The 2013 World Congress on
Advances in Nano, Biomechanics, Robotics, and Energy Research (ANBRE13)
Seoul, Korea, August 25-28, 2013

Magnetic and Structural Properties of Co doped ZnO Nanoparticles

Robina Ashraf[1)], *Saira Riaz[2)], Mahwish Bashir[3)], and Shahzad Naseem[4)]

[1), 2), 3), 4)] *Centre of Excellence in Solid State Physics,*
University of the Punjab, Pakistan
[2)] saira_cssp@yahoo.com

ABSTRACT

Semiconductor materials with dilute doping of transition metals are of great interest in spintronic applications. In order to investigate the magnetic properties of these diluted magnetic semiconductors, Co-doped Zinc Oxide nanoparticles and thin films are prepared by simple, economic and application oriented sol-gel method. Zinc acetate dihydrate and Cobalt nitrate are used as precursor materials. It is worth mentioning here that all the synthesis is carried out at room temperature. Thin films have been deposited by spin coating technique on glass substrates. Cobalt composition is varied in a range from 0-9wt%. The deposited thin films with the thickness of 80nm are then magnetically annealed at 300°C for 1 hour. XRD results show that Cobalt is successfully doped in zinc oxide crystal lattices while preserving the ZnO wurtzite structure. With increasing cobalt concentration peak broadening is observed in (101) peak which is high intensity peak. Surface morphology is studied by SEM and it indicates that the particle size less than 20 nm in case of nanoparticles and wrinkle network like structure with uniform distribution of size is clearly seen in case of thin films. With increasing cobalt concentration size of the nanostructure decreases well. The effect of cobalt doping on magnetic properties of the synthesized nanoparticles and thin films has been investigated by using VSM. Room temperature ferromagnetism is observed in almost all the samples. It is observed that the doping of cobalt plays important role in the presence of ferromagnetism as the difference in the radii of high spin cobalt (0.58 Å) and divalent Zinc (0.60 Å) is small. It is also observed that strong magnetic properties and crystal quality is obtained by doping with 1% to 10% Cobalt in ZnO to obtain diluted magnetic semiconductors while lower doping percentage results in the lower magnetization and higher doping percentage results in the presence of the secondary phase. Interaction of the transition metal (Cobalt in this case) and free carriers results in the ferromagnetism.

1. INTRODUCTION

Diluted magnetic semiconductors have gained much interest in spintronics due to the involvement of both spin and charge (Liang 2009). Practical devices require simultaneous control on spin state and charge of the electrons in semiconductors

[1), 3)] Graduate Student
[2), 4)] Professor

having room temperature ferromagnetism (Li 2012). Among these semiconductors ZnO lightly doped with transition metals (Mn, Fe, Co, Ni, In, V, and Cr) (Anghel 2010, Kang 2013, Hong 2005, 2012, Liu 2009, Liu 2009, Jiao 2011) have gain much interest in spintronics due to the presence of room temperature ferromagnetism. In recent years, tremendous experimental work have been done focusing Cobalt doped Zinc oxide as diluted magnetic semiconductors in order to observe ferromagnetism at room temperature as doping element and doping conditions effects on the required properties. Therefor it is important to know its structural and magnetic properties (Nair 2011).

Room temperature ferromagnetism in cobalt doped Zinc Oxide nanostructures is the topic of interest among various researchers since last few years. Kang (2010) reported that the expected reason of ferromagnetism in co doped ZnO is exchange mechanism in between donor electron of the impurity atoms and Zn lattice. Bound magnetic polaron (BMP) model describe that exchange interaction. Double exchange model and ruderman-kittel-kasuya-yosida (RKKY) interaction are also helpful in giving the explanation of the presence of room temperature ferromagnetism in diluted magnetic semiconductors. Increase in doping level results in the presence of dopant clusters or formation of secondary phases where as these two are also responsible or observable ferromagnetism. Hence, Co doping concentration effected on the composition, crystal orientation, morphology, and magnetic property of ZnO thin films and nanoparticles (Xian 2012). Ahmed (2012) reported the effect of co doping on ZnO nanoparticles. Cobalt doped ZnO is important material for room temperature ferromagnetism as the co showed high thermal stability in ZnO as well as difference in ionic radii between high spin divalent cobalt (0.58 Å) and divalent zinc in tetrahedral coordinate (0.60 Å) is small.

There are various methods described in the literature to synthesise ZnO thin films and nanoparticles, based on techniques like auto combustion, co-precipitation, spray pyrolysis, thermal plasma method, sputtering, and sol-gel method (Ahmed 2012, Shafique 2012, Reddy 2012, Nirmala 2011, Fukuma 2008, Xian 2012). We used sol-gel process as it is a low cost simple method for the synthesis of large number of samples with easier control on composition at low processing temperature. Also by using sol-gel method better homogeneity can be achieved with high solubility along with accurately controlled mole ratio of the precursors. From the point of view of deposition this method has a general advantage for controlled thickness with uniform large area growth of the films (He 2012).

In this research work, we report the synthesis of un-doped and Co-doped ZnO thin films and nanoparticles by simple and economic sol-gel method. Characterization of these samples was done in order to study their morphologies, structural and magnetic properties which indicate successful doping of cobalt in zinc oxide as well as room temperature ferromagnetism by using simple route of sol-gel. Main point to emphasize here is the complete Room Temperature synthesis of undoped and Co-doped ZnO sols.

2. EXPERIMENTAL DETAILS

Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] and Cobalt nitrate [$Co(NO_3)_2.6H_2O$] were used as precursor materials for ZnO sol and Cobalt sol, respectively. Zinc Oxide sol was synthesized by the sol gel method as reported somewhere else by (Riaz 2011).

Cobalt sol was synthesised by mixing cobalt nitrate in deionized water with magnetic stirring for 30 mints. After that cobalt sol was added drop wise to Zinc Oxide sol and after magnetic stirring of 30 mints we get transparent pink sol with pH 6. One set was kept undoped while other nine sets were doped with varying cobalt concentration in the range from 0-9wt%. Thin films of the prepared Co doped Zinc Oxide were prepared by spin coating on glass substrates. Substrates were cleaned by detergent, and then in Isopropanol alcohol and acetone by using ultrasonic cleaner for 15 minutes. Thin films of desired thickness were obtained by coating at 500 rpm for 10 sec. After each coating the film was dried at 45℃ for 10 minutes to evaporate the solvents. This process of drying and coating was repeated several times to get uniform thin films. The process is repeated for each set of Co doped ZnO sol. Fig. 1 show as series of synthesized sols. Whereas, nanopowders obtained from these sols are shown in Fig. 2.

Fig.1 Co doped ZnO sols with variation from x = 0.00 to x = 0.09

Fig. 2 Co doped ZnO nanopowder with variation from x = 0.00 to x = 0.09

Structural and magnetic properties of the prepared thin films and nanoparticles were studied after characterization by Bruker D8 Advance X-Ray diffrectometer. Diffractometer was operated at 35 kV/20 mA, using Cu Kα radiation with wavelength of 1.54056 Å in the Bragg's diffraction angle '2Θ' ranging from 20° to 80°. Hitachi S3400-N Scanning electron microscopy and Lake Shore's 7407 Vibrating sample magnetometer.

3. RESULTS AND DISCUSSIONS

3.1 Structural characterization

XRD patterns of Co doped ZnO thin films with different doping concentrations are shown in fig. 3. All these peaks match with the hexagonal wurtzite structure of ZnO. Co

ions are replaced by the ZnO lattice without changing the wurtzite structure of the ZnO which is also clearly seen from the XRD results as there is absence of peaks representing cobalt metal clusters and as well as for cobalt oxides. With the increase in the Co concentration, preferential orientation along c-axis becomes more and more observable. Effect of Co doping on c-axis orientation of ZnO nanoparticles are very different as reported earlier. Xian (2012) reported the synthesis of Co doped ZnO thin films and also report that c-axis orientation can be improved by Co doping. Growth method in this case is sol-gel. Growth method is important as effects of Co doping on the orientation of ZnO thin films is due to the states of Co ion's in ZnO.

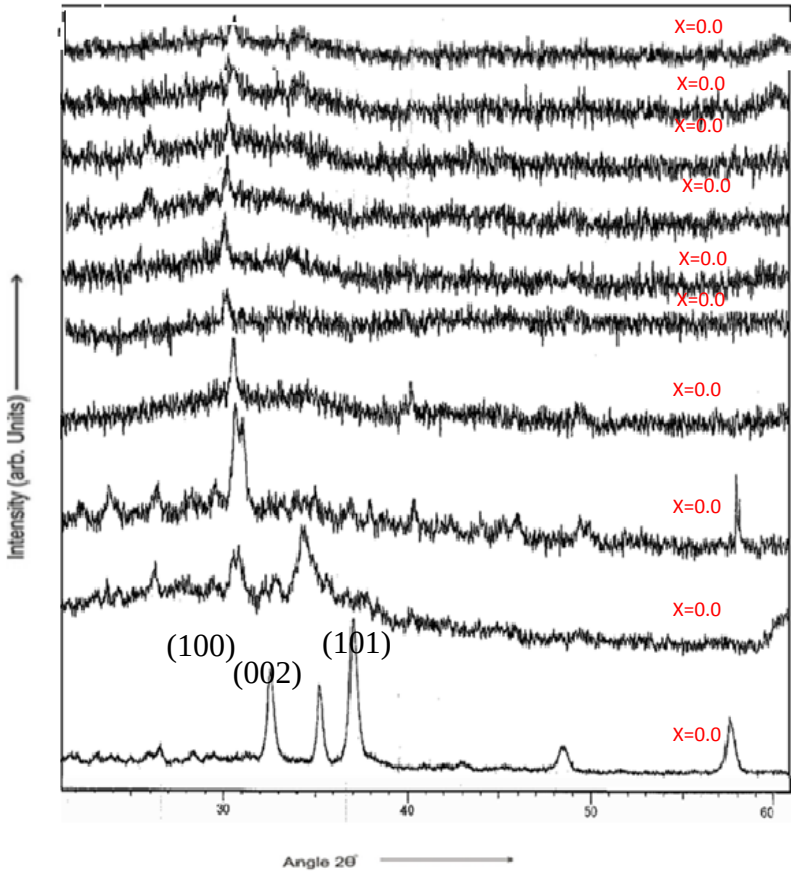

Fig. 3 XRD of the Co doped ZnO Thin films with Co varied from 0-9wt%

3.2 Magnetic Properties

Fig. 4 showed the graphs of magnetization (M) versus magnetic field (H) for Co doped ZnO thin films with variation in Co concentration from x = 0.00 to x = 0.09. The magnetization measurement was performed using Lakeshore 7407 vibrating sample magnetometer at room temperature for all the samples. Obvious ferromagnetism at room temperature for all the films was observed. From Fig. 4 it is also clear that Co doping effect the saturation magnetization as by the increase in the level of Co doping

saturation magnetization also increased. Song (2007) was also reported that the saturation magnetization was increased with the increase in the co doping concentration. The origin of room temperature ferromagnetism in Co doped ZnO thin films were due to two possible reasons. First one is the presence of the Cobalt oxides or the presence of clusters of cobalt metal. The second reason for room temperature ferromagnetism in Co doped ZnO thin films is the successful doping of the Co ions on Zn sites (Ahmad 2012) In our case ferromagnetism is due to the second reason as there is absence of secondary phases showing the presence of cobalt metal clusters and cobalt oxide as in accordance with the XRD results shown in Fig. 3. Hence, co-ordination of the VSM and XRD results showed that the presence of Co ions in ZnO thin films play an important role for the ferromagnetism at room temperature for all the samples. Song (2007) also reported the same reason for the presence of the ferromagnetism and states that random substitution of Co ion into hexagonal wutzite ZnO lattice, bound magnetic polarons are the possible it is possible to form, which may be the origin of room temperature ferromagnetism in co doped ZnO. Li (2012) also reported the presence of paramagnetism in ZnO doped with 10% cobalt but with the increase of doping level from 10% to 20% ferromagnetic behavior is observed.

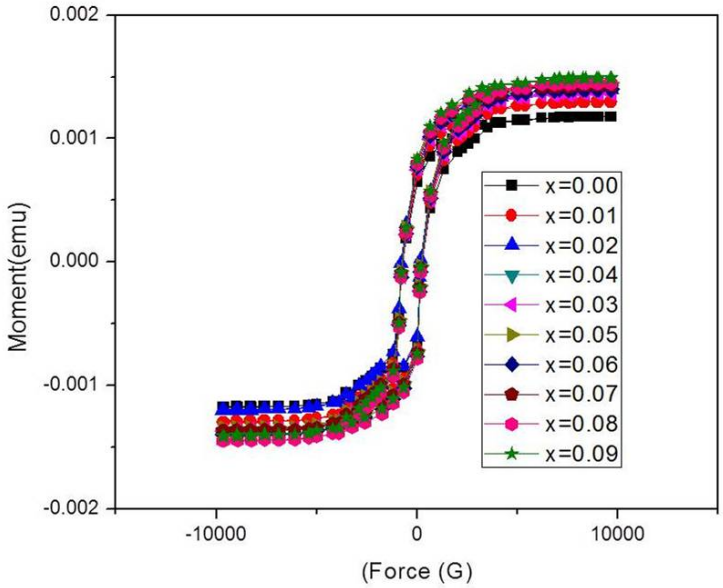

Fig. 4 Magnetic hysteresis loops of Co doped ZnO nanoparticles with variation from x = 0.00 to x = 0.09

4. CONCLUSIONS

Co doped ZnO thin films were successfully synthesized by using low cost sol-gel spin coating Technique and nanopowder was synthesised by centrifugation with variation of doping concentration of Cobalt in Zinc Oxide lattice. Effect of Cobalt doping was studies on structural and magnetic properties. XRD results showed that Co ions were replaced by Zn ions on the ZnO lattice, without changing the hexagonal wurtzite

structure of the ZnO. This also showed that the size distribution is uniform. VSM results showed room temperature ferromagnetism for all samples. The Co doping in ZnO nanoparticles play an important role for the origin of ferromagnetism at room temperature.

REFERENCES

Ahmed, F., Kumar, S., Arshi, N., Anwar, M.S., Koo, B.H. and Lee, C.G. (2012), "Doping effects of Co^{2+} ions on structural and magnetic properties of ZnO nanoparticles", *Microelectron. Eng.,* **89**, 129-132.

Anghel, J., Anghel, J., Thurber, A., Tenne, D.A., Hanna, C.B. and Punnoose, A. (2010), "Correlation between saturation magnetization, bandgap, and lattice volume of transition metal (M = Cr, Mn, Fe, Co, or N) doped $Zn_{1-x}M_xO$ nanoparticles", *J. Appl. Phys.,* **107**, 09E314-09E317.

Fukuma, Y., Odawara, F., Asada, H. and Koyanagi, T. (2008), "Effects of annealing and chemical doping on magnetic properties in Co-doped ZnO films", *Phys*. *Rev*., **78**, 104417.

He, R., Hocking, R.K. and Tsuzuki, T. (2012), "Local structure and photocatalytic property of sol–gel synthesized ZnO doped with transition metal oxides", *J. Mater Sci.,* **47**, 3150-3158.

Hong, N.H., Sakai, J. and Hassini, A. (2005), "Magnetic properties of V-doped ZnO thin films", *J. Appl. Phys.,* **97**, 10D312-10D314.

Jiao, B.C., Zhang, X.D., Wei, C.C., Sun, J., Huang, Q. and Zhao, Y. (2011), "Effect of acetic acid on ZnO:In transparent conductive oxide prepared by ultrasonic spray pyrolysis", *Thin Solid Films,* **520**, 1323-1329.

Kang, S., Kim, Y., Kim, S.E. and Kim, S. (2013), "The effects of heat treatment on room temperature ferromagnetism in a digitally Co Doped ZnO thin film", *Electron. Mater. Lett.,* **9**, 7-11.

Li, L., Guo, Y., Cui, X.Y., Zheng, R., Ohtani, K., Kong, C., Ceguerra, A.V., Moody, M.P., Ye, J.D., Tan, H.H., Jagadish, C., Liu, H., Stampfl, C., Ohno, H., Ringer, S.P. and Matsukura, F. (2012), "Magnetism of Co-doped ZnO epitaxially grown on a ZnO substrate",, *Phy. Rev.,* **85**, 174430.

Liang, W., Yuhas, B.D. and Yang, P. (2009), "Magnetotransport in Co-Doped ZnO Nanowires", *Nano Lett.,* **9**(2), 892-896.

Liu, H., Yan, J., Zhang, Y., Yang, L., Wei, M. and Ding, X. (2009), "Structure and magnetic properties of Fe-doped ZnO prepared by the sol–gel method", *J. Phys. Condens. Matter.,* **21**, 145803-14580.

Liu, Y., Yang, J., Guana, Q., Yang, L., Zhang, Y., Wang, Y., Feng, B., Cao, J., Liu, X., Yang, Y. and Wei, M. (2009), "Effects of Cr-doping on the optical and magnetic properties in ZnO nanoparticles prepared by sol–gel method", *J. Alloy Compd.,* **486**, 835-838.

Murugesan, N. and Achuthanunni, A. (2010), "Structural and optical properties of undoped and Co doped Zno nanostructured thin films", *J. Sci. Technol.,* **18**(1), 81-88.

Nair, M.G., Nirmala, M., Rekha, K. and Anukaliani, A. (2011), "Structural, optical, photo catalytic and antibacterial activity of ZnO and Co doped ZnO nanoparticles", *Mater. Lett.,* **65**, 1797-1800.

Nirmala, M., Smitha, P. and Anukaliani, A. (2011), “Optical and electrical properties of undoped and (Mn, Co) co-doped ZnO nanoparticles synthesized by DC thermal plasma method”, *Superlattice. Microst.*, **50**, 563-571.

Reddy, K.T.R., Supriya, V., Murata, Y. and Sugiyama, M. (2012), “Effect of Co-doping on the properties of $Zn_{1-x}Co_xO$ films deposited by spray pyrolysis”, *Surf. Coatings Technol.*, **12**, 234-238.

Riaz, S., Naseem, S. and Xu, Y.B. (2011), “Room temperature ferromagnetism in sol–gel deposited un-doped ZnO films”, *J. Sol-Gel Sci. Technol.,* **59**, 584-590.

Shafique, M.A., Shah, S.A., Nafees, M., Rasheed, K. and Ahmad, R. (2012), “Effect of doping concentration on absorbance,structural, and magnetic properties of cobalt-doped ZnO nano-crystallites”, *Int. Nano Lett.,* **2**, 31.

That, C., Foley,M., Phillips, M.R., Tsuzuki, T. and Smith, Z. (2012), “Correlation between the structural and optical properties of Mn-doped ZnO Nanoparticles”, *J. Alloy. Compd.,* **522**, 114-117.

Xian, F.L., Xu, L.H., Wang, X.X. and Li, X.Y. (2012), “Crystallographic, optical and magnetic properties of Co-doped ZnO thin films synthesized by sol gel route”, *Cryst. Res. Technol.,* **47**(4), 423-428.