Band Gap Tunability of Manganese (Mn) Doped ZinC Oxide (ZnO) Thin Film Nanoparticles

[1]Anup Kr. Kalita

[1]Senior Scientific Assistant
[1]Directorate of Forensic Science, Kahilipara, Guwahati-19
[1]anup1982.2015@rediffmail.com

Abstract: The optical properties of Manganese (Mn) doped ZnO nanoparticles prepared by chemical bath deposition technique at different molarities have been reported. Average particle sizes of Mn doped ZnO are found to be 33.4 nm, 35.2 nm and 22 nm at 473K at molarities 0.025M, 0.05M and 0.1M. Due to calcinations at 523K average particle size increased to 48 nm, 57 nm and 32 nm at the already mentioned molarities. The band gap of the prepared nanoparticles is calculated using UV-Vis Absorption spectroscopy. The band gap is found to decrease with increase in molarity as well as with increase in calcination. Because of different doping percentages the band gap of ZnO nanoparticles are decreased which may be applied for tunning of band gap of ZnO nanoparticles with Mn doping and can be applied for designing of various devices.

***Keywords*— Band Gap, Optical properties, Chemical Bath Deposition, Molarity.**

Introduction:

Polycrystalline ZnO doped with Manganese (Mn) with general formula MnZnO is applicable in medical diagnostic, sensors technology, microwave technology and antibacterial activity (1). Hence study of the effect of Manganese (Mn) doping on Zinc Oxide have attracted researcher in terms of particle size and optical properties. has been very important due to their potential response in transistors, LEDs and Non-volatile memory . From literature it has been found that ZnO is a wide band gap semiconductor with band gap 3.37 eV and large exciton binding energy 60 meV (2). During doping some of the Zinc ions can be replaced by Manganese ions. Therefore the Mn doped ZnO will be Ferromagnetic one . Doping of Metal can change band gap energy (E_g) of ZnO. Grain size of ZnO is controlled by the dopants . Therefore variation of optical, structural properties of ZnO [2] comes into effect. Surface defect of ZnO increases with the doping of transition metal. Again the structural and optical properties of the doped ZnO shift optical absorption edge. Numbers of processes are applied to synthesize Mn doped ZnO like Pulsed Laser Deposition [4], solid-state reaction etc. But all these methods can be applied only at high temperature, which makes the synthesis process more complex and costlier. Therefore we applied the Chemical Bath Deposition (CBD) technique which is more attractive due to the ability to maintain purity, crystallinity and low cost for large scale deposition for the fabrication of Mn doped ZnO. Manganese doped ZnO have got more importance now-a-days due to the structural and optical properties exhibited by it.

Experimental procedure:

Here Zinc Acetate Dihydrate $(CH_3COO)_2Zn.2H_2O$ of 0.025M, 0.05M and 0.1M solutions are stirred constantly for 1 hour at 343K. Now NaOH is slowly added drop by drop into the solution of Zinc Acetate Dihydrate and stirred at room temperature for half an hour and white solutions are obtained. Again to prepare Manganese (Mn) dopped ZnO we prepare Manganous Acetate solution separately of three different concentration 0.025M, 0.05M and 0.1M and mixed with the solutions of Zinc Acetate dihydrate and PVA of same molarity. In this resultant solution, already cleaned glass substrates are dipped for 24 hours. After 24 hours the glass substrates are removed from the final solutions and allowed to dry at room temperature. The characterization is done for as deposited and annealed films. The sample is annealed in order to improve the crystallinity as well as to clean the surface from probable absorbed impurities . Here we have annealed the Manganese doped ZnO at 473K and 523K respectively.

Characterization methods:

X-ray diffraction analysis

Manganese doped Zinc Oxide thin films prepared at room temperature and annealed at 473K and 523K respectively. The Manganese doped ZnO nannaoparticles are of amorphous nature at room temperature. On subsequent annealing at 473K and 523K the nanoparticles become crystalline and the XRD pattern is shown in Fig. 1 and Fig.2.

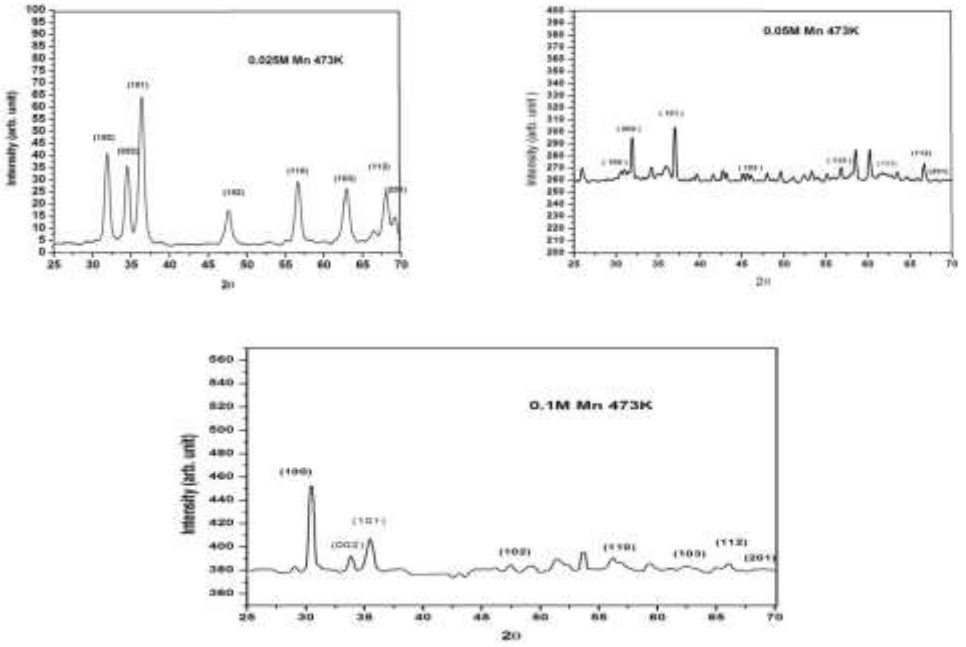

Figure 1. XRD pattern of Manganese doped ZnO nanaoparticles of molarity 0.025M, 0.05M and 0.1M at 473K

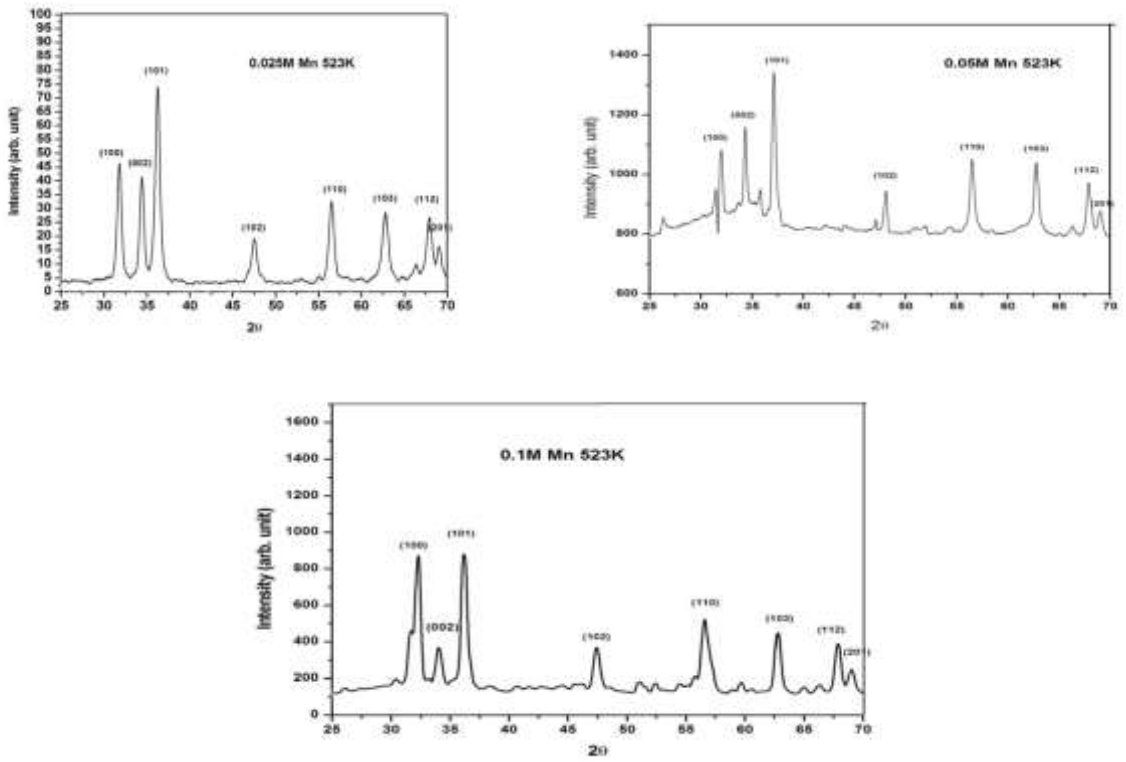

Figure2. XRD pattern of Manganese doped ZnO nanaoparticles of molarity 0.025M, 0.05M and 0.1M at 523 K.

From the above diffractograms it is seen that the peak positions are slightly shifted as that of undoped ZnO nanoparticles prepared at same temperature. The shifting of the peaks is due to the Mn doping effect. As the doping percentage is increased from 0.025M to 0.05M and 0.1M, some extra peaks are developed which are from Manganese oxide and those peaks are not indexed. In Figure.2 some Zn sites are replaced by Mn and all the peaks are prominent and no other peak from other species is observed. Doping leads to both peak shift and changes in intensity due to the difference in size of the atoms and cause the repeat distances in the crystal structure to expand or contract depending on whether the doped atom is larger or smaller than the host atom. The peak intensity is increased with increase in molarity and annealing temperatures but as the doping percentage is changed the peak centres are also changed. Due to shifts of the diffraction peaks small changes are observed in the length of the lattice axes of the prepared nanoparticles. It has been observed that with the increase in concentration the intensity of peaks are increased to 523K from 473K. This variation in peak intensity directly shows the impact of doping concentration on surface texture of

the nanoparticle. The intensity of various diffraction peaks is different, which confirms the anisotropic growth of ZnO nanoparticle. The crystalline quality has been degraded with increase in doping concentration. Due to annealing the crystalline quality has been improved and it has been observed that there is increase in intensity for the sample of different molarity which suggests that crystalline quality has improved again. The different results of the above experiments are due to the different distribution of Mn ions on ZnO thin films. No diffraction peaks from other species could be observed which indicates that no structural deformation occurred in ZnO lattice due to Manganese (Mn) doping. It summarizes that Mn has been successfully substituted in Zn lattice sites in ZnO matrix. The sharp peaks indicate that the products are well crystallized. X-ray peak intensities are weak and broad compared to bulk sample of ZnO, suggesting the small crystalline size. By using Scherrer formula the Average particle sizes of Mn doped ZnO are found to be of the order of 33.4 nm, 35.2 nm and 22nm at 473K at molarities 0.025M, 0.05M and 0.1M. Due to calcinations at 523K average particle size increased to 48 nm, 57 nm and 32 nm at the already mentioned molarities.

UV-Vis Study

UV-Visible Absorption spectroscopy is a very important technique for the investigation of energy band gap and optical properties of nanocrystals. The band gap energy of Mn doped ZnO is estimated from the graph of hν versus $(\alpha h\nu)^2$ through the absorption coefficient α which is related to the band gap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where hν is the incident light energy and k is constant. Figure 3. , Figure.4 and Figure.5 shows the plots of $(\alpha h\nu)^2$ Vs hν for 0.025 M, 0.05 M and 0.1 M at RT, 473K and 523K respectively.

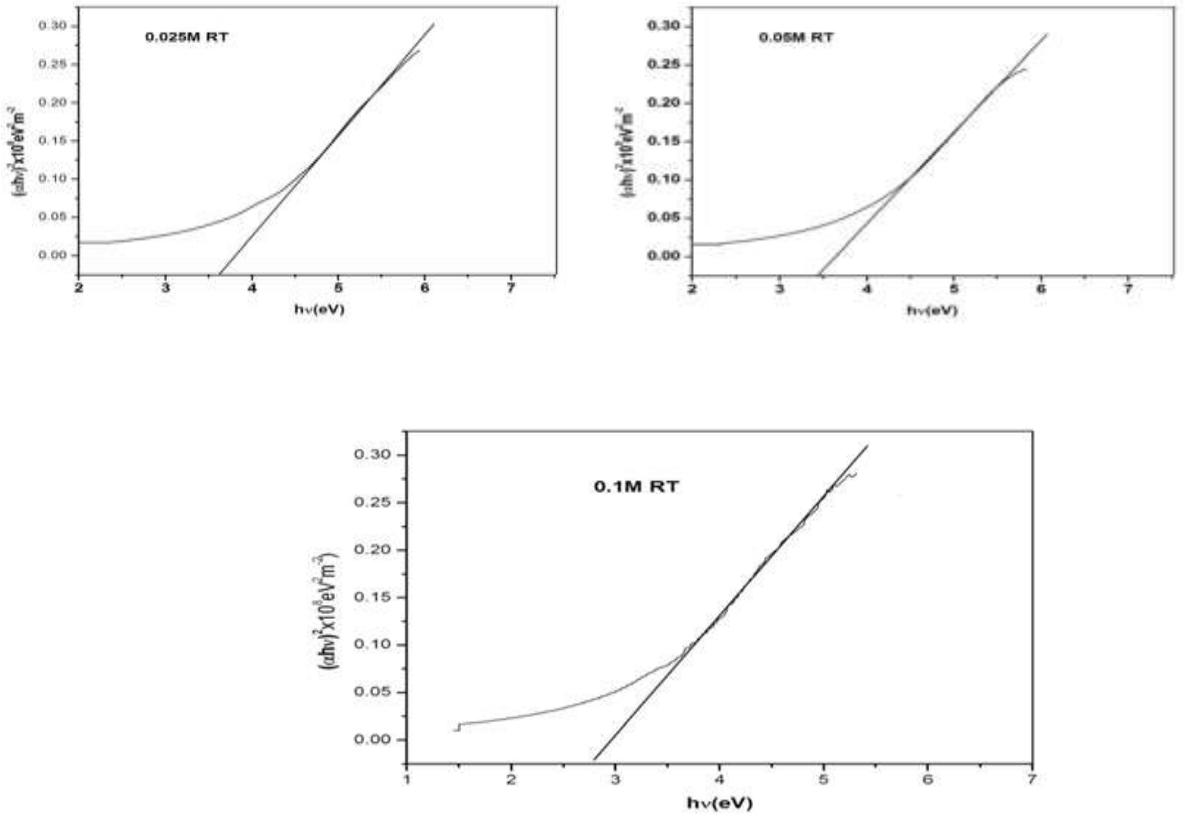

Fig. 3 Tauc plot between hν Vs $(\alpha h\nu)^2$ of Mn doped ZnO thin film nanoparticle of 0.025M. 0.05M and 0.1M at RT.

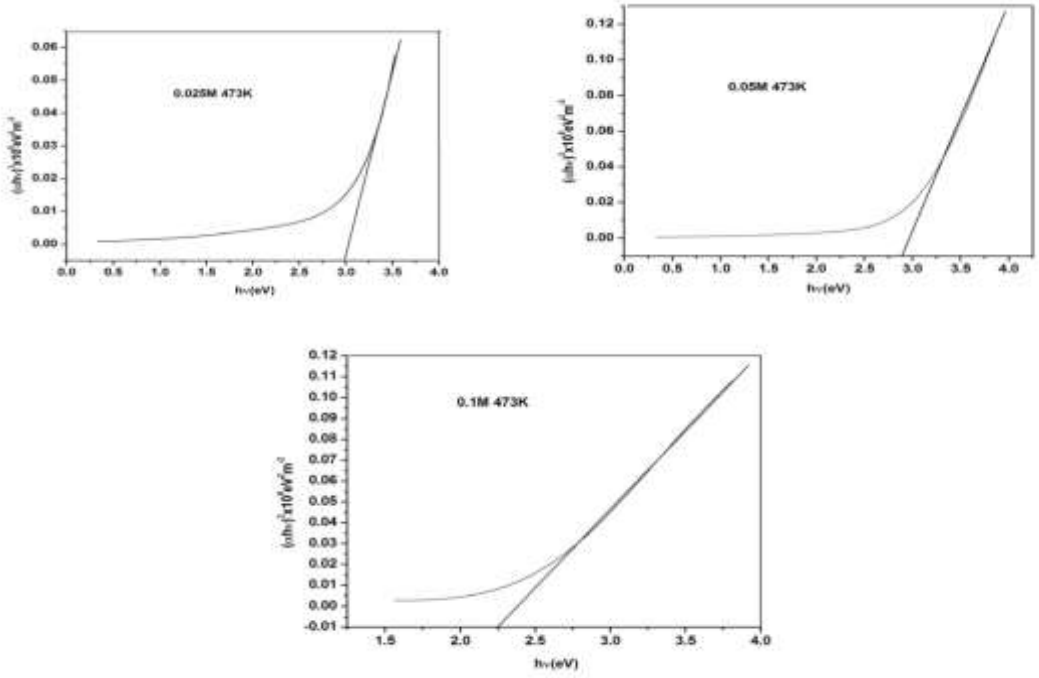

Fig. 4 Tauc plot between hν Vs $(\alpha h\nu)^2$ of Mn doped ZnO thin film nanoparticle of 0.025M, 0.05M and 0.1M at 473 K.

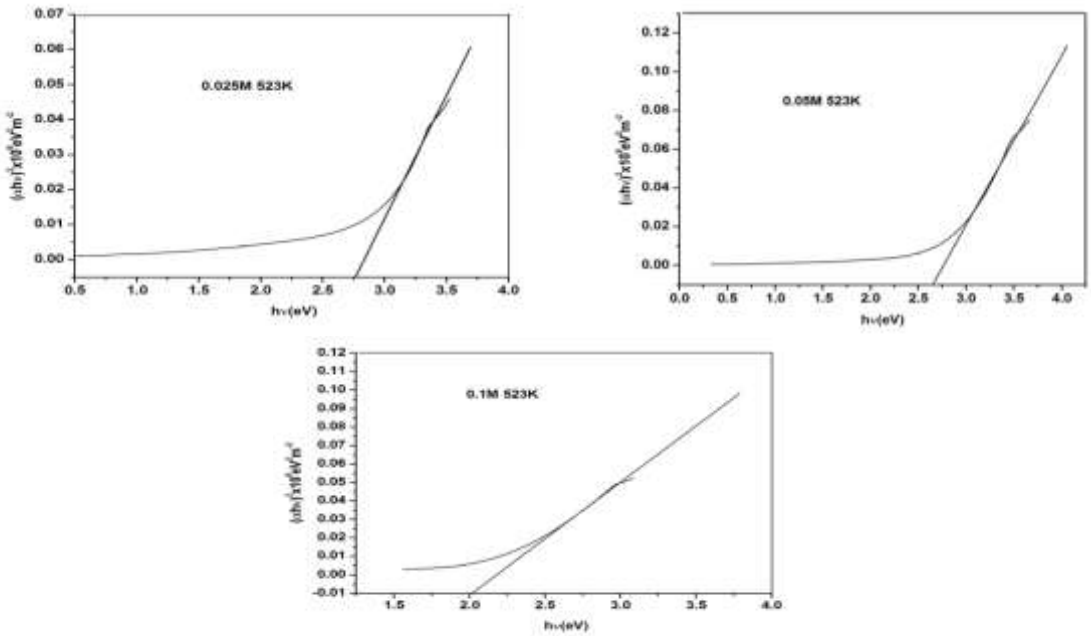

Fig. 5 Tauc plot between hν Vs $(\alpha h\nu)^2$ of Mn doped ZnO thin film nanoparticle of 0.025M, 0.05M, 0.1M at 523 K.

Table 1. Band Gaps of Mn doped ZnO at different molarity prepared at RT and annealed at 473K and 523K

Molarity(M)	Temperature(K)	Band Gap(eV)
0.025	RT	3.64
	473	2.98
	523	2.76
0.05	RT	3.43
	473	2.88
	523	2.65
0.1	RT	2.79
	473	2.25
	523	2.1

The linear nature of the plots give the idea of the direct transition and thus the prepared Manganese doped ZnO thin film nanoparticles comes in the group of direct band metal oxide. The band gaps are determined by extrapolating the straight line of the graph to the energy axis. The intercepts on energy axis gives the values of the band gap energies of all the samples. The optical band gaps are found to be size dependent and the band gap decreases as the particle size increases. The optical band gaps obtained from Figure.3, Figure.4 and Figure.5 are shown in Table1. The UV-Visible absorption study shows the optical band gap of Manganese doped ZnO decrease with increase in doping concentration as well as with increase in cacination temperature. The optical band gap at 0.025 M and 0.05 M at room temperature (RT) is found to be 3.64 eV and 3.43 eV which are greater than the bulk one (3.3eV). This concludes that a blue shift is shown by the nanoparticles at 0.025 M and 0.05 M. But 0.1 M band gap at RT is found to be 2.79 eV which confirms the red shift of the nanoparticle. This may be due to the presence of defects and vacancy present in the crystal structure and generating a new energy level which reduces the band gap energy [7]. Again absorption increases with increase in annealing temperature . The optical band gap of Mn doped ZnO nanoparticles increases from their bulk value with decrease in particle size.

Conclusion:

Mn doped ZnO nanoparticles have been prepared chemical bath deposition technique at doping percentage 0.025M, 0.05M and 0.1M at room temperature followed by calcination at temperature 473K and 523K respectively. Average particle sizes of Mn doped ZnO are found to be of the order of 33.4 nm, 35.2 nm and 22nm at 473K at molarities 0.025M, 0.05M and 0.1M. Due to calcinations at 523K average particle size increased to 48 nm, 57 nm and 32 nm at the already mentioned molarities.. The optical band gap of Mn doped ZnO thin film nanopareticles are found to be 3.64 eV, 2.98 eV, 2.76 eV at 0.025M at RT, 473 K and 523 K. With increase in molarity to 0.05 M band gap changes to 3.43 eV, 2.88 eV, 2.65 eV at 0.05 M at RT, 473 K and 523 K. Again at 0.1 M band gap shifts to 2.79 eV, 2.25 eV and 2.1 eV at 0.1 M at RT, 473 K and 523 K. Thus optical band gap is found to decrease with increase in molarity as well as with increase in calcination temperature. Because of different doping percentages the band gap of ZnO nanoparticles are decreased which may be applied for tunning of band gap of ZnO nanoparticles with Mn doping and can be applied for designing of various devices.

References:

1. K. Rekha, A. Anukaliani, Condensed Matter Electronic structure and magnetism of the Heusler alloy Mn2NiAl: A theoretical study of the shape–memory behavior. *Physica B* 2010, 405-15.
2. De paiva, J. A. C. Graca, M.P.F. Monteiro, J. Macedo, M.A. Valente, M.A. Niobium Oxide prepared by sol gel using poder coconut water J. Alloy Compd., 2009, 485, 637-641.
3. Verkey A Fort A F *Thin Solid Films* Vol (239) pp 211 1994
4. Behnajady, M.A., Modirshahla, N., Shokri, M., Zeininezhad, A, and Zamani, H. A. Synthesis of Iron doped Zinc Oxide by simple heating *Journal of Environmental Science and Health, Part A. Toxic/ Hazardous Substances and Environmental Engineering*. Vol. (44), No. 7, pp.666-672.
5. T, Dietl, H. Katayama- Yoshida, *Semi. Sci. Technol.*17, 367 (2002).
6. Adler, D. and Feinlieb, Electricaland Optical properties of narrow band material *J. Phys. Rev*. (1970) B. 2, 3112.
7. Bora A, Sarma K.C., Optical properties of cobalt doped Zinc Oxide material *IJST* 8 (**12**) 2015.