Mg doped ZnO Dilute Magnetic Oxides Prepared by Chemical Method. Mg doped ZnO Dilute Magnetic Oxides Prepared by Chemical Method

Article · April 2020

CITATIONS
3

READS
125

6 authors, including:

Akhil Maru
University of Tuebingen
3 PUBLICATIONS **6** CITATIONS
SEE PROFILE

Hrishikesh Kamble
Ramnarain Ruia College
5 PUBLICATIONS **6** CITATIONS
SEE PROFILE

Abhishek Kalarikkal
Somaiya Vidyavihar
5 PUBLICATIONS **32** CITATIONS
SEE PROFILE

Pratik Bhanuse
4 PUBLICATIONS **6** CITATIONS
SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Mg doped ZnO dilute magnetic semiconductor View project

Mg doped ZnO Dilute Magnetic Oxides Prepared by Chemical Method.

A.H. MARU[1], H. KAMBLE[1], A. KALARIKKAL[1], R. SHAH[1], P. B. BHANUSE[2], N. PRADHAN[1, a].

[1]Department of Physics, Ramnarain Ruia College, Mumbai, Maharashtra, India
[2]School of Mathematical Sciences, University of Nottingham, Nottingham, United Kingdom
Corresponding Author: nana.pradhan@gmail.com

Abstract

Mg doped ZnO dilute magnetic semiconductors prepared by chemical method for various doses from 1% to 5%. ZnO and Mg doped ZnO samples were characterized using XRD, SEM and SQUID techniques to study the structural, morphological and magnetic properties respectively. The XRD data of ZnO sample showed the peaks at 31.42^0, 34.16^0, 36^0, 47.46^0, 56.38^0, 62.66^0, 67.76^0 and 76.94^0 corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (112) and (202) respectively. The intensity of these peaks was found to be reducing with doping percentage. FWHM of samples varies with the doping percentage. SQUID technique showed ferromagnetic behaviors of all doped samples. The Curie temperature for doped samples showed ferromagnetism above room temperature. SEM technique showed the nano rods in the samples and size of nanorods were found to be in the range of 20-50 nm. As the doping is increased, agglomeration in ZnO takes place which changes its shape of nanorods.

Keywords Ferromagnetism, Mg doped ZnO, XRD, SQUID and SEM.

Introduction

Zinc Oxide (ZnO) is one of the most promising materials for spintronics devices, and other applications such as solar cells, Optoelectronics, laser systems etc. Since it has a high mechanical and thermal stability, and wide band gap (3.37 eV) with excitonic energy of 60meV [1-3].Spintronics devices require materials which have ferromagnetism well above room temperature, which means that the Curie temperature of the materials has to be greater than 300K. The dilute magnetic semiconductors (DMSs) are prepared such that they will have ferromagnetism at room temperature by introducing the atoms of the magnetic material into the host lattice which are mainly metal oxides. Semiconductor nanoparticles show unique size dependent optical properties due to quantum confinement effect [4].The properties of ZnO has been studied for various application such as ultraviolet (UV) light emitters, spin functional devices, gas sensors, transparent electronics, and surface acoustic wave devices. Synthesis of ZnO nanorods, n-type conductivity showed by ZnO due to residual hydrogen and application of ZnO in spintronics has been studied [5]. ZnO can be used for various applications and it has been doped with Al to study the electronic, electrical and structural properties. It was prepared using quantum-chemical approach and n type electrical conductivity was found due to the large radius electron polaron and the increase in the band gap was found [6]. Using various dopant different properties of ZnO are studied, ZnO N films were prepared by doping Nitrogen (N) in ZnO by reactive RF sputtering of a zinc metal target with different oxygen partial pressures method studied the electrical properties and defects in ZnO [7].DMSs have also been prepared by solution phase method in which ZnO doped with Cobalt (Co^{2+}) and Manganese (Mn^{2+})

showed ferromagnetic properties at room temperature. It has found that the synthesis conditions affect the magnetic behaviour of the doped ZnO and magnetism depended on the solvent used [8].Li-Doped ZnO prepared dilute magnetic semiconductor using pulse laser deposition method were found that the ferromagnetism in DMS, it is due to the cation vacancies and it can be used to tune the magnetic properties [9].Amongst the possible competing techniques, the chemical route method offers many advantages for the deposition of thin Mg doped ZnO film, such as customizable, microstructure, ease to compositional modifications, minimum variables to control the growth of film, simple and inexpensive equipment, and most important, the possibility of coating on large area substrates [10-11].
In this work, Mg doped ZnO dilute magnetic semiconductors prepared using chemical method. Magnetic properties were studied using SQUID technique and morphological and structural properties were studies using SEM and XRD techniques respectively.

Experimental Work

Magnesium doped ZnO were prepared with two separate procedures; firstly, $ZnSO_4$ and NaOH (to prepare ZnO) and then $MgSO_4$were added to introduce the doping agent Mg in the ratios of Zn Mg as 1001, 1003 & 1005 (as per weight of ZnO).0.1M of $ZnSO_4$ in 100ml of distilled water and solution of 0.2M of NaOH in 100ml of distilled water was kept for stirring on a magnetic stirrer for 30 min after which the $ZnSO_4$ solution was added drop wise to the NaOH solution with the latter still on magnetic stirrer which gives a white precipitate which is the resultant ZnO, now 0.1mM $MgSO_4$ is added to resultant solution and kept for stirring for 1 hour. As the doped precipitate solution is ready, it is transferred to tarsons tubes and centrifuged and filtered using filter paper; this filtered precipitate is heated in oven for 1 hour at 100^0 C. The solid layer of precipitate was grinded. Some part of grinded powder was kept for incineration in an incinerator for 1 hour at 250^0 C. Pristine ZnO, annealed and non-annealed samples doped with various percentages from 1 to 5 % Mg were characterized using XRD, SQUID and SEM techniques. SEM and SQUID techniques were carried out at Tata Institute of Fundamental Research,Mumbai. Morphological studies were performed using models ULTRA plus FESEM from ZEISS INCA Energy eEDS with pentafet detectors from OXFORD instruments and magnetic properties were studied using model SQUID 7 Tesla Quantum Design Mec MPMS 3 (QDUSA) in vibration mode. XRD technique was performed at Mumbai University which has model RIGAKU No.5020289, UltimaIV with wavelength of 0.1540nm.

Results and Discussions

XRD Studies

Fig 1 a. shows the XRD characterization of the samples for various doping percentages. The reflection peaks were observed from the graph are at angles 31.41, 34.16, 36.00, 47.36, 56.38, 62.66, 67.76 which corresponds to the lattice planes (100), (002), (101), (102), (110), (103), (112) respectively for the pristine sample [2,12]. As the percentage of Mg is increased in the ZnO the Intensity peaks were found to be decreased. The line broadening for the doped samples was found to be decreasing which is because of the uniform strain caused by dislocation of the atoms due to doping.The crystal structure of the ZnO was confirmed to be wurtzite structure [13]. The average crystallite size were found using Scherer Equation 1 given as [12],

$$d = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

It is also observed that the peak (101) reflection shifted to increasing 2□ by 0.02 degree in 3% Mg doped ZnO and 0.06 degree in 5% Mg doped ZnO. This indicates that Mg has either been substituted in the ZnO crystal or it has been placed interstitially. Due to the doping, the peaks shifted to the higher angle which depicts that there was strain produced in the crystal structure due to Mg.The lattice parameters for 1% Mg doped ZnO is a = 0.283 nm and c = 0.490 nm, for 3% annealed Mg doped ZnO is a=0.269nm and c=0.398nm, for 5% annealed Mg doped ZnO is a=0.266nm and c=0.385 nm and for the pristine sample it is a=0.27nm and c=0.389 nm which is slightly less due to the impurities present in the sample[3].The XRD parameters estimated shown in Table-I, it is revealed from the table-I that the size of doped samples is increased as the doping is increased.

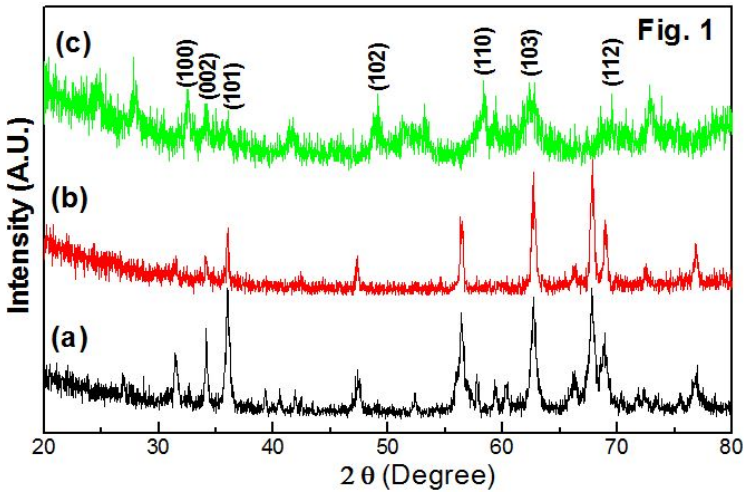

Figure1**.** XRD pattern for; (a) Pristine ZnO, (b) 3% Mg doped ZnO and (c) 5% Mg doped ZnO.

Table I. Estimated values for pristine ZnO and Mg doped samples; Intensity, FWHMat reflection (101) from XRD and diameter of nanorods.

Sample	Intensity (A.U)	FWHM (degree)	Size (nm)
Pristine ZnO	475.0	0.366	22.82
1% Mg	10423.3	0.549	17.06
3% Mg	195.8	0.187	44.66
5% Mg	112.5	0.196	42.62

SQUID Studies

Figure 2(a) - 2(b) shows the M-H curves at 339 K for ZnO samples doped with 3% and 5% respectively. It is observed from Fig. 2 that the magnetic properties for 3% Mg doped sample showed increased magnetization than that of 5% Mg doped sample. The magnetic properties estimated from the curves

shown in Table II. It is also observed that the magnetic properties such as remanence, saturation magnetization and coercivity field found to be decreasing with increase in temperature.

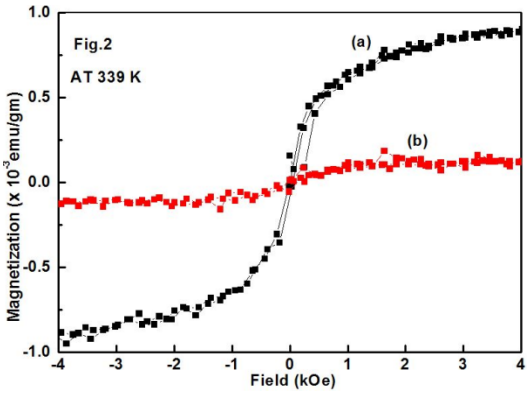

Figure2.Magnetization versus field (M-H) curves of ZnO samples doped with Mg; (a) 3% and (b) 5%

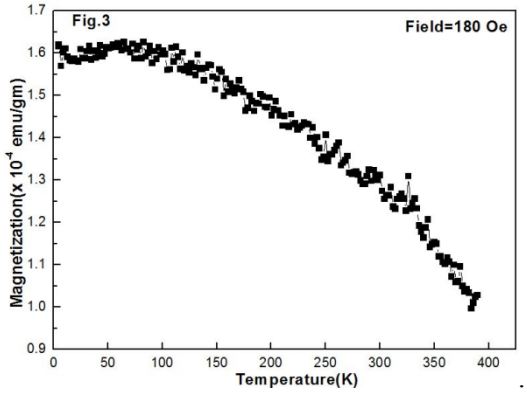

Figure3. Magnetization versus temperature (M-T)curve of ZnO sample doped with 3% Mg.

Figure 3 shows the M-T curve for ZnO doped with 3% of Mg. It is observed from the fig. 3 that the sample 3% Mg doped ZnO showed magnetization till 400 K. The extension of this curve intercepts at temperature axis showed Curie temperature at 423 K. however, pristine ZnO is paramagnetic at room temperature [8] and after doping with Mg it was found to be ferromagnetic at room temperature (fig. 3) [11]. The increase in the Curie temperature is due to the polarons surrounding the magnetic Mg ions in the ZnO crystals which leads to the Ferromagnetic nature of ZnO at room temperature [14].

Table II. Estimated values of remanence magnetization, coercivity field and saturation magnetization for Mg in ZnO samples at temperature 339K.

Samples	Remanence (R_m) (emu/gm)	Coercivity (H_c) (kOe)	Saturation magnetization (M_s)(emu/gm)
3% Mg doped ZnO	2.284×10^{-5}	0.00814	1.05×10^{-3}
5% Mg doped ZnO	1.805×10^{-6}	0.01148	1.049×10^{-4}

SEM Studies

Figure 3(a) – 3(e) shows the SEM scans at 20 nm of pristine ZnO, ZnO doped with 1%,3 %, 5% Mg and EDX of 3% Mg doped ZnO samples respectively. The surface properties of ZnO found to be influenced due to incorporation of dopant [13]. Especially the amount and kind of dopant played an important role on the surface properties. Impurities such as sulphur, aluminium and silicon were found. The size of nanorods of Mg doped ZnO samples were found in ranges from 20-50 nm [Table-I] [15].As the concentration of Mg in ZnO is increased, agglomeration of nanorods was observed [3].

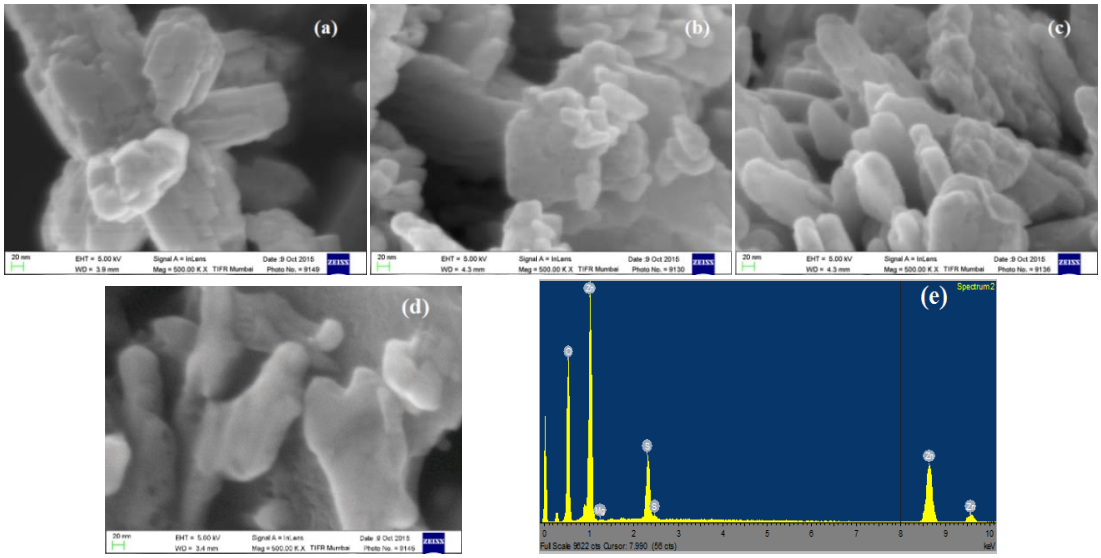

Figure 3 SEM scans of ZnO for Mg doping percentages at 20 nm; (a) Pristine ZnO, (b) 1 %, (c) 3 %, (d) 5% and (e) EDX of ZnO doped with 3 % Mg.

Conclusions

Mg doped ZnO have been prepared by chemical method. The prepared ZnO was found to have Wurtzite crystal structure. The crystallite size of ZnO and the doped samples were in the range of 20-60 nm from XRD studies. There was no deformation in the structure due to doping. Increase in the concentration of Mg lead to the agglomeration in the doped sample. From SEM results, the crystallite size was found to be in the range 20nm-50nmwhich is in accordance with the XRD results. Due to doping with Mg, the intensities of the peaks varied with the different percentages of doping as observed in XRD results. As ZnO being paramagnetic at room temperature, on doping with Mg it showed ferromagnetic properties at room temperature.

Acknowledgements

We thank Dr. P. A. Sathe, Head, Department of Chemistry, Ruia College,Mumbai for synthesis support, Dr. S. K. Dubey, Department of Physics, Mumbai University, Mumbai and Prof. Paulose, Tata Institute of Fundamental Research (TIFR) for their help in samplecharacterization techniques.

References

[1] N. Kılınç, L. Arda, S. Öztürk, and Z. Z. Öztürk,"Structure and electrical properties of Mg-doped ZnO Nanoparticles", Cryst. Res. Technol. 45, No.5, 2010,529-538.

[2] R. Viswanatha, T.G. Venkatesh, C.C. Vidyasagar, Y. ArthobaNayaka, "Preparation and Characterization of ZnO and Mg-ZnO nanoparticle",Archives of Applied Science Research, 4 (1), 2012, 480-486.

[3] R.Viswanatha, Y. ArthobaNayaka, C. C. Vidyasagar and T. G. Venkatesh, "Structural and optical properties of Mg doped ZnO nanoparticles", Journal of Chemical and Pharmaceutical Research, 4(4), 2012, 1983-1989.

[4] RathinamChandramohanPillai, ThirukondaAnandhaVijayan and JagannathanThirumalai, "Growth of Undoped and Metal Doped ZnO Nanostructures by Solution Growth", Nano crystals,2010,Yoshitake Masuda 978-953 - 307-126-8.

[5] D.P. Norton, Y.W. Heo, M.P. Ivill, K. Ip, S.J. Pearton , M.F. Chisholm, T. Steiner, "ZnO growth, doping & processing", Materials Today, 7(6),2004, 34-40.

[6] Frank Maldonado, ArvidsStashans, "Al-doped ZnO Electronic, electrical and structural properties", Journal of Physics and Chemistry of Solids, 71(5),2010, 784-787.

[7] Se-Hee Lee, Yanfa Yan, Seokhyun Yoon, Craig Perkins, Edwin Tracy, and J. Roland Pitts, "Effective Nitrogen Doping of Zinc Oxide", Electrochemical Society Proceedings, Volume 2004-06, 312-315.

[8] G. Clavel, M.-G.Willinger, D. Zitoun, N. Pinna, "Solvent dependent shape and magnetic properties of doped ZnO Nanostructures", Advanced Functional Materials, 17, 2007, 3159-3169.

[9] Sreekanth K. Mahadeva, Zhi-Yong Quan, Jin-Cheng Fan, Hasan B. Albargi, Gillian A Gehring, Anastasia, et al., "Room Temperature Ferromagnetism and Band Gap Engineering in Mg Doped ZnO RF/DC Sputtered Films", Material Research Society Symposium Proceedings, 1577, 2013, 509.

[10] J. B. Yi, C. C. Lim, G. Z. Xing, H. M. Fan, L. H. Van, S. L. Huang, et al., "Ferromagnetism in Dilute Magnetic Semiconductors through Defect Engineering Li-Doped ZnO", Physical Review Letters, 104(13), 137201, 2010.

[11] Amanpal Singh,D. Kumar, P. K. Khanna, Anuj Kumar and Mukesh Kumara,"Dielectric Anomaly in Mg Doped ZnO Thin Film Deposited by Sol–Gel Method", Journal of The Electrochemical Society, 158(1),2011, G9-G12.

[12] Amritpal Singh, Rajesh Kumar, Mrs. NeeruMalhotra and Suman, "Preparation of ZnO nanoparticles by sol gel thermal process", International Journal for Science and Emerging Technologies with latest Trends, 4(1),2012,49-53.

[13] Chien-YieTsay, Min-Chi Wang and Shin-Chuan Chiang, "Effects of Mg Additions on Microstructure and Optical Properties of Sol-Gel Derived ZnO Thin Films", Materials Transactions, Vol. 49, No. 5,2008, 1186 – 1191.

[14] Rathinam Chandramohan, JagannathanThirumalai and Thirukonda Anandhamoorthy Vijayan, "NanocrystallineMn and Fe Doped ZnO Thin Films Prepared Using SILAR Method for Dilute Magnetic Semiconductor Application", Materials Science - Advanced Topics, Prof. Yitzhak Mastai (Ed.), 978-953-51-1140-5, 2013, InTech, 10.5772/54327.

[15] Surya PrakashGhosh, "Synthesis and Characterization of Zinc Oxide Nanoparticles by Sol-gel Process", National Institute of Technology, Rourkela, 410PH2126, 2012.