

Optical Studies of Swift Heavy Ion Irradiated Nanostructured CdS Films

P.K. Mochahari¹, F. Singh² and K.C. Sarma³

¹Department of Physics, D.K.D. College, Dergaon, Assam, India

²Inter University Accelerator Centre, New Delhi-110067

³Department of Instrumentation & USIC, Gauhati University, Guwahati, India

E-mail: ¹mochaharip@rediffmail.com

Abstract—Nanostructured cadmium sulphide (CdS) films have been synthesized chemically on glass substrates at room temperature. Synthesized samples have been subjected to swift heavy ion (SHI) irradiation using 100 MeV Si⁸⁺ ion beams. X-ray diffraction (XRD) study exhibits both pristine and irradiated CdS films have cubic phase structures and peak shifting towards lower diffraction angle are observed on irradiated samples. Crystallite size is found to be increased upon SHI irradiation. The irradiated samples are found to exhibit shift in fundamental absorption edge of optical spectra and the band gap energy decreases due to irradiation. Refractive index is found to increase upon irradiation.

1. INTRODUCTION

Nanostructured materials of II-VI group especially with large band gap energy have received much attention during recent years because of their various unique mechanical, optical, electrical properties as well as for their potential applications in different areas [1]. CdS has direct band gap of 2.42eV (bulk form) at room temperature and it has attracted widespread attention among researchers due to its unique size dependent optical properties, chemical stability and easy synthesis techniques. Nanostructured CdS films find extensive uses in various areas. Some of them are in solar cells, piezo-electronic, light emitting diodes, luminescence devices, optoelectronic, photo-electrolysis, biotechnology, communication display devices, and many more [2-3]. Swift heavy ions (SHI) irradiation is an promising field in material research which can cause different phenomena in the materials. The use of SHI irradiation to the material can bring various effects such as creation of defect, generation of surface nanostructure, crystallization and amorphization [4-5], phase modification, nullify the pre existing defect, etc. As a result, the materials subjected to SHI irradiation undergo various material properties and the method is useful to study the stability of the material exposed to various ions, energetic particles, etc. Although, great number of works have been reported about low energy implantation on CdS, but study on chemically prepared CdS films using SHI irradiation have been reported by few. In our work, preparation of nanostructured CdS films using chemical bath deposition

(CBD) method and effect of 100 MeV Si⁸⁺ ion on the samples have been studied. Modifications of various properties of nanostructured CdS film, viz. structural and optical properties due to ion irradiation are reported in this present paper.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation and swift heavy ion irradiation

In order to prepare nanostructured CdS films CdCl₂.H₂O, Na₂S.9 H₂O were taken as the source materials of Cd²⁺ and S²⁻ ions respectively and polyvinyl alcohol (PVA) as the capping agent. 0.25 molarity CdCl₂ solution was added to an aqueous solution (4wt %) of PVA in equal volume at stirring rate 200 rpm for 3 hours at constant temperature 700°C and the solution was kept for 12 hours. 0.25 molarity Na₂S solution was added to the above solution till the whole solution turns into yellow colour. The final solution was casted on cleaned glass substrates and are allowed to dry in a closed chamber to produce nanostructured CdS films. The prepared samples were subjected to SHI irradiation with 100 MeV Si⁸⁺ ions at fluences viz. 1x10¹¹ ions/cm² using the 15 UD Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi. The samples of size 1cmx1cm were mounted on a copper ladder in an irradiation chamber evacuated at a pressure of 4x10⁻⁶ Torr at room temperature. The ion beam current was maintained at 0.7 particle nano ampere during irradiation and the beam was scanned over 10 mmx10mm area of the samples with an electromagnetic scanner.

2.2 Instrumental analysis

In order to perform structural characterization of the sample, X-ray diffractometer pattern were taken in XRD Bruker (AXS D8 Advance) with CuK α radiation ($\lambda=1.5406\text{\AA}$). To undertake optical analysis, optical absorption spectra were recorded in CARY 300 Scan UV-Visible spectrophotometers in 350nm-800nm range.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

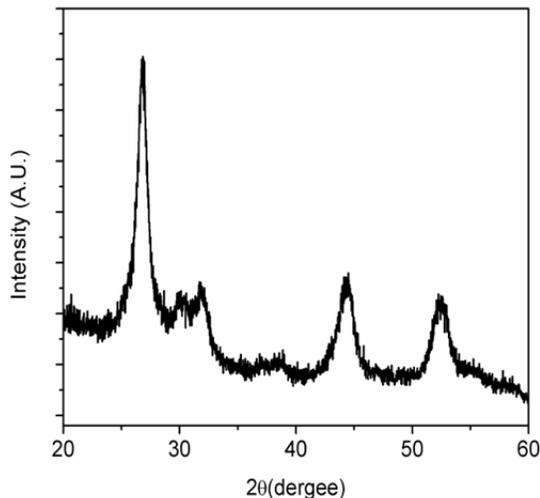


Fig. 1 (a) XRD pattern of pristine CdS films

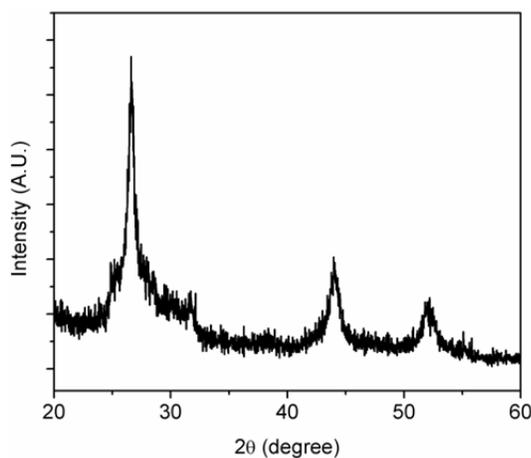


Fig. 1 (b) XRD pattern of 1×10^{11} ions/cm² irradiated CdS

Fig. 1 (a-b) shows the glancing angle X-ray diffraction (GAXRD) pattern of pristine and irradiated nanostructured CdS films at ion fluences 1×10^{11} ions/cm² respectively. Fig.1(a) exhibits intense diffraction peak of pristine CdS centered at $2\theta=26.69$, 44.09 and 52.21 which are assigned to (111), (220) and (311) planes respectively of CdS cubic crystalline phase (JCPDS: 800019). It is observed that peak of (111) is shifted by 0.143 towards higher diffraction angles compared to that of bulk CdS ($2\theta=26.547^\circ$; JCPDS 800019) indicating compressive stress. This may be due to residual stress generated in the sample during deposition and also may be because of lattice mismatch existing in film and substrate [19]. Fig.1(b) exhibits diffraction pattern of irradiated CdS film at fluence 1×10^{11} ions/cm². The diffraction pattern shows three distinct peaks at $2\theta=26.58$, 44.018 and 52.04

respectively which can be assigned to (111), (220) and (311) planes respectively of cubic phase CdS (JCPDS: 800019). The diffraction patterns of irradiated films shows small peak shift towards lower 2θ compared to that of pristine CdS. From 1(a-b) it is observed that small increase in intensity occurs because of due SHI irradiation which may be due to development of defect clusters or generation of additional grain boundaries [6]. Intense and broad diffraction peaks confirms good crystallinity and formation of nanoparticles in the samples.

The plane spacing (d) for the prepared samples is found using Bragg's law. d values for pristine CdS are 3.341 \AA , 2.004 \AA and 1.701 \AA corresponding to 1st, 2nd and 3rd peak respectively. And that for irradiated CdS are 3.311 \AA , 2.001 \AA and 1.681 \AA corresponding to 1st, 2nd and 3rd peak respectively. Crystallite size of the samples is estimated using Scherrer formula [7]

$$D = \frac{K\lambda}{\beta_D \cos\theta} \quad (1)$$

where K is a constant equal to 0.94 , λ is the wavelength of the radiation which is 1.54056 \AA for CuK_α radiation, β_D (in radian) is the full width at half maximum (FWHM) of the peaks and θ is the Bragg's diffraction angle. Crystallite size of pristine CdS film is found to be 10.67 nm and that of irradiated CdS is 10.85 nm showing increase in crystallite size due to irradiation. The increase in crystallite size is because during irradiation the kinetic energy of the electrons ejected from the target atom is transferred to the lattice which increases local lattice temperature forming non equilibrium state in grain volumes, thereby, the grain volumes are increased and agglomeration of grains on the surface take place [8].

3.2 Optical study

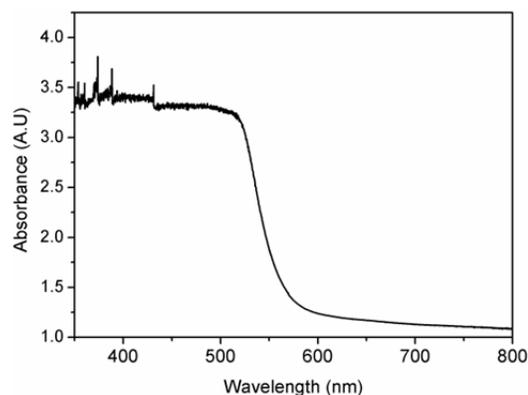


Fig. 2(a) Absorption spectra of pristine CdS film

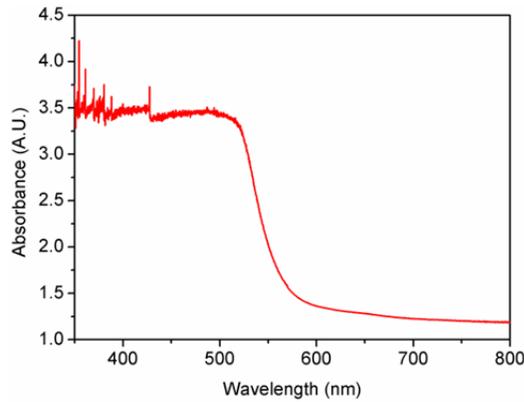


Fig. 2 (b) Absorption spectra of CdS irradiated at 1×10^{11} ions/cm²

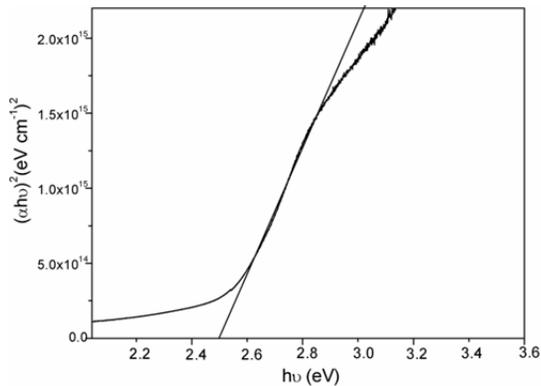


Fig. 3(a) Plot of $(\alpha hv)^2$ versus hv for pristine CdS

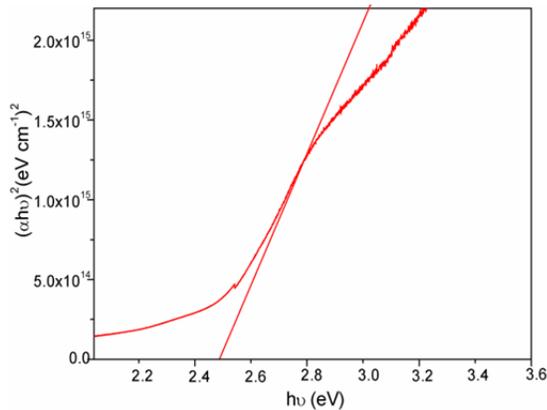


Fig. 3 (b) Plot of $(\alpha hv)^2$ versus hv for CdS irradiated at 1×10^{11} ions/cm²

Fig. 2(a-b) show the optical absorption spectra of pristine and irradiated CdS films at fluencies 1×10^{11} ions/cm² respectively. Due to irradiation a shift in the band edge towards higher wavelength region along with slight increase in absorbance occur. These may be due to the creation of defect levels in the band gap [9].

The band gap energy (E_g) is estimated using Tauc's formula [10]

$$(\alpha hv)^2 = A(hv - E_g) \quad (2)$$

where A is a constant, α is the absorption coefficient and hv is incident photon energy. Band gap energy is found by extrapolating the linear region of the plots $(\alpha hv)^2$ versus hv on the energy axis as in Fig. 3 (a-b). The band gap energy of pristine CdS film is found to be 2.48 eV showing it is blue shifted compared to that of bulk CdS (2.42 eV) due to size confinement effect. The band gap energy of irradiated sample is found to be 2.45 eV which shows decrease of band gap energy due to irradiation. This may be due to creation of intermediate energy levels and increase in the carrier concentration [11].

In order to calculate refractive index (n), relation proposed by T. S. Moss [12] has been used.

$$E_g n^4 = k \quad (3)$$

where k is a constant equal to 95 eV according to Moss. According to this relation refractive index for pristine and irradiated CdS films are 2.488 and 2.496 respectively.

Refractive index for all the samples is also found by the relation given by Herve and Vandamme (H-V) [13]

$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2} \quad (4)$$

where $A=13.6$ eV and $B=3.4$ eV are constants. According to H-V relation, refractive index for pristine and irradiated CdS films are 2.519 and 2.531 respectively. From both Moss and H-V relations refractive index is found to increase upon irradiation.

4. CONCLUSIONS

Good quality nanostructured CdS films have been synthesized using chemical bath deposition method at room temperature and they are subjected to SHI irradiation with 100 MeV Si⁸⁺ ion beams. Both the pristine as well as irradiated films are of cubic phase structure indicating good crystalline stability. Growth in crystalline size but decrease in bandgap energy is obtained due to irradiation. The modified material properties using SHI irradiation are important which can be applied in photosensors, solar cell, etc.

5. ACKNOWLEDGEMENTS

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REFERENCES

- [1] Mallick, P., Rath, C., Biswal, R. and Mishra, N.C., *Indian J. Phys.* **83** (2009) 517.
- [2] Todorov, T.K., Gunawan, O., Gokmen, T., Mitzi, D. B., *Progress in Photovoltaics: Res. and Appl.* **21** (2013) 82
- [3] Kumar, P., Kukkar, D., Deep, A., Sharma, S.C., Bharadwaj, L.M., *Adv. Mat. Lett.* **3** (2012) 471
- [4] Ison, V.V., Rao, A.R., Dutta, V., Kulriya, P.K., et al., *J. Appl. Phys.* **106** (2009) 023508
- [5] Kumar, P., Saxena, N., Chandra, R., et al., "SHI induced enhancement in green emission from nanocrystalline CdS thin films for photonic applications", *Journal of Luminescence* **147** (2014) 184–189
- [6] Agarwal, D.C., Kumar, A., Khan, S.A., et al., "SHI induced modification of ZnO thin film: Optical and structural studies", *Nucl. Instrum. Meth. Phys. Res. B* **244** (2006) 136-140
- [7] Sen, S., Halder, S.K. and Sengupta, S.P., *J. Phys. Soc. Jpn.* **38** (1975) 1641
- [8] Ghosh, S., Khan, S.A., Ganesan, V., et al., "Surface studies on 100 MeV Ag⁷⁺ ions and 150 MeV Ni¹¹⁺ ions irradiated nanocrystalline ferrite thin films", *Nucl. Instr. Meth. B* **244** (2006) 34-39
- [9] Senthil, K., Mangalaraj, D., Narayandass, S.K., et al., "Argon and nitrogen implantation effects on the structural and optical properties of vacuum evaporated cadmium sulphide thin films", *Semicond. Sci. Technol.* **17** (2002) 97-103
- [10] Tauc, J., (ed.) *Amorphous and liquid semiconductors* (London and New York: Plenum press) Chapter 4 (1974) 171
- [11] Sayed, S.M.El., "Electron beam and gamma irradiation effects on amorphous chalcogenide SbSe₂:5 films", *Nucl. Instr. Meth. Phys. Res. B* **225** (2004) 535-543
- [12] Moss, T.S., "Relations between the Refractive Index and Energy Gap of Semiconductors", *Physica Status Solidi (B)* **131** (1985) 415-427
- [13] Herve, P., Vandamme, L.K.J., "General relation between refractive index and energy gap in semiconductors", *Infrared Phys. Technol.* **35** (1994) 609–615