Synthesis and characterization of Mn composition effect on CdSe thin films

Sarika Singh*, A.K. Shrivastava, Swati Tapdiya

School of studies in Physics, Jiwaji University, Gwalior 474 011, India

*Corresponding author: E-mail: sarikasingh4june@gmail.com

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Abstract

Cadmium Selenide (CdSe) doped with (Mn) Manganese Chloride grown, on commercial glass substrate using Chemical Bath Deposition Method. Growth time was kept at 1-2 hours. Magnese Chloride ($Mncl_2$) was used for dopant. CdMnSe films so obtained were characterized using X-Ray Diffraction, Scanning Electron Microscopy, EdAX, and UV-Visible spectrophotometer and photoluminescence studies respectively. XRD study confirms that CdSe films are polycrystalline in nature and have cubic structure. The Debye-Scherer formula was used to calculate average particle size of pure and doped CdSe film. Thus, the particle size was decrease on doping. The effect of doping concentration Mn on the luminescence spectra of CdSe was studied. The emission spectra revealed that the intensity increased considerably in the presence of dopant ions. It is clearly observed from the surface morphological studies by SEM that the as-deposited CdSe and doped Mn concentration films are nanocrystalline, homogenous, without cracks or holes and well covered to the glass substrate. FE-SEM images show spherical particles having uniform distribution. Roughness of the films were totally eliminated. EDAX patterns confirms the presence of Cadmium, Selenide and Magnese chloride elements (2%, 5%) in sample. Optical band gap of pure CdSe film comes out to be 2.1 eV.After doping energy band gap was decreasing.

Keywords: CBD, photoluminescence, XRD, absorbance.

Introduction

CdSe is one of the most important II-VI semiconductor materials, which has interesting optical, electrical and optoelectronic properties via quantum confinement in nanocrystals [**1, 2**]. There by being a promising candidate for the potential applications in various fields such as optoelectronics, biosensors, laser diode, solar cells, biomedical labelling and so forth [**3**]. Formation of a junction structure by controlled doping or combining different semiconductors is essential for promoting charge separation and making photo electrochemical with superior performance. CdSe and CdMnSe are considered as two most important nanomaterials with interesting electronic and photonic properties [**4**]. CdSe nanocrystalline films have prepared by various techniques including chemical bath deposition (CBD). CBD is a well-known method for preparing semiconductor and has been used mainly for metal Selenide. In the present work, we have successfully synthesized nanograins in CdSe and nanosphere in CdSe: Mn (2%), (5%) films on glass substrates. Pure and Mn doped CdSe thin films were then subjected to measure their Structural, Morphological and Optical properties and PL studied respectively [**5**].

Experimental

Materials

All the Chemicals used in present investigation, like Cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) Magnese Chloride($MnCl2.4H_2O$), Sodium Sulphite, Selenium metal powder were analytical grade agents and used without further purification. Double distilled water was used as solvent.

Growth mechanism of the films

In the present study, CdSe and Mn: CdSe films ($Cd_{1-x}Mn_xSe$; x = 0.02 and 0.05) were deposited on glass slide by Chemical bath deposition method in aqueous phase at 80°C. In a typical process, stoichiometric amount (x = 0.02 and0.05)1M of reaction mixtures of (Cd $(CH_3COO)_2{\bullet}2H_2O$ (20ml.), SeO_2 (25 ml) and $Mncl_2$ (5ml.) were prepared separately. Triethanolamine (TEA) was used as complexing agents. Selenium Selenosulphate solution was then added slowly into the mixture of Magnese Chloride and Cadmium Acetate solution with constant stirring till it turn in to yellowish orange solution. Thereafter 5 ml. of Triethanolamine was added to this solution. The PH of resulting solution was maintained in alkaline medium by adding the 30% ammonia. Growth of films were kept at 2 to 3 hours. After the depositions were completed on the films were taken out and cleaned with double distilled water and dried in open atmosphere at room temperature. Dry films were subjected to annealed in the vacuum (10^{-1} Tore) for about at 400°C. The annealed samples were subjected to Morphological and structural characterization using Scanning Electron Microscope, EDAX, Photoluminescence and XRD.

Table 1. Structural parameter of pure and doped Mn 2%, 5% CdSe films.

S. No.	2θ (degree)	d-values	Lattice Constant a(Å)	FWHM (rad.)	Average particle size(nm)	Plane (hkl)
1.	25.90°, 42.07° 49.69°	3.4720 2.1437 1.8433	6.07	0.1235 0.119 0.0421	15 nm	111 220 311
2.	24.80°, 41.83° (Mn2%)	0.051 0.0022	5.56	0.116 0.105	9 nm	111 220
3.	24.96° 41.69° (Mn5%)	0.02 0.049	5.99	0.034	7 nm	111 220

Results and discussion

Structural studies

Structure of the deposited CdSe and doped with Mn 2%, 5% thin films were confirmed by X-ray diffractometer using CuKα radiation (λ=1.5418A) within the 2θ range 20° to 80°. Pure CdSe film peaks are detected at 2Θ values equal to 25.90°, 42.07° and 49.69°, respectively. Whereas in Mn 2%, 5% doped films, the peaks are shifted to 24.80°, 41.83° respectively (**Table 1**). Particle sizes of the films were determined using Debye-Scherer formula.

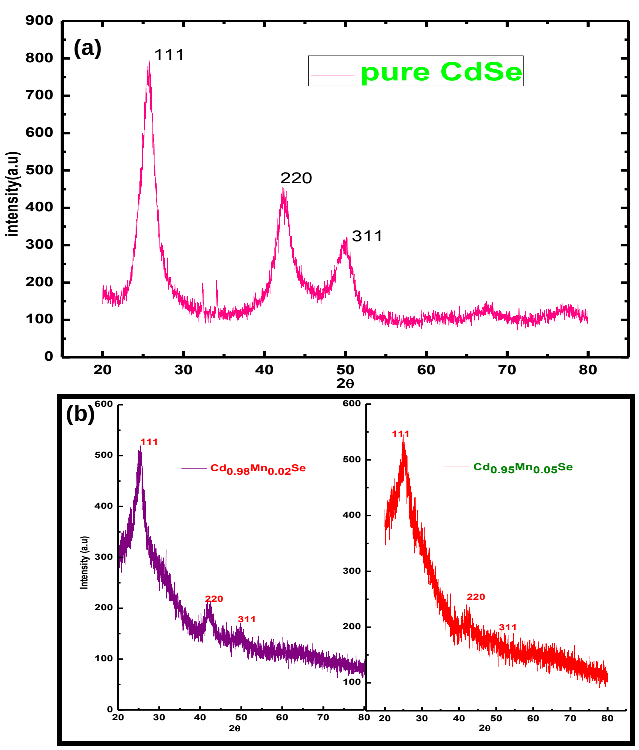


Fig. 1. (a), (b) XRD pattern of pure CdSe films, Mn 2%, 5% films.

Fig. 1 it can be concluded that the crystalline of the film increases with the addition of dopant material ($Mncl_2$) in the depositing solution. The well-defined peaks are observed in the XRD pattern. XRD results shows that the deposited CdSe thin films are polycrystalline in nature with cubic structure having (111) 25.90° plane as the preferred growth and in well agreement with JCPDS data file number 00-019-0191.

The low intensity peaks show that the CdSe thin films are coarse crystallites. Thus, there is a shifting of peak position on doping.

The particle sizes of the films were determined using Debye-Scherer formula,

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta}$$

where, k is a constant and taken to be 0.94. β is the full width half maxima (FWHM) of the XRD peaks at 2Θ. XRD was recorded with wavelength λ (=1.54Å). The particle size calculated using the prominent peak indexed as (111) plane. It comes out to be 15nm. The FWHM of the XRD peaks may also contain contributions from the lattice strain.

Scanning electron microscopy

Scanning Electron Microscopy (SEM) is a versatile technique for studying the nano structure of thin films. It is clearly observed from the surface morphological studies by SEM that the CdSe films are homogenous, without cracks or holes and well covered to the glass substrate (**Fig. 2**). These studies reveal that particle size decrease, it has been observed that increase with Mn concentration as compared to XRD study.

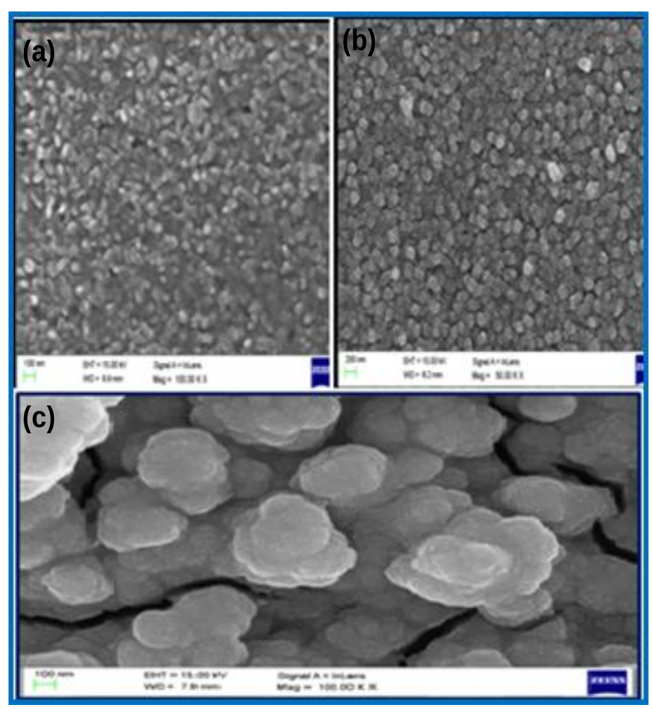


Fig. 2(a), (b), (c). SEM image of pure CdSe and Mn 2%, 5% films.

E-DAX analysis

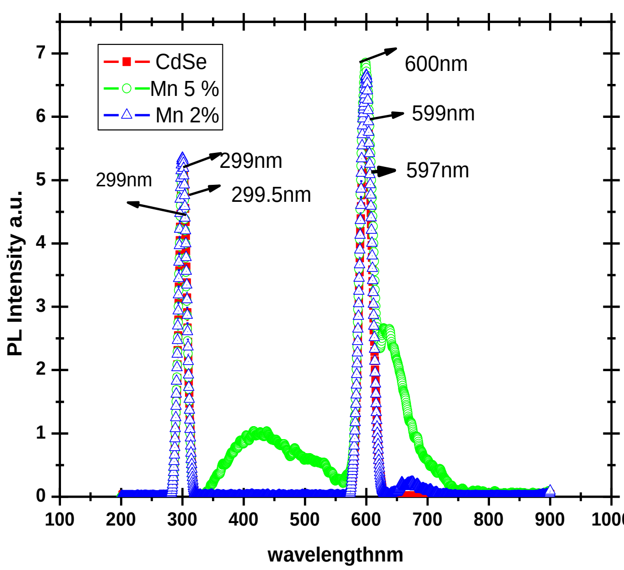
E-DAX shows that presence of CdSe and Mn in **Fig. 3**(**a, b, c**). Result indicates that material depositions are exactly CdSe and CdMnSe (2%, 5%).

Optical studies

Fig. 4 (**a, b**) shows the transmission data of n-CdSe thin films deposited at 80°C of bath solutions. Energy band gap of pure and doped, CdSe thin films was measured using UV-VIS spectrophotometer. Plots of $(\alpha h\upsilon)^2$ with photon energy $h\upsilon$ are shown in **Fig. 4**(**c, d**). Using the plots optical band gap of CdSe was calculated by Tauc relation. For pure films, it comes out to be 2.1 eV whereas for doped with Mn 2%, 5% films it is 1.9eV, 1.75eV respectively. Thus, the optical band gap of CdSe thin film decreases on doping. CdSe film has good absorption in short wavelength region as compared to dopant Mn content 2%, 5% respectively. **Fig. 4**(**a, b**) shows that absorption was decreasing with the increasing the wavelength in visible region and **Fig. 4 (e)** shows variation of energy band gap of CdSe with Mn content.

Photoluminescence studies

Photoluminescence (PL) studies of CdSe doped with Mn composition 2%, 5% were carried out at room temperature (**Fig. 5**). PL intensity was defined the radiative recombination of electron and holes interact to each other. PL spectra for all samples show two peaks. Peaks regarding CdSe film was obtained at lower wavelength at 299nm. From the spectra observed that PL intensity was improved when sample were doped with CdSe:Mn. Thus, peaks became more intense from doping.



Conclusion

In this Present work, we have shown that CdSe films have been successfully chemically deposited on glass substrate in alkaline medium. Annealed films were found to increase the crystallinity of the films. The films

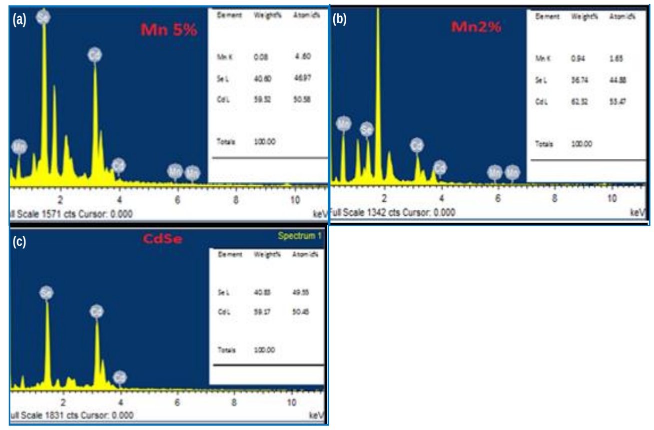


Fig. 3 (a), (b), (c) EDAX image of of pure CdSe and Mn 2%,5% films.

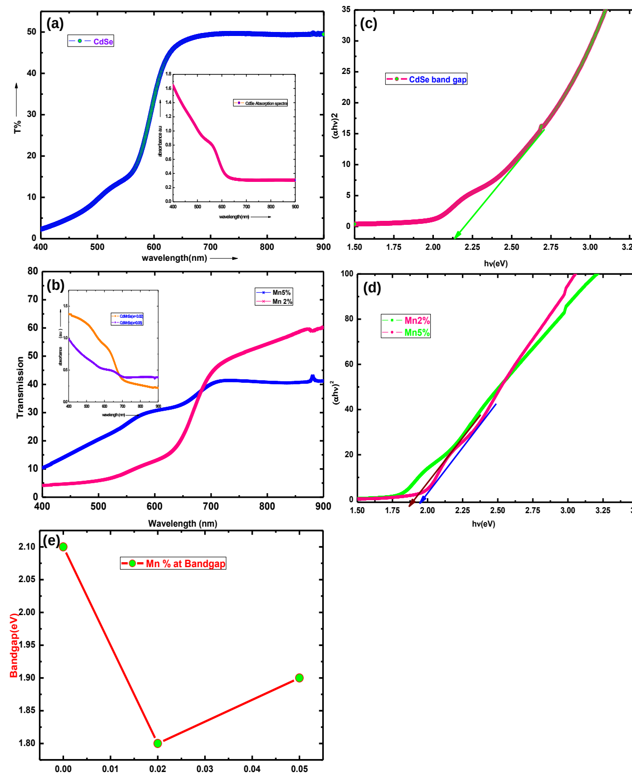


Fig. 4. (a), (b) Transmission and absorption spectra of CdSe and doped Mn2%, 5% thin films, **(c), (d**) Plots of photon energy $(\alpha hv)^2$ vs (hv) CdSe and doped Mn2%, 5% thin films and **(e)** Variation of energy band gap of CdSe with Mn content.

are polycrystalline in nature with cubic structure. XRD study confirms that the particle size decreases on doping with Mn. The FE-SEM confirms the uniform spherical distribution of particles. Optical study shows the band gap decreased down to the Mn concentration increases up to 2%, 5%. PL spectra show an increase in PL intensity on doping.

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Author's contributions

Conceived the plan: ss,aks; Performed the expeirments: ss; Data analysis: ss, st; Wrote the paper: ss. Authors have no competing financial interests.

References

1. Lewis, N.S.; Toward Cost-effective solar energy use, *Science;* 315, 5813, **2007**, 798. **DOI**:10.1126/science.1137014
2. Murray, C.B.; Kagan. C.R.; Bawendi, M.G.; *Science*, 270 **1995**, 1335. **DOI**-10.1126/qscience.270.52401335.
3. Huynh, X. Peng, A.P. Alivisatos; *Adv. Mater.* 11 **1999**, 923.
4. Chopra, K. L.; Das, S. R.; *Thin film solar cells*, Plenum Press: New York, London, **1983,** pp. 283. ISBN-9780306411410
5. Le, D.Alessia.; Jana, S.K.; Banerjee,S.; Basu, S.; and Binetti,S; *J. Appl. Phys.*,**2013,** 113, 014903. **DOI:** http://dx.doi.org/10.1063/1.4772668
6. Shinde, K.; Dubal,D.P.; Ghodake. G.S.; Fulari. V.J; *J. Electroanal. Chem.*, **2014,** 727, 179–183. **DOI:** dx.doi.org/10.1016/j.jelechem.2014.04.005
7. Khomane.A. S.; Hankare, P. P.; *J. Alloys Compd*, **2010**, 489, 605. **DOI:** 10.1016/j.jallcom.2009.09.122
8. Chate, P. A.; Sathe, D. J; Hankare, P.; Lakade, S.D.; *J. Alloys Compd.*, **2013**, 552, 40. **DOI:** 10.1016/j.jallcom.2012.10.012
9. Ichimura, M.; Takeuchi, K.; Nakamura, A.; Arai, E.; *Thin Solid Films.*, **2001**, 384, 157. **DOI:** 10.1016/S0040-6090(00)01826-5
10. JCPDS File No: 19 – 0191.
11. Kale, R. B.; Sartale, S. D.; Chougule, B. K.; Lokhande, C. D; *Semicond. Sci. Tech.* **2004**, 19, 980. **DOI:** 10.1088/0268-1242/19/8/006
12. Lokhande; C. D; Lee, E.-H; Jung, K.-D; Joo, O.-S.; *Mater. Chem. Phys.*, **2005**, 91, 399.
13. **DOI:** 10.1016/j.matchemphys.2005.03.051
14. Pawar, S.M.; Moholkar, S. M; A.V; Bhosale, C. H. *Mater. Lett.* **2007**, 61, 1034. **DOI:** 10.1016/j.matlet.2006.06.044
15. Mondal, A.; Chaudhuri, T. K.; Mondal, P. P; *Sol. Energ. Mater.* **1983**, 7, 431.
16. Panday,G.; Dixit,S.; Shrivastava,A.K.; *Mater. Sci. Eng., B,* **2015,** 59. **DOI**: 10.1016/j.mseb.2015.06.007
17. Hone, F.G.; Ampong, F.K.; Nkrumah, T. I.; Nkum, R.K. and Boakye,F.; *Int. J. Thin. Fil. Sci. Tec*., **2015,** 4, No. 2, 69. **DOI:** 10.12785/ijtfst/040202
18. JCPDS data file number 00-019-0191.
19. Hodes, G.; *Chem. Sol. deposition of semicon. Films*, Marcel Dekker, Inc., New York, **2002.** **DOI**-10.1002/1616-302820020805
20. Kale, R.B.; Lokhande, C.D.; *Semicond. Sci. Technol.*,**2005,** *20*, 1. **DOI:**10.10881/02682-12423/20/1/001
21. Shrivastava,P.; Singh,K.; *Adv. Mat. Lett.* **2012**, *3*, 340-344. **DOI:** 10.5185/amlett.2012.5341
22. Shinde, S. K.; Dubal, D. P.; Ghodakec G. S.; Fulari, V. J.; *RSC Adv*., **2014**, *4*, 33184 **DOI:** 10.1039/c4ra02791d
23. Luan, W.; Yang, H.; Tu, S.; Wang, Z. *Nanotechnology* **2007**, *18*, 175603. **DOI:** 10.1088/0957-4484/*18*/17/175603
24. Rolo, A. G.; Vasilevskiy, M. I. *J. Raman Spectroscopy* **2007**, *38* , 618. **DOI:** 10.1002/jrs.1746
25. Borah, M. N.; Baruah, B. J.; Chaliha, S.; Gogoi, D. P.; Mcfarlane, U Dutta ,S.; *J.Exp. Nanoscience*., **2015**, 1745. **DOI:**10.1080/17458080.2012.667162
26. Pandey, G.; Dixit, S.; Shrivastava, A. K.; *Mater. Chem. Phys.***2014** **DOI:** http://dx.doi.org/10.1016/J.matchphy.2014.05.010
27. Proshchenko, V.; Dahnovsky, V. J. *J. phys. chem*., **2014** 118, 28314. **DOI**: http://dx.doi.org/10.1021/jp5103324
28. Singh, S.; OJha,C. B.; Shrivastava, A. K.; Tapdiya, S.; **DOI**:10.15373/22778160