STRUCTURAL, ELECTRICAL AND OPTICAL INVESTIGATIONS OF CdSe NANOPARTICLES

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Cadmium selenide nanoparticles are grown on to glass substrate by using chemical bath deposition method at room temperature. The samples are annealed in air for 4h at various temperatures and characterized by structural, electrical and optical properties. The as-deposited CdSe nanoparticles are in cubic phase with optical band gap 'Eg' 2.3eV and electrical resistivity of the order of $10^8 \Omega cm$. After annealing meta stable nanoparticles cubic phase transformed into stable polycrystalline hexagonal phase. Depending upon temperature, decease up to 0.6V and $10^3 \Omega cm$ were observed in the Eg and electrical resistivity, respectively. These changes have been attributed to the increase in the grain size of the CdSe nanoparticles. Optical absorption studies have been recorded. Dependence of optical band gap on crystallite size has also been studied.

1. Introduction

Presently nanoparticle materials have opened new chapter in the field of electronic applications, since material properties could be changed by changing the nanoparticle size and/or thickness of the film. New applications in various fields are also emerging. Development of such materials, whose structural, electrical and optical properties could be controlled, will be useful in many ways. For example optoelectronic devices, particularly solar energy conversion devices could be modified accordingly [1]. The synthesis of binary metal chalcogenide of groups II-VI semiconductors in a nanoparticle form has been a rapidly growing area of research due to their important non-linear optical properties, luminescent properties, quantum-size effect and other important physical and chemical properties [2-4]. The semiconductor nanoparticles belong to state of matter in the transition region between molecules and solids. There physical and chemical properties are found to be strongly size dependent. The properties of materials prepared by different methods are critically dependent on the nature of preparation technique and subsequent heat treatments like annealing in air, vacuum or different gaseous environments like H_2, N_2, Ar. etc. The micro structural features of nanoparticles are found to govern their electro-optical behavior. Cadmium selenide (E_g=2.3 eV) is one of the promising semiconducting material that has been studied for application in solar cells [5]. γ ray detectors [6], thin film transistors [7] etc. A number of workers have studied chemically prepared CdSe thin film [8-10]. However, little attention has been paid to the various properties of chemically deposited CdSe thin films. In the present work we have studied structural, electrical and optical properties of CdSe nanoparticles by chemical bath deposition method.

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2. Experimental techniques

Commercially available glass micro slides of dimension 26 mm x 75 mm x 2 mm have been used for deposition of thin film by chemical bath deposition method. The CdSe film thickness was measured with commonly used weight difference method by using a sensitive microbalance. Crystallographic study was carried out using Phillips PW-1710, X-ray diffractometer using Cu-Kα radiation in the range from 20 to 100^0. The microstructure of the CdSe thin films on the glass substrate was studied by using a scanning electron microscope (Cambridge Stereoscan 259MK-III). The dark electrical resistivity and thermoelectric power of films were measured using dc two-probe method in the temperature range 300-500 K. In order to study optical properties, optical absorption spectra were recorded in the wavelength range 300-850 nm using UV-Vis-NIR spectrophotometer (Hitachi model-330, Japan).

3. Results and discussion

3.1 XRD studies

Cadmium selenide can be formed having the hexagonal, wurtzite-type structure or the cubic, zincblende-type structure [11]. Many workers have reported that chemically deposited CdSe thin films onto the glass substrates are either hexagonal [9] or cubic [8]. Fig. 1 shows XRD patterns of as-deposited and annealed CdSe thin films at different temperatures. As-deposited CdSe thin film onto glass substrates were cubic, zincblende-type structure, which showed any one intense reflection peak (111). The low intensity peaks show that the as-deposited CdSe thin films are coarsely fine crystalline nanoparticle. The thin films annealed at 373 K were nanopartiles cubic with slight improvement in crystallinity, whereas films annealed at 473 K becomes polycrystalline with cubic structure. Further, CdSe thin films annealed at 573 K were polycrystalline with a mixture of cubic along with hexagonal (more dominating) structure with highest intense reflection peaks (100). The nanoparticle size of CdSe thin films was calculated by using Scherrer's formula,

$D = \dfrac{K\lambda}{\beta\cos\theta}$ where 'D' is the crystalline size, 'λ' the X-ray wavelength used, 'β' the angular

line width of half maximum intensity and 'θ' is Bragg's diffraction angle, 'K' is some constant 0.9 for CdSe. From Table – 1, it is clear that the average crystalline size of as-deposited CdSe thin film was 40 Å which increased up to 180 Å with increasing annealing temperatures.

Table 1. Crystalline size, band gap 'Eg' and electrical resistivity of as-deposited and annealed CdSe thin films.

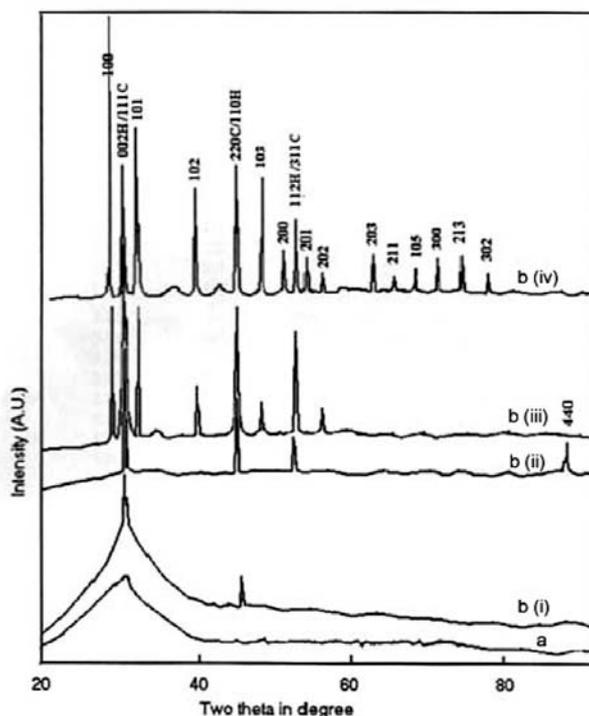| Thin films	Crystalline size (Å)	Band gap 'Eg' (eV)	Electrical resistivity (Ω cm)
As-deposited	40	3.0	3.25×10^8
373 K	60	2.9	9.58×10^4
473 K	80	2.8	5.38×10^4
573 K	120	2.7	8.23×10^3
673 K	180	2.6	1.17×10^3

Fig. 1 XRD patterns of CdSe thin films (a) as-deposited (b) annealed at (i) 373 K, (ii) 473 K, (iii) 573 K and (iv) 673 K

3.2 Surface morphology

Scanning electron microscopy (SEM) is a convenient technique to study microstructure of thin films. Fig. 2(a) and (b) shows the SEM micrographs of as deposited and annealed (at 673K) CdSe thin films. From SEM studies, it is observed that the as-deposited CdSe films are nanocrystalline, homogeneous, without cracks or holes and well covered to the glass substrate. The SEM of CdSe thin film annealed at 673 K clearly shows the needle like micro crystals of larger size, confirms transformation of sphalerite (cubic phase) to wurtzite (hexagonal phase) structure.
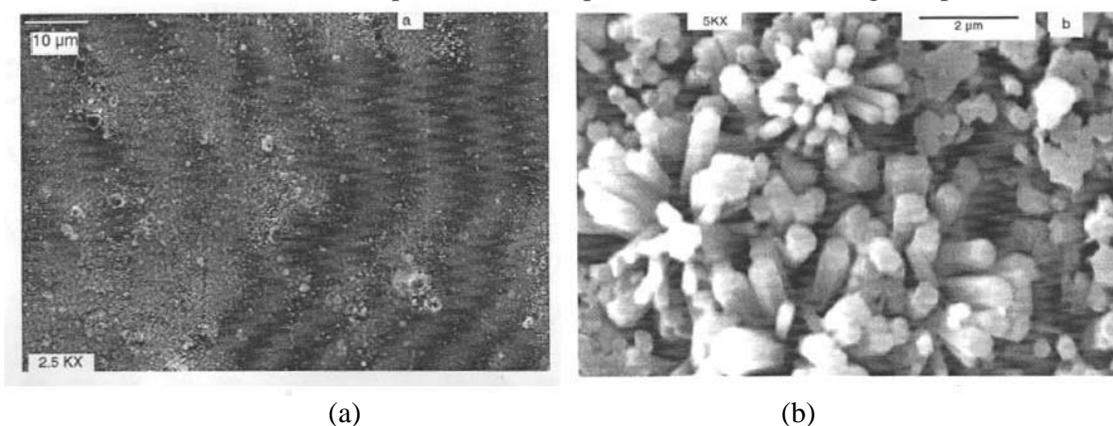

(a)   (b)

Fig. 2 SEM of CdSe thin films (a) 'as-deposited' and (b) annealed at 673 K.

4. Electrical properties

Fig. 3 shows the variation of band gap 'E_g' vs. crystalline size of CdSe thin films. As the annealing temperature was increased, the crystalline size of CdSe films was increased resulting in

to decrease in band gap. The normal bulk value is attained at annealing temperature 573 K. This is attributed to the crystalline size-dependant properties of the energy band gap.
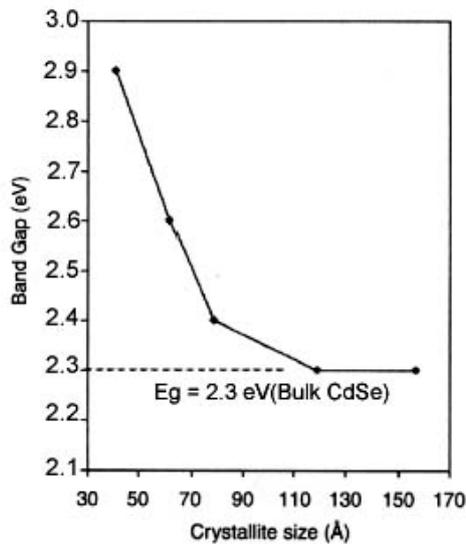

Fig. 3 Plot of band gap vs. grain size of
CdSe thin films.

Fig. 4 shows the variation of electrical resistivity (ρ) with inverse of temperature for CdSe thin films. From Fig. 4, it is observed that the resistivity of as-deposited and annealed CdSe thin films decreases with increase in temperature. The room temperature electrical resistivity, $3.25 \times 10^8 \Omega$cm, of as – deposited CdSe thin films was decreased to $1.17 \times 10^3 \Omega$cm after annealing at temperature 673 K. The high value of resistivity for as-deposited CdSe thin film may be attributed to the nanocrystalline nature of thin film.
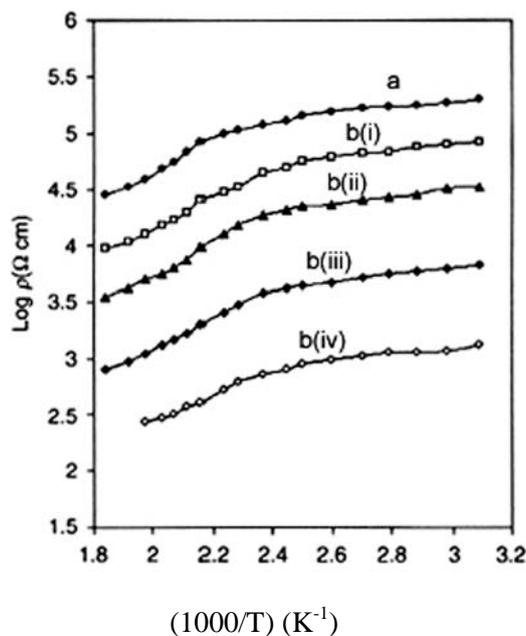

$(1000/T) (K^{-1})$

Fig. 4 Plot of log ρ vs. (1000/T) of CdSe thin films (a) as-deposited, (b) annealed at
(i) 373K, (ii) 473 K, (iii) 573 and (iv) 673K

5. Optical absorption studies

The absorption spectra of as-deposited and annealed samples were studied without taking into account the reflection and transmission losses. Fig. 5 shows the variation of optical absorbance (αt) with wavelength (λ). It shows that optical absorption increases with increase in annealing temperature. It may be due to increase in crystallite size, decrease in defects and change in color from red-orange, dark brown to dark black. The absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors.

$$\alpha = \frac{K^{'}\left(h\nu - E_g\right)^{n/2}}{h\nu}$$

Where $K^{'}$ is a constant, E_g is the band gap, n is a constant equal to one for direct gap semiconductors and four for indirect gap semiconductor materials. The variation of $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 6) is linear at the absorption edge which confirms that CdSe is a semiconductor with a direct band gap. Extrapolating the straight-line portions of the plot $(\alpha h\nu)^2$ versus $h\nu$ for zero absorption coefficient value give the 'E_g', which are listed in Table 1. The 'E_g' for as-deposited CdSe nanoparticles was found to be 2.3 eV which gradually decreased to 1.7 eV after annealing the CdSe to 673 K. Fig. (3) shows the variation of band gap 'E_g' versus crystallite size of CdSe nanoparticles. As the annealing temperature was increased, the crystallite size of CdSe films was increased resulting in to decrease in band gap. Therefore, annealing the films, exhibits strong red shift in their optical spectra due to localization of charges in individual nanocrystals. Annealing of the films caused a gradual shift of the film spectra to that characteristic of bulk CdSe, due to sintering of the nanocrystallites into effectively larger crystallites. The normal bulk value is attained at annealing temperature 57 K. This is attributed to the crystallite size-dependant properties of the energy band gap. Similar 'blue/red shift' in band gap energy 'E_g' values for the films with smaller thickness and/or crystallite sizes have been reported for chemically deposited thin films [9, 12-13]. It is important to note that there is no significant change in band gap due to structural phase transform of CdSe from metastable cubic to stable hexagonal. Since previous workers have also reported that there is very small difference between the band gaps of both the phases [12]. Previous workers reported two band gaps for hexagonal medication due to spin orbit interaction [14]. In the present case, no such phenomenon was observed.
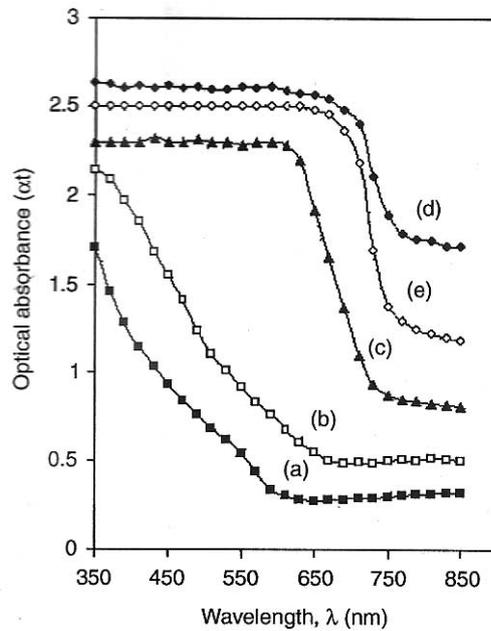
Fig. 5 Plot of absorbance (αt) *vs. wavelength for CdSe thin films (a) as deposited, and annealed at (b) 373 K, (c) 473 K, (d) 573 K and (e) 673 K.*
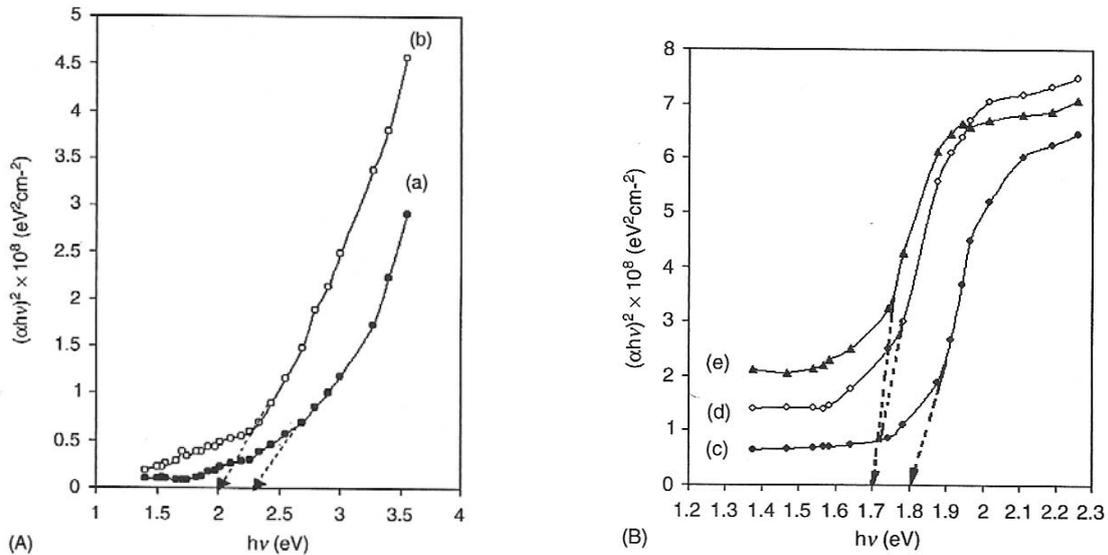

Fig. 6   (A) Plot of $(\alpha h \nu)^2$ *vs.* $h\nu$ *of CdSe thin films (a) as deposited, and   (b) annealed at 373 K, (B) Plot of* $(\alpha h \nu)^2$ *vs.* $h\nu$ *of CdSe thin films annealed at (c) 473 K, (d) 573K and (e) 673 K.*

6. Conclusions

CdSe thin films have been successfully deposited onto glass substrate by chemical bath deposition technique. The as-deposited CdSe nanoparticles are in cubic phase. After annealing meta stable nanoparticles cubic phase transformed in to stable polycrystalline hexagonal phase. The electrical resistivity is of the order of $10^8 \Omega cm$ with optical band gap 2.3 eV. Air annealing was found to increase crystallinity of the CdSe films along with recrystalization process that changed nanocrystalline to metastable cubic to stable hexagonal phase (673 K) at higher annealing temperature. The crystalline size of the particles increases as a result of increasing the

annealing temperature. Consequently, the electrical resistivity decreases and CdSe film shows 'red shift' of 0.6 eV. No significant change has been recorded in optical band gap due to structural phase transform of CdSe from metastable cubic to stable hexagonal phase.

Acknowledgement

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