

Raman, PL And Hall Effect Studies Of Cdse Thin Film Deposited By Chemical Bath Deposition

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Abstract: CdSe thin films were fabricated on glass substrate by chemical bath deposition method. The films were deposited by keeping the deposition time a constant and also by keeping solution bath temperature a constant. Some of the deposited films were annealed. The as-deposited and annealed films were subjected to various spectroscopic studies such as Raman Spectroscopy and Photo luminescence spectroscopy. The hall effect measurement shows that CdSe is an n-type semiconductor and its resistivity decreases on annealing

Key words: CdSe, Raman Spectroscopy, Photo luminescence, Hall effect, Mobility, Carrier concentration

1. Introduction:

The II-VI binary semiconducting compounds belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe) are important materials for photovoltaic applications [1-3]. CdSe is a good photovoltaic material due to its high absorption coefficient and nearly optimum band gap energy for the efficient absorption of light and conversion into electrical energy. Its applications in solar cells, Optical coating, Optoelectronic devices and light emitting diodes are experienced [4]. Other areas of successful applications include photo detectors, light amplifiers, lasers, gas sensors, large –screen liquid crystal display and photoluminescence response [5]. CdSe thin film can be deposited either by Physical or Chemical methods. The Chemical bath deposition (CBD) is relatively simple and economic. CBD technique was employed by several researchers for the deposition of CdSe thin film on glass substrate [6-8] In the present work CdSe thin films were fabricated on glass substrate at various deposition times and also at various solution bath temperatures. The film deposited at 70 °C, 1 hour was annealed for two different temperatures 150°C and 200 °C in air for 1.5 hrs and the film deposited at 70 °C, 2 hour was also annealed under the same condition. The Raman and PL spectrum of the samples were taken and the Hall effect measurements were done for detecting the type of conductivity and for measuring the electrical properties.

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2. Experimental:

CdSe thin films have been prepared by Chemical bath deposition method. The principle underlying the deposition of CdSe thin films have been discussed by Chopra and Das [9]. It is based on the slow release of Cd²⁺ and Se²⁻ ions in aqueous solution of P^H greater than 10 and subsequent condensation of these ions on glass substrate vertically mounted in the solution bath.



Sodium Selenosulphate (Na₂SeSO₃) was used as Selenium source and CdCl₂ as Cadmium source [10] The reduction of Na₂SeSO₃ to elemental Se was through the following reaction in the aqueous ammoniacal medium.



The Cd²⁺ ions released in the bath and the selenium ions condense to give CdSe solid phase provided that the ionic product is greater than the solubility product of the compound. The solubility product of CdSe is very low and hence even very low concentration of Cd²⁺ and Se²⁻ ions are sufficient to yield the solid phase. The rate of growth of film depends on the temperature, P^H value and the relative concentration of Cd²⁺ and Se²⁻ ions in the reaction mixture. By controlling these parameters uniform films of desired thickness can be grown. Preparation of Sodium Selenosulphate was as follows: Elemental Selenium in the form of fine powder was added to an aqueous solution of Sodium sulphite heated to 90 °C. The solution was stirred well until all the selenium was dissolved. It was then cooled to room temperature and filtered to get a clear solution of Na₂SeSO₃. The films were deposited on glass slides of size 7.5mmX2.5mmX1.2mm. Before deposition; the substrate should be cleaned in the following way: the slides were first dipped in hot trichloroethylene for 15 mins and then in acetone to remove oily impurities on the glass slides. They were then cleaned in detergent, chromic acid and deionized water and finally dipped in acetone and dried in air. The chemical bath was constituted from 0.2M solutions of CdCl₂ and Na₂SeSO₃. The chemical bath was prepared by the following sequence of addition of reactants: 20 ml of 0.2M CdCl₂, few drops of triethanolamine and 25% NH₄ and 20 ml of Na₂SeSO₃. The P^H of the solution was adjusted to be more than 10 by adding more NH₄, if required. The solution was thoroughly stirred using a magnetic stirrer with a hot plate. The solution bath temperature was maintained at a

constant temperature of $50\pm 2^\circ\text{C}$, $60\pm 2^\circ\text{C}$, $70\pm 2^\circ\text{C}$ and $80\pm 2^\circ\text{C}$ respectively. The glass slide was mounted vertically inside the bath with a substrate holder. Each time the deposition time was assigned to be 2 hours. After deposition the films were removed from the bath and then washed in distilled water and dried in air. Then three samples were also deposited by maintaining solution bath temperature at $70\pm 2^\circ\text{C}$ for three different deposition times 1 hour, 1.5 hour and 3 hrs respectively. The films deposited at 70°C , 1 hour and at 70°C , 2 hour were annealed for two different temperatures, 150°C and 200°C in air for 1.5 hrs

3. Results and discussion

3.1. Thickness measurement:

The thickness of the as-deposited and annealed samples were measured using Stylus Profiler at CUSAT. The observed thicknesses were listed in table -1

Sample	Sample Code	Thickness in nm
CdSe 50°C , 2 hrs	CdSe 1.1	1790
CdSe 60°C , 2 hrs	CdSe 1.2	1840
CdSe 70°C , 2 hrs	CdSe 1.3	1465
CdSe 80°C , 2 hrs	CdSe 1.4	1811
CdSe 70°C , 1 hrs	CdSe 2.1	1400
CdS 70°C , 1.5 hrs	CdSe 2.2	1465
CdS 70°C , 3 hrs	CdSe 2.3	1750
CdSe 70°C , 1 hrs annealed at 150°C	CdSe 2.1.1	1376
CdSe 70°C , 2 hrs annealed at 150°C	CdSe 1.3.1	1320

Table -1

3.2. Photoluminescence studies

The Principle of PL measurements is to create carriers by optical excitation with photon energy above the band gap of the film. The optical luminescence spectra were recorded at room temperature in the range of 450 – 600 nm with excitation wavelength of 325 nm using PL spectrometer. Figure shows the emission spectra for the as-deposited samples Fig 1 and Fig 2 and annealed samples Fig 3 and Fig 4

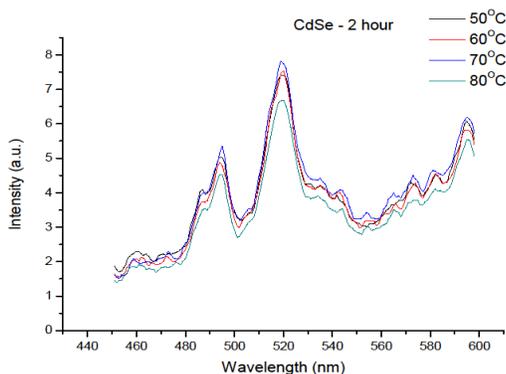


Figure 1: PL spectrum of CdSe deposited at different solution bath temperature at a constant deposition time -2 hours

The PL intensity is determined by the radiative recombination of excitons. The interaction between electrons and holes as well as the electron-hole attractive interaction are taken. The photoluminescence process is a charge transfer process, since the photoluminescence emission is associated with the combination of electrons from the conduction band and holes in the valence band and the change of the near- band- edge [11-12].

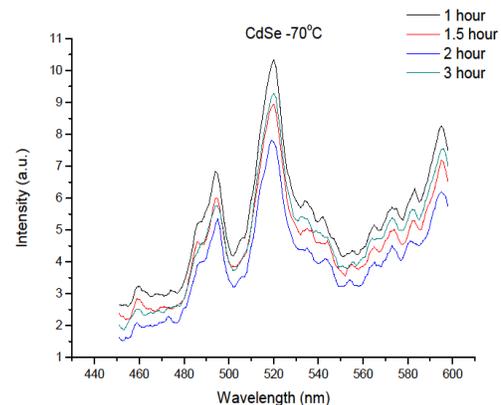


Figure 2. PL spectrum of CdSe deposited at different deposition times at a constant solution bath temperature

The Photoluminescence spectra of CdSe thin film deposited at different solution bath temperatures (fig 1) shows a sharp emission at 520 nm (green region) and a less intense one at 495 nm (blue region) and 595 nm. The sharp emission in the green region (531nm) and a less intense emission in the blue region(485 nm) were reported earlier [13]. The same measurements with slight change in intensity of the emission peaks were observed in the PL spectrum of the CdSe thin film deposited at different deposition times (Fig 2). The Fig 3 and Fig 4 indicate the effect of annealing on PL spectrum. No accountable change was observed in the wave length corresponding to the emission peaks , but it was observed that the intensity of sharp emission peak (520 nm) increased greatly for the film annealed at 200°C in both the cases

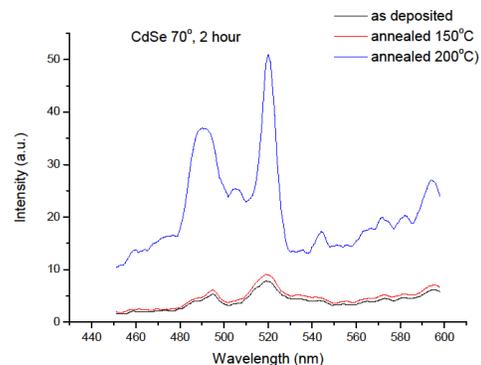


Figure 3. PL spectrum of as deposited and annealed CdSe film deposited at 70°C , 2 hour

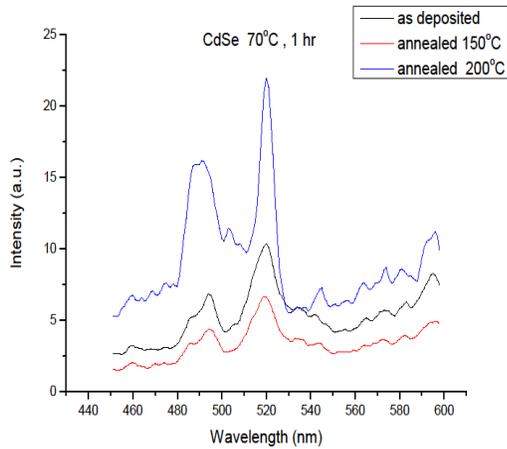


Figure 4 PL spectrum of as deposited and annealed CdSe thin film deposited at 70° C, 1 hour

3.3. Raman Spectroscopy:

Raman spectroscopy has been recognized as a very sensitive tool for characterizing crystalline structure of CdSe including lattice defect, grain boundaries and stacking faults. The standard Raman spectrum for bulk CdSe is characterized by two peaks at 209 cm⁻¹ and its overtone at 420 cm⁻¹ which are assigned to the longitudinal optical phonon mode (LO mode) [14-16]. In another study the LO and its overtone were reported at 209 cm⁻¹ and 410 cm⁻¹ respectively [17-18]. In the present study Fig 5. shows the Raman spectra of CdSe thin films deposited at different solution bath temperatures with deposition time maintained at 2 hours in each time. For all the films, the first order LO phonon modes were observed at 203 cm⁻¹ with a shift of 6 cm⁻¹ as compared with earlier reported values. The second order LO phonon modes were observed at 418 cm⁻¹, 413 cm⁻¹, 409 cm⁻¹ and 413 cm⁻¹ respectively for films deposited at 50° C, 60° C 70° C, 80° C. The small Raman shift, both LO and 2LO, might be due to the strain developed in CdSe layers during deposition. The higher intensity corresponding to the film deposited at 60° C and 70° C indicates a better crystalline structure of the film [19].

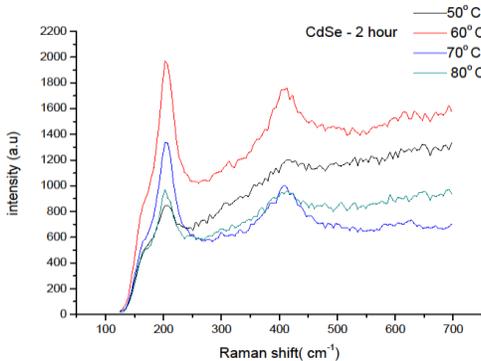


Figure 5. Raman spectra for CdSe thin film deposited at different solution bath temperatures at a constant deposition time (2 hours)

Fig 6. Shows the Raman spectra for the CdSe thin film deposited at different deposition times with solution bath temperature maintained at 70° C in each time. Here also the first order phonon modes were observed at 203 cm⁻¹ for all

films and their overtones are observed at 413 cm⁻¹ except for films deposited for 2 hour (408 cm⁻¹) The Figures 7&8 show the annealing effect on Raman spectra. In both the cases the films annealed at 150 °C shows the first order LO phonon mode at 208 cm⁻¹ and no considerable changes are observed in their overtones.

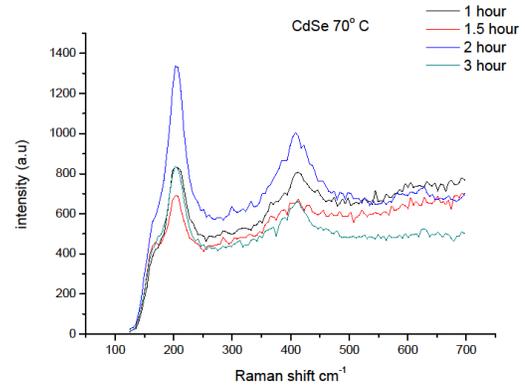


Figure 6. Raman spectra for CdSe thin films at different deposition times at a constant solution bath temperature 70° C

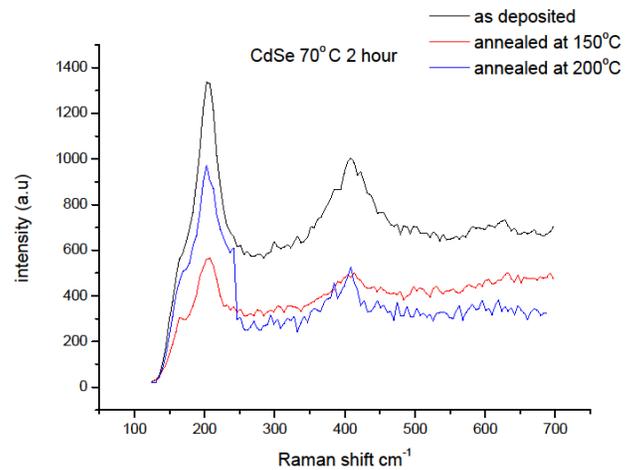


Figure 7. Raman spectra for as deposited and annealed CdSe thin film deposited at 70° C, 2 hour

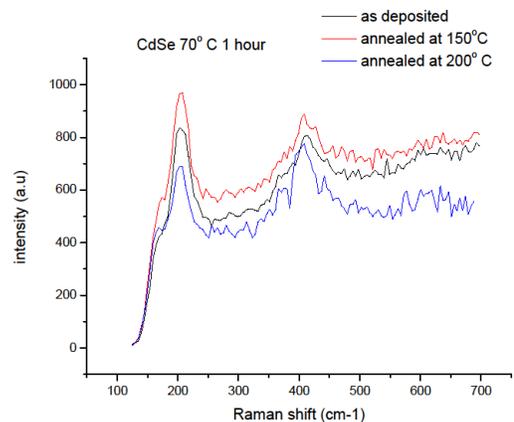


Figure 8. Raman spectra for as deposited and annealed CdSe thin film deposited at 70° C, 1 hour

3.4. Hall effect measurement:

The electric properties of the materials are of great importance in determining the use of films in photovoltaic field. The electric parameters can be determined by studying the Hall effect of the sample. The Hall effect measurement were carried out at room temperature using Ecopia Hall Effect Measurement System (HMS- 3000). The measurement includes Carrier concentration, Hall coefficient, Hall mobility, resistivity and conductivity. The observed data for as- deposited and for annealed samples

of CdSe thin films are recorded in table -2. The negative value of Hall coefficient confirms the n-type conductivity of the as-deposited and annealed samples. The data also confirms that the resistivity decreases on annealing. The resistivity of the films was increased for films deposited at solution bath temperatures 70°C and 80°C due to the decrease in non-stoichiometry in the films [20]. It was also observed that resistivity decreases with increases in deposition time

Sample	Sample Code	Carrier concentration /cm ³	Mobility cm ² /VS	Resistivity Ohm cm	Conductivity Ohm ⁻¹ cm ⁻¹	Hall Coefficient cm ³ /C
CdSe 50°C, 2 hrs	CdSe 1.1	-6.561E+16	8.589E-2	1.108E+3	9.029E-4	-95.13
CdSe 60°C, 2 hrs	CdSe 1.2	-2.857E+16	2.011E-1	1.086E+3	9.207E-4	-218.42
CdSe 70°C, 2 hrs	CdSe 1.3	-1.118E+15	2.209E-1	2.529E+4	3.955E-5	-5.585E+3
CdSe 80°C, 2 hrs	CdSe 1.4	-1.668E+15	1.706E-1	2.193E+4	4.560E-5	-3.742E+3
CdSe 70°C, 1 hrs	CdSe 2.1	-1.029E+15	1.096E-1	5.535E+4	1.807E-5	-6.067E+3
CdS 70°C, 1.5 hrs	CdSe 2.2	-2.791E+14	4.17	5.358E+3	1.866E-4	-2.236E+4
CdS 70°C, 3 hrs	CdSe 2.3	-2.622E+14	7.791	3.055E+3	3.273E-4	-2.381E+4
CdSe 70°C, 2 hrs annealed at 150°C	CdSe 1.3.1	-5.031E+15	3.866E-1	3.209E+3	3.116E-4	-1.241E+3
CdSe 70°C, 1 hrs annealed at 150°C	CdSe 2.1.1	-2.26E+14	33.18	8.326E+2	1.201E-3	-2.763E+4

Table -2

4 Conclusion:

Chemically deposited CdSe films have a strong PL emission peak at 520 nm with two less intense peaks. The Raman spectra showed the presence of LO and its first overtone (2LO) phonon peaks. PL and Raman analysis enabled the researchers to show the evidence for good crystalline quality of the films. The Hall effect measurements confirm the n-type conductivity of the CdSe thin films and also the resistivity of the film which decreases on annealing.

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