Structural And Optical Characterization Of Cdse Nanoparticles

D. Kalita, K. C. Sarma

Department of Instrumentation and USIC, Gauhati University, Assam, India

H. L. Das

Department of Physics, Gauhati University, Assam, India

Corresponding author:

D. Kalita

Department of Instrumentation and USIC,
Gauhati University, Assam, India

ABSTRACT

The optical properties of chemical bath deposited CdSe thin films at temperature 293 K (Room Temperature) and annealed in air for 6 hours at various temperatures were investigated. The optical band edge of investigated CdSe thin films having different grain distributions was estimated from absorption data. The reflectances, transmittances and absobance were obtained by measurement. Dependance of optical absorption on the intensities of illumination for different incident radiation was studied. Accordingly the variation of optical co-efficients against the intensities of illumination for a given radiation was also observed. The absorption co-efficient in the (333-1050) nm range of the films were measured on the as grown and annealed films. It is seen that annealing transformed meta stable nanoparticle cubic phase into stable polycrystalline hexagonal phase. The exact numerical relationships between the absorption co-efficient and photon energy are estimated.

KEYWORDS

Chemical bath depotion, CdSe thin film,nanoparticle, band gap, polycrystalline, annealing.

INTRODUCTION:

At present there is a great interest in the the study of the physicochemical properties of nanometricsized compound semiconductor particles. Nanocrystalline form of compound semiconductor has been a rapidly growing area of research due to its non-linear optical properties, luminescent properties, quantum size effect and other physical and chemical properties. The semiconductor nanoparticles belong to the state of matter in transition between molecules and bulk solids in which the relevant dimension changes. The equilibrium and dynamic properties of nanomaterials are completely different with their bulk materials. The nanocrystaline size affects the spacing between energy levels, which becomes the cause of increase of energy gap.

Cadmium selenide belongs to the binary metal chalcogenides of group II-VI semiconductors and it is an important material among other II-VI semiconductors for the development of various modern technologies of solid-State devices such as solar cells, high-efficiency thin film transistors, light emitting diodes etc. CdSe is a promising photovoltaic material because of its high absorption co-efficient and nearly optimum band gap energy for the efficient absorption of light and conversion into electrical power .

Presently at RGU, Arunachal Pradesh

In recent years, major attention has been given to the investigation of electrical and optical properties of CdSe thin films in order to improve the performances of the devices and also for finding new applications

CdSe thin films have been prepared using a variety of methods including physical vapour deposition, sputtering, chemical bath depositoin, electro deposition etc. The chemical bath depositoin, in its variant is offen used because it offers many possibilities to modify the deposition parameters and to obtain films with pre-determined structures and properties.

EXPERIMENTAL:

Chemical bath depositin method was adopted for the preparation of CdSe thin film. All chemicals used for deposition of CdSe thin film were of analytical reagent (A.R) grade supplied by M/S Merck.The deposion solution were prepared by a process similler to that used by K.Girija et.al . The required CdSe thin film were allowed to grow on ordinary glass substrates (size 26mm x 7.6 mm x 2 mm). Before deposition the glass substrate were cleaned thoroughly.

The reaction mixure was prepared by adding ammonia solution in 0.1 M of cadmium acetate till a pH of 11 attained under controlled stirring. The solution initially become milky and further addition of excess ammonia made the solution clear and transperant. The fresly prepared 0.25 M sodiumselenosulphite of equal volume was added to the solution slowly. After mixing, the pH of the solution became 11 ∓ 0.5. The thickness of the CdSe thin film were calculated by commonly used weight difference method with the help of a sensitive microbalence.

XRD was done using Cu radiation in the range from 20° to 90°. The microq structure of the CdSe thin film was studied by using scanning electron microscope Carl Zeiss, Sigma VP). To record optical absorption spectra and other properites both UV-Vis-NIR spectrophotometer (Hitachi model-330,Japan) as well as CZ metal interference filter were used. An Aplab luxmeter (model 5011S) is used to measure the transmitted as well as reflected monochromatic radiation from the thin films

RESULT AND DISCUSSION:

XRD STUDIES

CdSe can form having the hexagonal,wurtzite-type structure or the cubic zincblende-type sructure. The x–ray diffraction pattern of as deposited [Fig.1(a)] and annealed [Fig.1(b)] CdSe thin films indicate that the studied films were polycrystalline and had a haxagonal (wurteire) structure. The as deposited CdSe thin films on glass substrates were found to be cubic, zincblende-type structure and likely oriented with the (111) plane parallel to the substrate. The observed low intensity peaks of CdSe thin film are nothing but fine crystaline nano particle.The crystalline quality of CdSe thin film improved when the film is annealed.

As the annealing temperature was increased the film became poly crystalline with cubic structure. Finally annealing transformed meta stable nanoparticle cubic phase into stable polycrystalline hexagonal phase.

The lattice parameter (a) for cubic structure is determined using relation

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$

where d is the spacing between the planes in the atomic lattice, hkl are the miller indices (13,6).

The average grain size of the samples can be evaluated by using the well known Deby-Scherrer formula
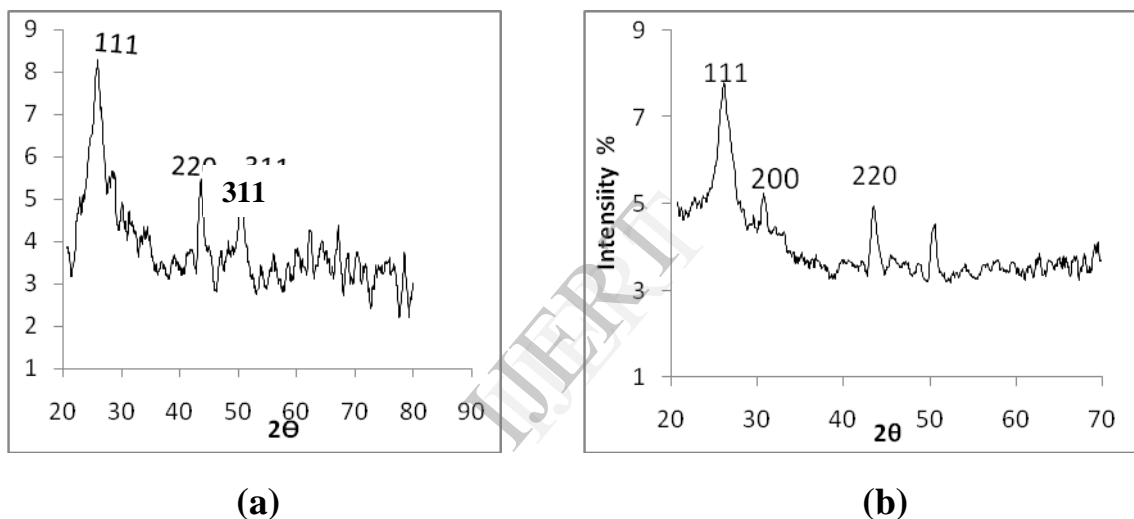
$$D = k\lambda/\beta cos\theta$$

Fig:-1 XRD pattern of CdSe thin flim (a) as deposited, (b) annealed at 473 K

where k is a constant of order unity, λ is the wave length of x-ray, θ is the Bragg's angle and β is full width at half maxima.

The dislocation density (δ) is evaluated from Williamson and Smallman's formula

$$\delta = \frac{1}{D^2} \ lines/m^2$$

Micro steain is obtained from

$$\varepsilon = \beta \ cos\theta$$

The obtained result is shown in the table

Table1. Different structural parameterts of CdSe thin films.

Material {Temp. in K)	Nos. of Peaks	2θ (degree)	D (spacing)	β FWHM	(hkl)	Lattice (a) Å	Grain Size (D) nm	Density (δ) x 10^{15} lines/m^2	Micro Strain (ε) x 10^3
CdSe Film as deposited	4	25.65	3.48	0.81	111	6.02	11.14	8.06	3.46
		30.13	2.95	0.63	200	5.02	14.53	4.74	2.65
		43.09	2.1	0.72	220	5.94	13.16	5.77	4.49
		50.25	1.81	0.69	311	6.01	14.08	5.04	2.74
CdSe Annealed	3	25.77	3.46	1.21	111	5.99	7.46	17.95	5.17
		42.81	2.11	1.05	220	5.98	9.00	12.33	4.28
		49.65	1.84	0.94	311	5.09	10.36	9.31	3.72

Structural Morphology

SEM is a convenient versatile technique to study microstructure of thin films Figs. 2(a) and 2(b) are the micrographs of as-deposited and annealed CdSe thin film.The SEM observations of as deposited CdSe thin film reveal that the films are composed of homogeneous nanosize grains. Needle like micro crystals of large size result are obtained from the SEM patterns of annealed CdSe thin film .
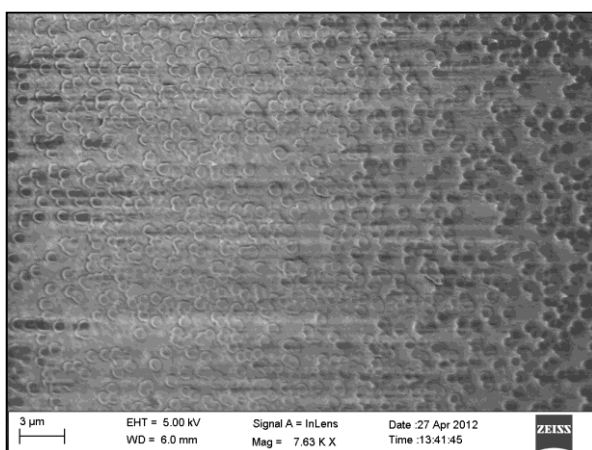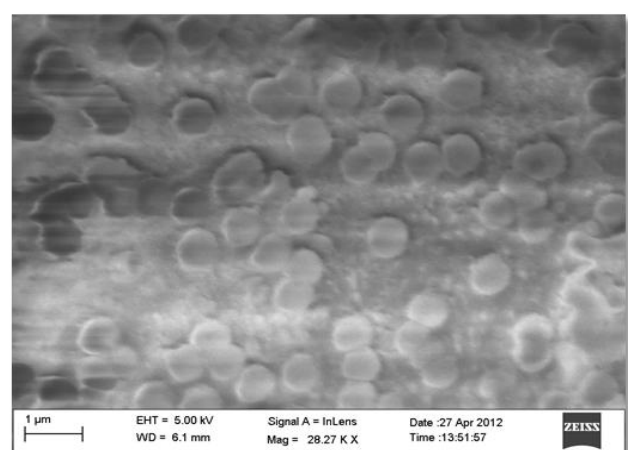
(a)   **(b)**

Fig. 2 SEM of CdSe thin films (a) as deposited, (b) annealed at 473 K

Spectral Properties

The typical transmission spactra of observed CdSe thin film is shown in Fig.3. The maxima and minima of interference due to superimposition of multiple reflected light waves were investigated.The transmission co-effient strongly depends on annealing temperatures. For heat treated samples the transmission co efficient is greater than that of fresh samples.
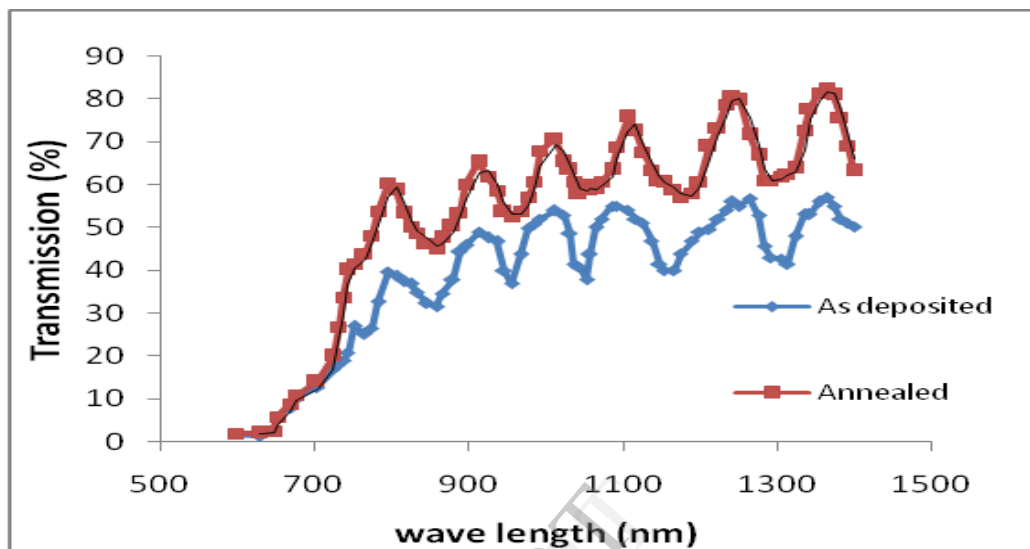

Fig. 3 : Transition spectra before and after the heat treatment

The dependence of the absorption co-efficient α, on the illuminating radiation, has been investigated for a range of energies from 1.71 ev -.22 ev.
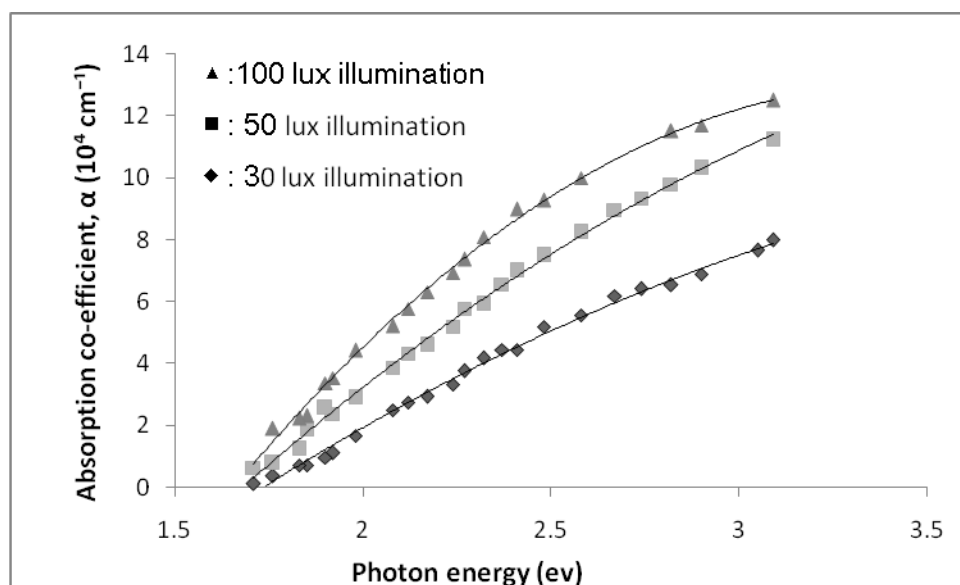

Fig.4.- Variation of absorption co-efficient with photon energy for different intensity of illuminating radiation .

Due to the absorption of illuminating radiation free electrons and holds were generated. But thin films of CdSe , grown at elevated temperature, were found to be polycralline having grains of different size with its boundery potential barrier. The photogenerated carriers recombined with respective opposite charges localized at grain boundery depletion regions, thereby reducing the grain boundery potential barriers along with the depth of trap centres. Thus the increase of intesity of illumination controlled the defect mechanism of CdSe thin films and became the cause of increase of optical absorption. In Fig.4, the smooth rise of optical absorption with increase of energy for different illuminating incident intensity radiation namely 30 lux , 50 lux and 100 lux are shown. From the plot band edges are calculated as 1.75 ev for 30 lux. 1.7 ev for 50 lux and 1.66 ev for 100 lux.

The intensity of incident radiation has a direct impact on photoabsorption. For a selective radiation, absorption co-efficients were caculated for different incident intensities. Fig.5. gives that absorption increases with the increase of intensityof radiation.
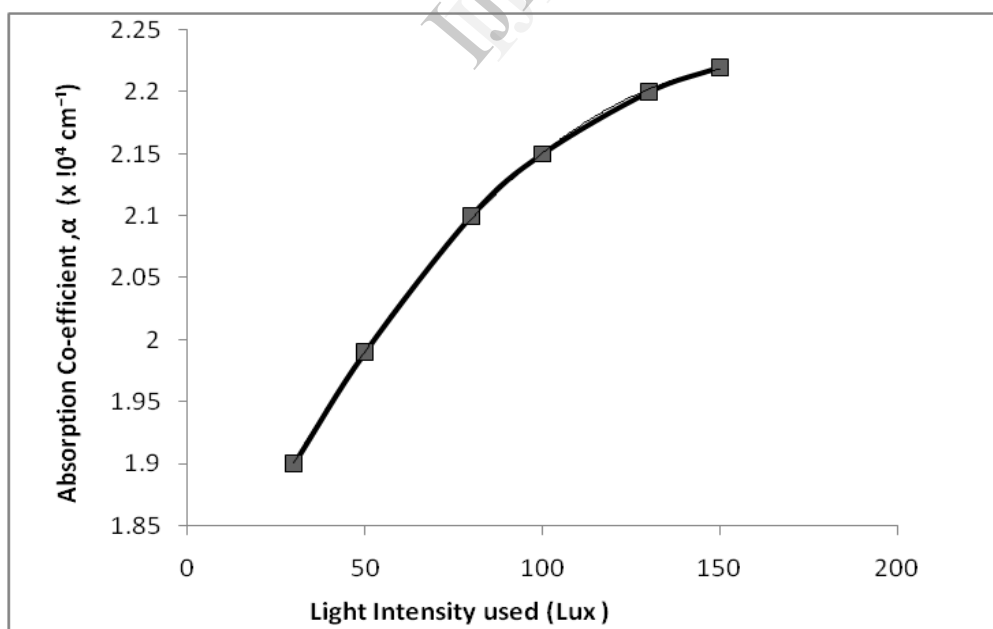

Fig.5: Variation of absorption co-efficient with intensity of selected monochromatic radiation (at constant W.L. 652 nm)

Optical absorption Studies:

The optical absorption spectra of as deposited and annealed CdSe thin films are shown in fig.6. It shows that optical absorption increases with the increase in annealing temperature. In this case it can be observed that absorption spactra were blue shifted which may be due to increase in crystallite size, decrease in deffect, change into color from red-orrange to dark black.
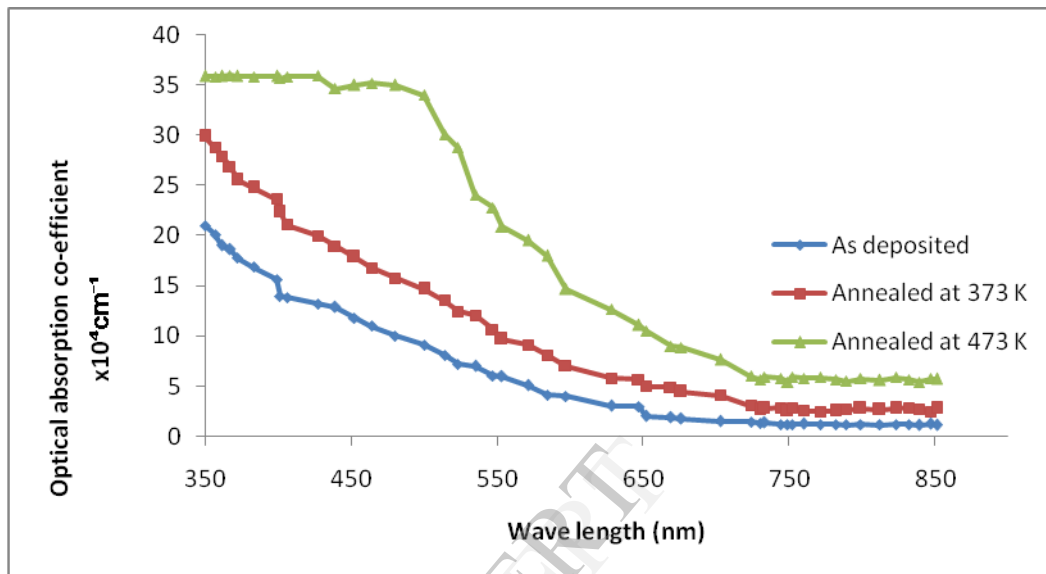

Fig. 6 : Plot of absorption coefficient vs. wavelength for CdSe thin films

The absorption datas were analyzed using the classical relation for near edge optical absorption of semiconductor as
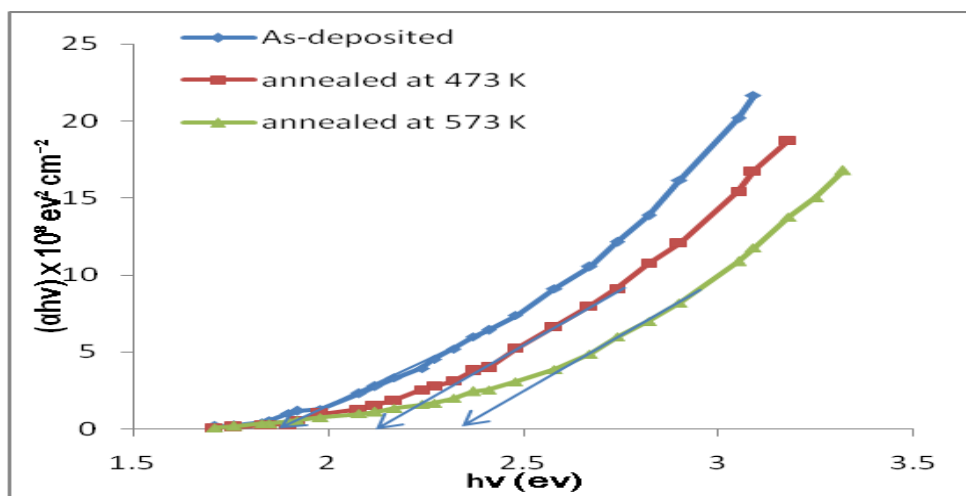
$$\alpha h\nu = A(h\nu - E_g)^{n/2}$$

Fig. 7: Plot of $(\alpha h\nu)^2$ vs. hν of CdSe of as deposited and annealed thin films

Where A is a constant, Eg is the optical band gap at which optical transition occurs, the nature of transition is determined by the value of n.The value of Eg have been calculated at and beyond the absorption edge. For direct transition n=1 and indirect transition for n=4.

The variation of $(\alpha h\nu)^2$ vertus $h\nu$ (fig.7) is linear at the absorption edge which indicates that CdSe is a semiconductor with a direct band gap. The extrapolation of sraight portion of the graph to $((\alpha h\nu)^2 = 0$ axis gives the value of the band gap. The Eg for as deposited CdSe nano particle was found to be 2.4 ev which greadually decreases to 2.1 ev and 1.71 ev after annealing to 473K and 573 K.

The annealing of CdSe fhin films caused a gradual red shift of the film spactra towards respective characteristic value of bulk CdSe due to sintering of nano crystallites into effective largeer crystallites. The all other samples studied in this work have shown similar behaviour.

CONCLUSION :

Thc crystaline size of vacuum deposited CdSe thin films increases when the films are treated by using heat. The absorption spectra are strongly iinfluenced by the annealing temperature as well as the intensities of illumination of the incident photon. A higher transmission coefficient is observed after a heat treatment. A direct optical band gaps of 1.71 ev, 2.1 ev and 2.4 ev were found for the films of annealed at 573 K, 473 K and as-grown from absorption spectra. The as-deposited CdSe nanoparticles are in cubic phase. Due to the annealing meta stable nanoparticles cubic phases transformed in to stable polycrystalline hexagonal phase.The crystalline size of the particle increases as a result of increasing the annealing temperature.

Acknowledgement:

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