΔH). Strong dipole interactions give a large resonance linewidth and g-value while strong superexchange interactions produce a small line width and g-value. The superexchange interactions generally increases when the distance between the magnetic ions and oxygen ions decreases and the corresponding bonding angles are close to 180º EPR spectra of these films derived from different sol concentrations (5%, 10% and 25%) were recorded at ambient temperature and their spectra are presented in Fig. 4 (a,b,c).

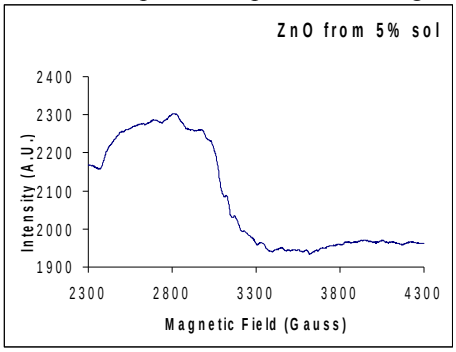

Fig. 4 (a): EPR spectrum of nc-ZnO thin film derived from 5% sol concentration

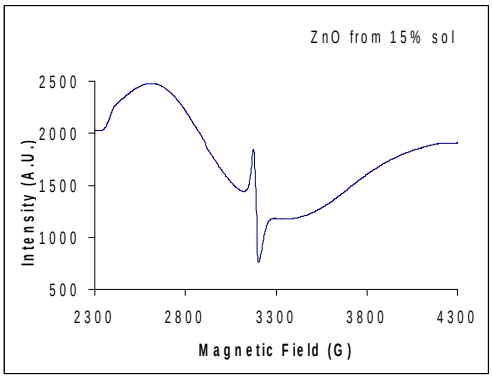

Fig.4 (b): EPR spectrum of nc-ZnO thin film derived from 15% sol concentration

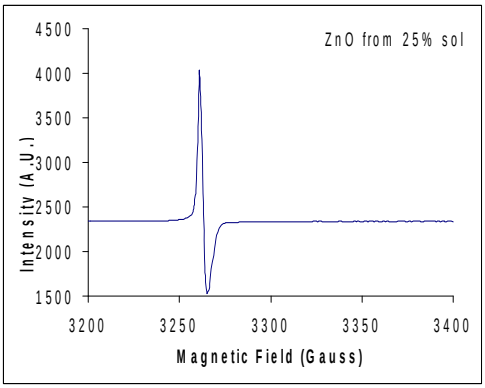

Fig. 4 (c): EPR spectrum of nc-ZnO thin film derived from 25% sol concentration

Two EPR signals with g-values at 1.9649 and 2.0015 were observed in these films. EPR signal pertaining to g-value 1.9649 corresponds to the ZnO with wurtzite structure having singly ionized oxygen vacancies with electron The oxygen vacancies are formed in the films during growth process when oxidation of zinc takes place by the atmospheric air. At that time, under suitable conditions unstable neutral oxygen vacancies are formed which are easily decomposed to singly ionized oxygen vacancy and single electron. The broad EPR resonance signal has g-value about 2.0015 i.e. close to free electron value (2.0023) is attributed to basically to the zinc vacancies [12]. The appearance of these signals at room

temperature confirms the formation of nanocrystalline particles/ grains in these films because in ZnO single crystal the shallow donor signal is not observed above 150 K due to thermal release of the donor electrons in the conduction band. While in nanocrystalline system the electrons are confined in the nanocrystals which prevents macroscopic conduction and EPR signals appear at ambient temperature. EPR spectroscopy has characterized ferromagnetism in the 5% sol concentration derived nanocrystalline ZnO films while in 15% sol derived ZnO thin film a narrow line signal superimposed on broad resonance signal was observed with a g-value 1.9264. The appearance of this narrow line signal is obtained due to the presence of oxygen vacancies in film network. In 25% sol concentration ZnO thin film only narrow line signal of oxygen vacancies is observed with a preferred c-axis orientation of these films.

II. CONCLUSION

EPR spectroscopy has been sucessfully used in the characterization of ferromagnetic behaviour in nanocrystalline ZnO thin films prepared by sol-gel process using different zinc acetate sol concentrations. This behaviour is observed as a broad resonance signal in EPR spectrum of 5% zinc acetate sol concentration thin film. The appearance of this broad signal is attributed to the presence of zinc vacancies. While oxygen vacancies signal appeared as a narrow line in higher sol concentration ZnO thin films with g-value 1.9264. Improvement in preferential orientation with the increase in sol concentration is also observed in these nanocrystalline ZnO thin films.

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REFERENCES

[1] Z. L. Wang, "Zinc oxide nanostructures: growth, properties and applications", J. Phys.: Condens, Matter vol. 16, R829 (2004).

[2] S.C. Pillai, J.M. Kelly, D. E. McCormack and R. Ramesh, "Self assembeled arrays of ZnO nanoparticles and their applications as varistir materials", J. Mter. Chem. Phys. vol. 14, 1572 (2004).

[3] C.-C Hasio, K.-Y. Huang and Y.-C. Hu, " Fabrication of a ZnO pyroelectric sensor", Sensors vol. 8, 185 (2008).

[4] J.-S. Huang and C.-F. Lin, " Influence of ZnO sol-gel thin film characteristics on ZnO nanowire arrays prepared at low temperature using all solution based processing", J. Appl. Phys. vol. 103, 014304 (2008).

[5] P. X, Gao and z. L. Wang, "Nanoarchitectures of semiconducting and piezoelectric zinc oxide", J. Appl. Phys. vol. 97, 044304 (2005).

[6] M. Dutta, S. Mirdha and D. Basak, " Effect of sol concentration on the properties of ZnO thin films prepared by sol-gel technique" Appl. Surface Sci. vol. 221, 462 (2007).

[7] H. Zhang, J. Feng, J. Wang and M. Zhang, " Preparation of nanorods through wet chemical method", Materials Lett. vol. 61, 5202 (2007).

[8] J. Z.- Perezi, A. Rahm, C. Czekalla, L. Lenzer, M. Lorenz and M. Grundmann, "Ordered growth of tilted ZnO nanowires: morphological structural and optical characterization", Nanotechnology vol. 18, 195303 (2007).

[9] Z. Jia,. l. Yue, Y. Zheng and Z. Xu, " Rod like Zinc oxide constructed by nanoparticles: synthesis, characterization and optical properties", Mater. Chem. Phys. vol. 107, 137 (2008).

[10] P. Erthart and K. Albe, "Diffusion of zinc vacancies and interstials in zinc oxide", Appl. Phys. Lett, vol. 88, 201918 (2006).

[11] A.O. Ankiewicz, W. Gehlhoff, J. S. Martins, A. S. Pereira, S. Perira, A. Hoffmann, E. M. Kaidasshev, A. Rahm, M. Lorenz, M. Grundmann, M.C. Carmo, T. Trindade and N.A. Sobolev, "Magnetic and structural properties of transition metal doped zinc - oxide nanostructures", Phy. Stat. Solidi B 1-5 (2009).

[12] X. Zuo, S.-D. Yoon, A. Yang, W. H. Duan, C. Vittoria and V.G. Harris, " Ferromagnetism in pure wurtzite zinc oxide", J. Appl. Phys. vol. 105, 07C508 (2009).

[13] A.O. Ankiewicz, M.. Carmo, N.S. Sobolev, W. Gehlhoff, E.M. Kaidashev, A. Rahm, M. Lorenz and M. Grundmann, " Electron paramagnetic resonance in transition metal -doped ZnO nanowires", J. Appl. Phys. vol. 201, 024324 (2007).

[14] J. Alaria, M. Bouloudenine, G. Schmerber, s. Colis, A. Dinia, P. Turek and M. Bernard, "Pure paramagnetism behaviour in Mn-doped ZnO semiconductors", J. Appl. Phys. vol. 99, 08M118 (2006)

[15] T. Jungwirth, K. Y. Wang, J. Mašek, K. W. Edmonds, J. König, J. Sinova,M. Polini, N. A. Goncharuk, A. H. MacDonald, M. Sawicki, A. W. Rushforth, R. P. Campion, L. X. Zhao, C. T. Foxon, and B. L. Gallagher, ", Phys. Rev. B vol.72, 165204 (2004).