------ Raf. J. Sci., Vol. 25, No.3, pp. 90- 98, 2014------

The Effect of γ-Irradiation on the Structural and Physical Properties of CdSe Thin Films

Nawfal Y. Jamil **Suha A. Najim**

Department of Physics/ College of Science/ University of Mosul

Abid Al-karem M. Muhammed

Department of Physic/ College of Electronics and Informatics, Nanotechnolog Sumy State University Technica, Sumy /Ukraine

(Received 16 / 7 / 2013 ; Accepted 28 / 10 / 2013)

ABSTRACT

Thin film of CdSe has been deposited on to the clean glass substrate by using CBD technique at room temperature. The samples are irradiated by γ-ray with various doses (0.25,0.5,1.0,1.5) Gy. These films are characterized by XRD, which indicated that as-deposited CdSe layers and irradiated films at 0.25 and 0.5 Gy of γ- ray grow in cubic phase having preferred orientation along (111) plane in c-direction. Further, the irradiated films at 1.0 and 1.5 Gy of γ- ray show polycrystalline in nature with a mixture of cubic along with hexagonal structures. Optical absorption spectra of these thin films have been recorded using spectrophotometer. The energy band gap has been determined using these spectra. It is found that the energy band gap of CdSe film is 2.09 eV and it is increased with the increase of γ- irradiation dose. The electrical conductivity measurements gave a decrease in conductivity with the increase of γ- irradiation dose.

Keywords: CdSe thin films, γ-irradiation, optical properties.

تأثير تشعيع γ على الخواص التركيبية والبصرية لأغشية CdSe الرقيقة

الملخص

رُسبت أغشية CdSe الرقيقة على أرضية نظيفة من الزجاج باستخدام تقنية الترسيب بالحمـام الكيميـائي Chemical Bath Deposition (CBD) عند درجة حرارة الغرفة. العينات تم تـشعيعها بواسـطة أشـعة γ عنـد جرعـات مختلفـة (1.5,1.0,0.5,0.25)Gy.

هذه الأغشية تم وصفها بواسطة XRD التي تشير إلى أن طبقات أغشية CdSe الرقيقة المرسبة والمشعة عنـد 0.25 و0.5 كراي لأشعة γ تنمو في الطور المكعبي وبالاتجاه المفضل عند المستوي (111) وبالاتجاه العمودي c. الأغشية المشعة عند 1.0 و1.5 كراي لأشعة γ تبين أنها متعددة البلورات في طبيعتها وخليط مـن التراكيـب المكعبـة والـسداسية. طيـف الامتصاص البصري لهذه الأغشية الرقيقة تم تحليله باستخدام المطياف. فجوة الطاقة تم تحديدها بهذا الطيف. ووجد أن فجـوة الطاقة لغشاء CdSe 2.09 الكترون فولت وتزداد بزيادة جرعة تشعيع γ. القياسات الكهربائية للتوصيلية أعطت نقـصاناً فـي التوصيلية مع زيادة جرعة تشعيع γ.

الكلمات الدالة: أغشية CdSe الرقيقة، التشعيع بأشعة γ- الخصائص البصرية.

INTRODUCTION

The II-VI semiconducting compounds, especially the cadmium chalcogenides, have been extensively studied due to their potential applications in semiconductor devices and solar cells fabrication (Mahapatra and Dubey, 1994), (Masumdar *et al.*, 2003), (Shahane and Deshmukh, 2001).

Cadmium Selenide with some additives is nowadays attracting a great deal of attention owing to its potential, fundamental, experimental and applied interests in a variety of thin film devices such as laser screen materials, projection colour TVs, nuclear radiation detectors, light emitting diodes, etc. (Burger and Roth,1984), (Basam *et al.*,1988),(Krishnan *et al.*,1992),(Gupta *et al.*,1995), (Samarth *et al.*,1990). Many studies have focused on cadmium selenium, because of its high luminescence quantum yield, a suitable band gap and a variety of optoelectronic conversion properties (Empedocles and Bawendi, 1997).

Several physical and chemical techniques are available for the growth of CdSe thin films. CdSe thin films have been deposited using different techniques such as electro deposition (Murali *et al.*,1994), (Murali *et al.*, 1991), molecular beam epitaxy (Samarth *et al.*, 1989), spray pyrolysis (Elango *et al.*, 2000), successive ionic layer adsorption and reaction method (Lokhande *et al.*, 2001), vacuum deposition and chemical bath deposition (CBD) (Erat *et al.*, 2008). Among these methods chemical bath deposition has several overriding advantages with other techniques such as uniform film deposition, control of thickness, precise maintenance of deposition temperature, low cost (Salem, 2002), (McAleese and O'Brien, 1998). In this paper, CdSe thin films deposited on the glass substrates by chemical bath deposition, then we demonstrated the effect of γ-irradiation on the optical, electrical and structural properties of CdSe films. The synthesized films were characterized and analyzed with scanning electron microscope (SEM), X-ray diffraction (XRD) patterns and ultraviolet- visible (UV–vis) spectrophotometer.

EXPERIMENTAL

Solutions were prepared by dissolving an appropriate amount of analytically Selenium metal and Sodium sulphite in 10 ml distilled water. Sodium selenosulphite (Na_2SeSO_3) can be synthesized by refluxing selenium powders in a sodium sulphite. In the experiments, (0.5M) Cadmium Chloride dissolved in 10 ml distilled water and ammonia was used as complexing agent. The temperature of the solution was allowed to rise slowly up to 35˚C. The substrates were removed from the beaker after about 20 h. After the deposition, the substrates were taken out of the bath, rinsed with distilled water, dried in air and kept in a desecrator (Pawar *et al.*, 2012).

In order to accelerate the irradiation process, the available γ-ray source was used, namely a ^{137}Cs source with the activity of 0.132 Ci, emitting (662 keV) γ rays (Sumy state university/ Ukraine). The dose average at the irradiation was (6Gy/h) and the irradiation time was (2.5,5,10,15) min at doses (0.25,0.5,1.0,1.5) Gy respectively. Thickness of the films was measured by gravimetric method and it was around 1 μm, the surface area was about (5.5×1) cm^2. The samples were on the distance 8 mm from the radiation source. The samples were characterized by X-ray diffraction patterns (XRD, Bruker/D8-advance with CuKα radiation λ = 1.54178 Å, Germany) at 40 kV and 20 mA employing in 2θ range from 20˚ to 80˚. The morphology and particle sizes were determined by Scanning Electron Microscopy (SEM) (FESEM, HITACHI S7900, Japan). UV–vis spectroscopy (Systronics-119 model) was carried out at room temperature using spectrophotometer in the range 400–1100 nm. The conductivity of these films (without radiation and irradiation) has been determined by I-V measurements using the electrometer.

RESULTS AND DISCUSSION

The crystal form of the CdSe film was characterized with XRD patterns and results are shown in (Fig.1). XRD studies revealed that these samples are polycrystalline in nature exhibiting the hexagonal (wurtzite) and cubic (zinc blend) structures.

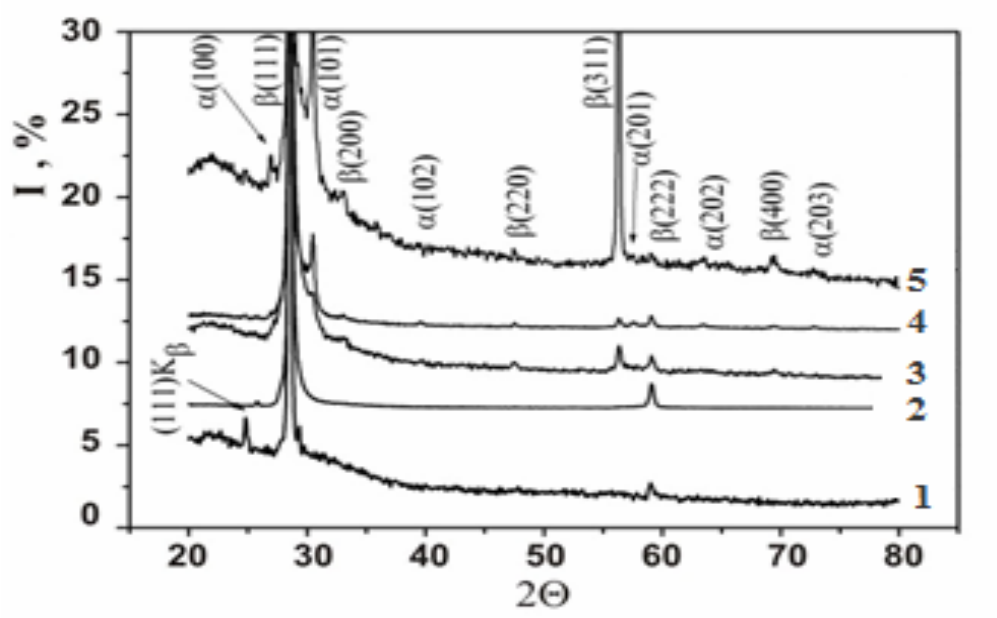

Fig. 1: XRD pattern of CdSe thin films 1-without γ-ray 2- 0.25 Gy, 3-0.5 Gy, 4-1.0 Gy, 5- 1.5 Gy

(Fig. 1) shows XRD patterns of as-deposited and irradiated CdSe thin films at different doses (0.25,0.5,1.0,1.5) Gy of γ-radiation. As-deposited CdSe thin films were cubic structure, which showed only one intense reflection peak at 2θ=(29), corresponding to cubic (111) plane, which coincide well with the Joint Committee on Powder Diffraction Standards JCPDS Data No.(8-459) (Frank, 1976). The thin films irradiated at 0.25 Gy of γ-ray were cubic with a slight improvement in crystallinity, whereas films irradiated at 0.5 Gy of γ-ray become polycrystalline with cubic structure. Further, CdSe thin films irradiated at 1.0 Gy of γ-ray were polycrystalline with a mixture of cubic along with hexagonal structure with highest intense reflection peaks at (2θ=29) corresponding to cubic (111) and with lowest reflection peaks corresponding to cubic and hexagonal structures. The film irradiated at 1.5 Gy of γ-ray was also polycrystalline with a mixture of cubic along with hexagonal structures with highest intense reflection peaks at (2θ=29) and (2θ=56.5) corresponding to cubic (111) and (311) planes respectively.

Scanning electron microscopy (SEM) is a convenient technique to study the microstructure of thin films. (Fig. 2) shows the SEM micrographs without irradiated and irradiated with γ-ray CdSe thin films.

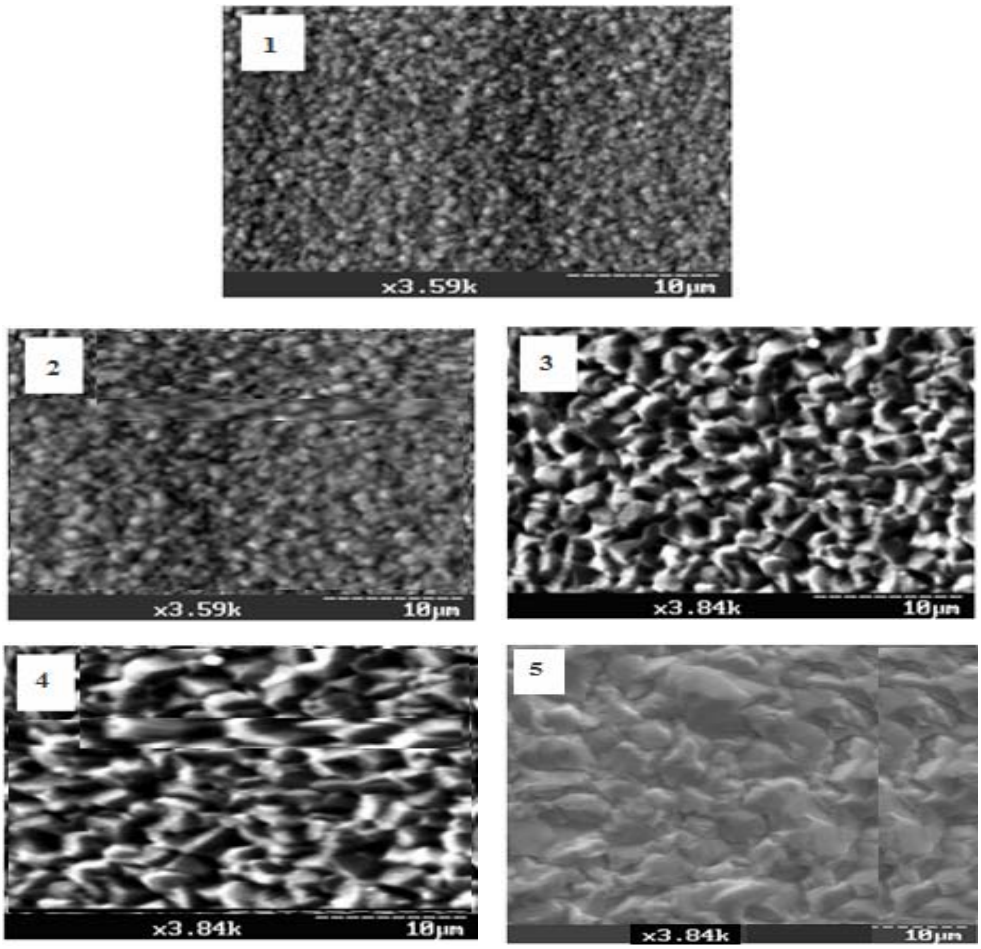

Fig. 2: SEM of deposited & irradiated with γ-ray CdSe thin films without γ-ray 2- 0.25 Gy 3- 0.5 Gy 4- 1.0 Gy 5- 1.5 Gy

It is observed that CdSe films without irradiation are non homogeneous, the grains are densely packed, well defined and quasi- spherical having different sizes. Whereas the film irradiated at 0.25 Gy of γ-ray was nearly similar that as-deposited CdSe films with presence simple distortion in picture. Further, films irradiated at 0.5 Gy of γ-ray clearly show that the effect of γ-irradiation on CdSe and observed that the grains become nearly similar to crystals. In (Fig 4), it was observed that the distortion in the crystals non homogenous. The SEM of CdSe thin film irradiated at 1.5 Gy of γ-ray clearly shows microcrystals of larger size, more crystalline behavior and well covered to the glass substrate.

The transmittance spectrum of the CdSe film was recorded using UV–vis spectrophotometer at room temperature in the wavelength range 400–1100 nm. Optical transmittance of the film is shown in (Fig. 3 a,b). (Fig. 3a) shows that the transmittance of CdSe film increases with the increasing wavelengths in the visible region and near IR region. In (Fig. 3 b), it is observed that the transmittance of CdSe thin films increases as increasing the irradiation at doses (0.25, 0.5, 1.0, 1.5) Gy.

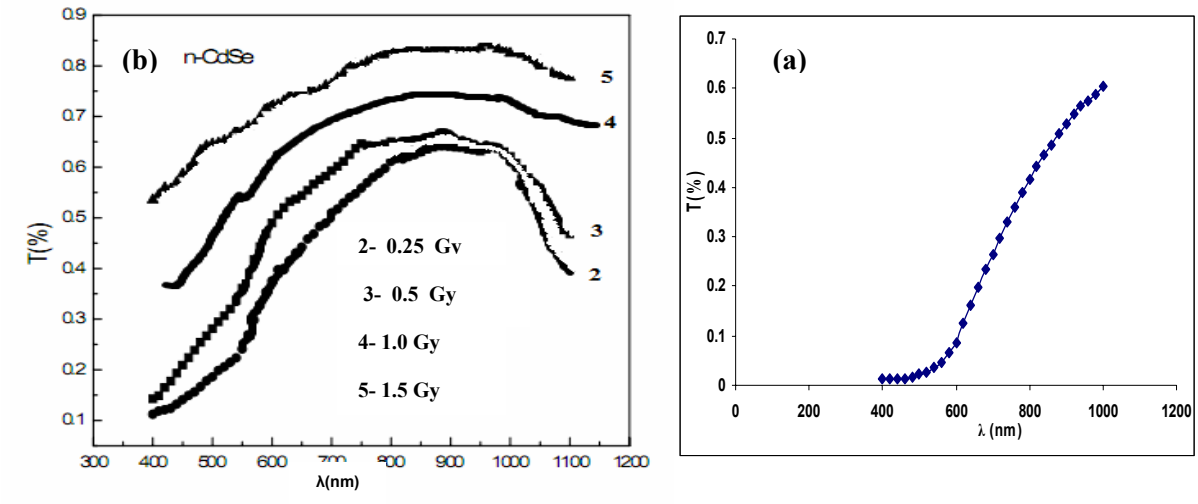

Fig. 3: Optical transmittance spectra of CdSe thin film (a) without irradiation (b) 2- 0.25 Gy 3- 0.5 Gy 4-1.0 Gy 5- 1.5 Gy

From (Fig. 3b) the maximum transmittance (T_{max}) at wavelength (880 nm) and the relation between T_{max} and doses is shown in (Fig. 4).

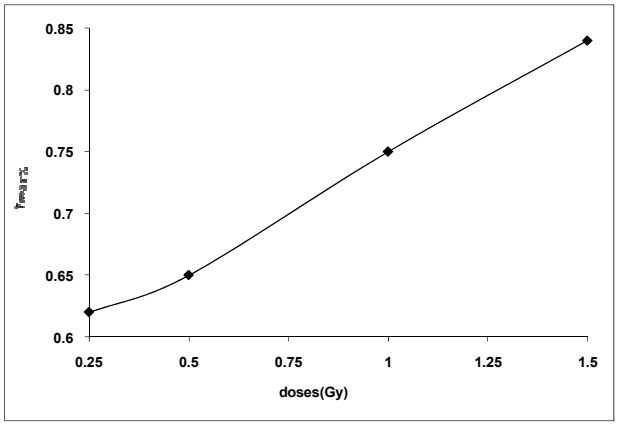

Fig. 4: Variation of (T_{max}%) versus the doses of irradiated CdSe films

The optical band gap energy E_g can be determined from the experimental values of absorption coefficient α as a function of photon energy hν using the following relation (Pankove,1971).

$$\alpha h\nu = A\left(h\nu - E_g\right)^n$$

where hν is photon energy, E_g is band gap and A is constant. Now n can have values 1/2 for direct transition. The value of absorption coefficient is found to be of the order of 10^4 cm^{-1} as shown in (Fig. 5).

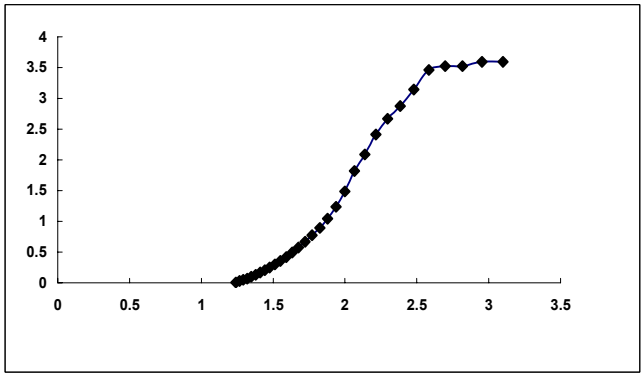

Fig. 5: Variation of absorption coefficient as a function of photon energy

The plot of $(\alpha h\nu)^2$ versus $(h\nu)$ is shown in (Fig. 6a) which is linear at the absorption edge, indicating a direct allowed transition. The straight line portion was extrapolated to the energy axis and when $(\alpha h\nu)^2 = 0$, the intercept gives the band gap energy of CdSe.

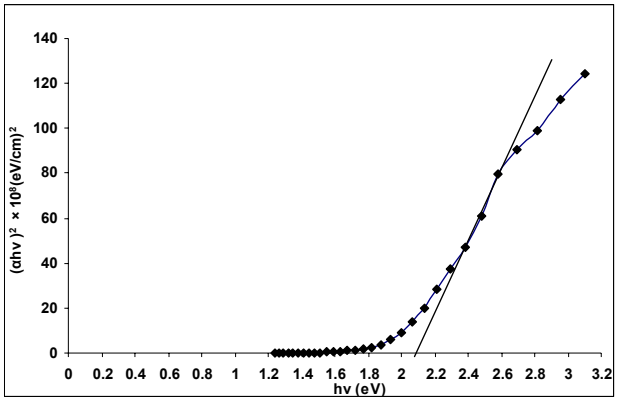

Fig. 6 a: Variation of $(\alpha h\nu)^2$ versus hν of deposited CdSe films

It is found to be 2.09 eV for CdSe thin film without irradiation and in the range of 2.15-2.35 eV for irradiated samples respectively. It is believed that the increas in the band gap after irradiation due to the increasing in the grain size as shown in SEM pictures and expectation of forming CdS material, as shown in XRD pattern. Then the variation is depicted as in (Fig.6b) and the band gap energy calculations are shown in Table (1).

Table 1: Band gap energy calculations of CdSe thin film:
1-without irradiation 2- 0.25 Gy, 3- 0.5 Gy , 4- 1.0 Gy, 5- 1.5 Gy

No.	E_g *(eV)*
1	2.09
2	2.15
3	2.3
4	2.33
5	2.35

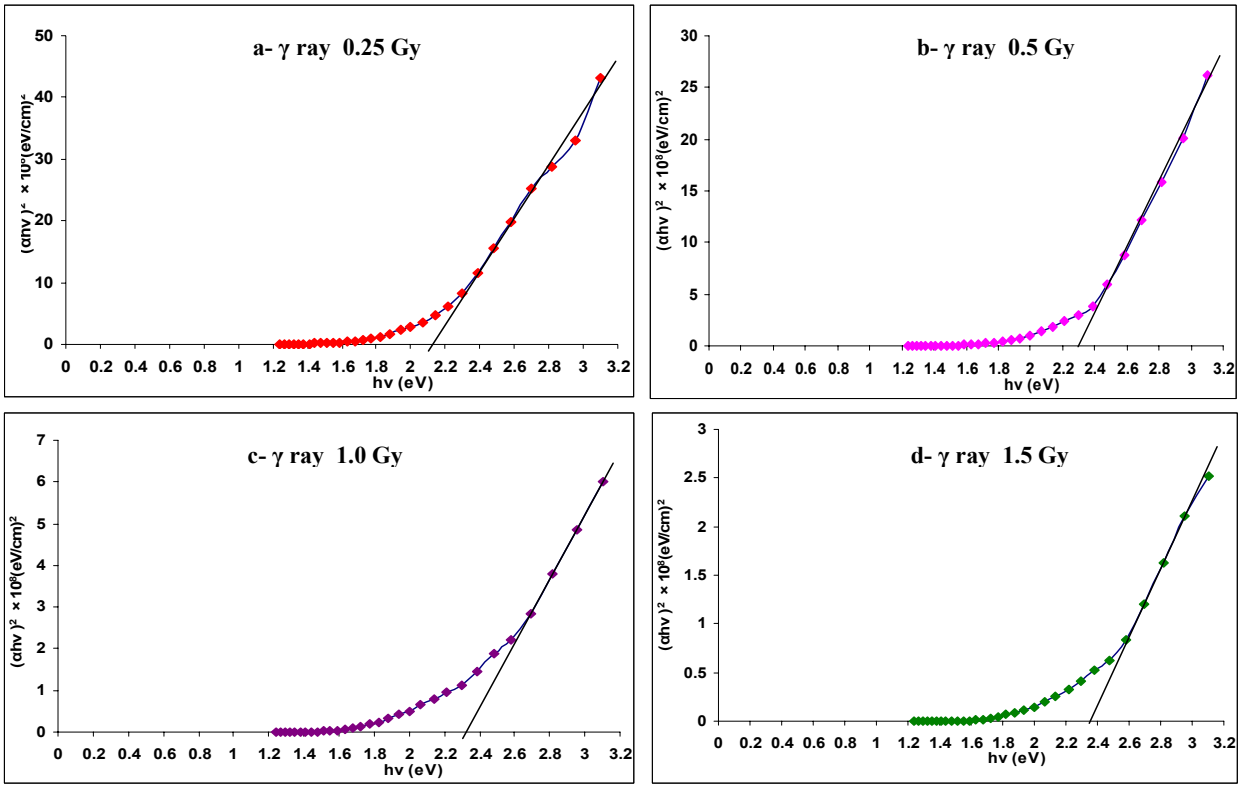

Fig. 6 b: Variation of $(\alpha h\nu)^2$ versus hν of irradiated CdSe films a- 0.25 Gy b- 0.5 Gy c- 1.0 Gy d- 1.5 Gy

The electrical conductivity of CdSe thin films is determined using four- point prop measurements at room-temperature as shown in Table (2). It is found that the conductivity decreases with the increase in irradiation dose. This is explained in terms of structural changes and defects creation occurring in the irradiated films (Sharma and Garg, 1990). In as-deposited CdSe films, there is some lattice defects, geometrical, and physical imperfections randomly distributed on the surface and within the volume of the film (Sharma and Garg, 1990). The roughness of the surface, grain boundaries and inclusions in the volume are the main components of the geometrical imperfection. The important factor, which is responsible for the physical properties of thin film, is the structure. So it is expected that the decrease in the conductivity is due to an increase in the mean size of the grain (Cristian and Rusu, 2003) and a decrease in the grain boundary area as shown in SEM pictures in addition to the increase of defects like vacancies and interstitial. Also our expectation of forming CdS which added the factor of decreasing in conductivity. The electrical conductivity of CdSe films are found to be n-type.

Table 2: Conductivity of thin film CdSe: 1-without irradiation 2- 0.25 Gy, 3- 0.5 Gy , 4- 1.0 Gy , 5- 1.5 Gy

No.	$\sigma \times 10^2 (\Omega\ cm)^{-1}$
1	1.3
2	0.5
3	0.2
4	0.03
5	0.07

CONCLUSION

In summary, the influence of irradiation on the optical, structural and electrical properties of the chemically deposited CdSe thin films was investigated. The optical energy band gap has been increased from 2.09 to 2.35 eV with the increasing irradiation doses. The structure of the films has been transformed slightly from cubic to a mixture of cubic and hexagonal structure at 1.0 and 1.5 Gy of γ-ray. The films show typical semiconductor characteristics with conductivity of the order 1.3×10^{-2} $(\Omega cm)^{-1}$ at room temperature and the electrical conductivity decreases down to 7×10^{-4} $(\Omega\ cm)^{-1}$ at 1.5 Gy.

REFERENCES

Basam, A.A.; Brinkman, A.W.; Russell, G.J.; Woods, K.J. (1988). Electrical properties of Zn_x Cd_{1-x} Se ($x<0.45$). *J. Cryst. Growth,* **86**, 667-672.

Burger, A.H.; Roth, M.J. (1984). Temperature gradient solution zoning growth and characterization of $Zn_xCd_{1-x}Se$ single crystals. *J. Cryst. Growth*, **70**, 386-392.

Cristian, B.; Rusu, G.I. (2003). On the structural and optical characteristics of CdSe thin films. *J. Appl. Surf. Sci*., **211**, 6-12.

Elango, T.; Subramanian, S.; Murali, K.R. (2000). Characteristics of spray-deposited CdSe thin films. *Surf. Coat. Technol*., **123**, 8-11.

Empedocles, S.A.; Bawendi, M.G. (1997). Quantum-confined stark effect in single CdSe nanocrystallite quantum dots. *Science*, **278**, 2114–2117.

Erat, S.; Metin, H.; Ari, M. (2008). Influence of Nitrogen anneling on the Xrd, Edx, sem and electrical properties of chemical bath deposited Cdse thin films. *Mat. Chem. and Phys*., **111**, 114-120.

Frank McClune, W. (1976). "Powder Diffraction File". Search Manual printed in U.S.A.

Gupta, P.; Maity, B.; Maity, A.B.; Choudhari, S.; Pal, A.K. (1995). Optical properties of $Zn_xCd_{1-x}Se$ films. *Thin Solid Films*, **260**, 75-85.

Krishnan, V.; Mishra, K.K.; Rejeshwar, K. (1992). Electro synthesis of Thin Films of CdZnSe: Composition Modulation and Bandgap Engineering in the Ternary System. *J. Electrochem. Soc.*, **139**(1), 23-27.

Lokhande, C.D.; Sankapal, B.D.; Sartale, S.R.; Pathan, H.M.; Giersig, M.; Ganesan, V. (2001). A novel method for the deposition of nanocrystalline Bi2Se3, Sb2Se3 and Bi2Se3–Sb2Se3 thin films — SILAR. *J. Appl. Surf. Sci.*, **182**, 413-417.

Mahapatra, P.K.; Dubey, A.R. (1994). Photoelectrochemical behavior of mixed polycrystalline n-type CdS-CdSe electrodes. *Sol. Ener. Mater. Sol Cells.*, **32**, 29-35.

Masumdar, E.U.; Gaikawad, V.B.; Pujari, V.B.; Patil, V.B.; Deshmukh, L.P. (2003). Some studies on chemically synthesized antimony-doped CdSe thin films. *Mat. Chem. Phy*.,**77**, 669-676.

McAleese, J.; O'Brien, P. (1998). Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS. *J. Mater. Chem.*, **8**, 2309-2314.

Murali, K.R.; Subramanian, V.; Rangarajan, N.; Lakshmanan, A.S.; Rangarajan, S.K. (1994). Brush plated CdSe films and their photoelectrochemical characteristics. *J. Electroanal. Chem.*, **368**, 95-100.

Murali, K.R.; Subramanian, V.; Rangarajan, N.; Lakshmanan, A.S.; Rangarajan, S.K. (1991). Photoelectrochemical studies on pulse plated CdSe films. *J.Electroanal. Chem.*, **303**,261-266.

Pankove J.J. (1971). "Optical Processes in Semiconductors".Dover Publications, Inc., New York.

Pawar, R.R.; Bhavsar, R.A.; Sonawane, S.G. (2012). Structural and optical properties of chemical bath deposited Ni doped Cd-Se thin films. *Ind. J. Phys.*, **86**, 55-68.

Salem, A.M. (2002). Structure, refractive-index dispersion and the optical absorption edge of chemically deposited ZnxCd(1-x)S thin films. *J. Appl. Phys.*, A, **74**, 205-211.

Samarth, N.; Luth Fardyan, J.K.; Alonso, R.G.; Lee, Y.R.; Ramdas, A.K.; Qadri, S.B.; Otsuka, N. (1990). Molecular beam epitaxy of $Zn_{1-x}Cd_xSe$ epilayers and $ZnSe/Zn_{1-x}Cd_xSe$ super lattices. *J. Appl. Phys. Lett.*, **56**, 1163.

Samarth, N.; Luo, H.; Furdyna, J.K.; Qadri, S.B.; Lee, Y.R.; Ramdas, A.K.; Otsuka, N. (1989). Growth of cubic (zinc blende) CdSe by molecular beam epitaxy. *J. Appl.Phys.Lett.*, **54**, 2680.

Shahane, G.S.; Deshmukh, L.P. (2001). Structural and electrical transport properties of $CdS_{0.9}Se_{0.1}$: In thin films: effect of film thickness. *Mat. Chem. Phy.*, **70**, 112-116.

Sharma, K.C.; Garg, J.C. (1990). Influence of thermal annealing in air on the electro-optic characteristics of chemical bath deposited non-stoichiometric cadmium zinc selenide thin films. *J. Phys.*, **23**, 1411-1419.