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Studies on optical and electrical properties of PVA capped nanocrystalline CdSe thin film prepared by chemical bath deposition method

S. R. Devi[a], P. J. Saikia[b], M. A. Hussain[c,*]
[a]*Department of Physics, Presidency College, Motbung-795107, Manipur, India*
[b]*Department of Electronics, J. B. College (Autonomous), Jorhat-785001, Assam, India*
[c]*Department of Physics, Imphal College, Imphal-795001, Manipur, India*

PVA-capped nanocrystalline CdSe thin films are deposited on chemically clean glass substrates by chemical bath deposition technique using Cadmium acetate [$Cd(CH_3COO)_2.3H_2O$ and Sodium Selenosulfate (Na_2SeSO_3) as Cd^{2+} and Se^{2-} ions sources respectively. Polyvinyl Alcohol (PVA) is act as a capping agent. Films of five different molarities (0.1 M–0.50M) of same pH value 8 were prepared at room temperature 298 K. The characteristics of the prepared CdSe thin films are investigated in detail by measuring their optical and electrical properties. The band gap energy of 2.16–2.49 eV was determined from the optical absorption spectra. The optical band gap decrease with increase in molarities. The electrical conductivity measured using two co-planar Aluminium electrodes are found to increase with increase in temperature showing semiconducting nature of the films. The electrical conductivity at room temperature is found to be of the order of 10^{-4} Ω^{-1} cm^{-1}.

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1. Introduction

The studies about the semiconductor thin films have received much attention due to their various applications in electronic devices. Different semiconducting materials are employed to study their suitability in different solid-state devices depending on their band gaps and properties. CdSe is a wide band gap material and suitable candidate for the solar energy conversion devices as its forbidden energy gap 1.65 -1.85 eV [1-2]. The band gap energy of CdSe (1.74eV bulk form) can increased to higher values by decreasing the size of the grains into the nanoregime. This property makes it capable of absorbing a major portion of solar energy and hence provides ample scope for the fabrication of solar cells and other electronics devices. The optical properties of the semiconducting nanoparticle can be determined from the absorption spectrum of the semiconducting nano particles. Recently many extensive works are going on in the optical properties of semiconducting CdSe nanocrystals as they exhibit strong size dependent optical properties. In order to develop the new device and applications in electronics deivices, main concentration have given to the study of their electrical and optical properties of CdSe thin films [3]. Many deposition techniques have been developed to synthesize CdSe in thin film such as vacuum evaporation [4], electrodeposition [5], spray pyrolysis [6], successive ionic layer adsorption and reaction (SILAR) [7] and chemical bath deposition (CBD) [8]. However, among these various techniques of deposition, CBD technique is suitable for the synthesis of PVA-capped CdSe nanoparticles thin film as it is easy to handle, cost effective, and convenient for large area deposition [9, 10]. In the present work, we have prepared PVA- capped nanocrystalline CdSe thin films by chemical bath deposition and studied their optical and electrical properties.

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[*] Corresponding author: hussainmakak@gmail.com
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2. Experimental procedure

2.1. Substrates cleaning

For the deposition of thin film by chemical bath deposition (CBD) technique, cleaning of glass substrates is very important factor. The substrates of appropriate sizes of 3 x 2 cm^2 is cut from glass slide and wash with detergent solution and treated in a mixture of nitric acid and isopropyle alcohol for 30minutes. Then, glass substrates are taken out from the solution and ultrasonically cleaned with deionised water for another 30 min and wiped with acetone and heated in a oven at 200^{0}C for about an hour for drying.

2.2. Preparation of nanocrystalline CdSe thin films in PVA matrix

Nanocrystalline CdSe thin films are deposited on glass substrates by chemical bath deposition (CBD) technique using Cadmium acetate [$Cd(CH_3COO)_2.3H_2O$ and Sodium Selenosulfate (Na_2SeSO_3) as Cd^{2+} and Se^{2-} ions sources respectively whereas Polyvinyl Alcohol (PVA) was used as capping agent. For the preparation of nanocrystalline CdSe thin films in PVA matrix involves in three steps. First steps, Preparation of PVA matrix solution. For this, 2 wt% (i.e. 2gm of PVA dissolve in 100ml of distilled water) of PVA solution was prepared in double distilled water and stirred with the help of a magnetic stirrer at constant temperature at 348K until a transparent solution was formed. Different concentrations of Cadmium acetate [$Cd(CH_3COO)_2.3H_2O$ were used to get different matrix solution. Second steps, 0.25M of Sodium Selenosulfate (Na_2SeSO_3) was prepared by refluxing 4g of Se powder with 20g of sodium sulphite (Na_2SO_3) in a three necked round bottom flask containing 100ml of deionized water at 70^{o}C in N_2 atmosphere for 5hrs and filtered. The filtrate solution was use as stock solution of Se^{-2} source. Finally, equal amount of PVA matrix solution and Se^{-2} source are add together. The pH value (8) of the solution is adjust by drop wise addition of aqueous ammonia (NH_3) and then kept at room temperature (298K) for further deposition. The cleaned glass substrates are vertically put into the solution, supported by the wall of the beaker. The colour of the solution slowly changes to orange red. This indicates the initiation of chemical reaction and formation of CdSe films. After deposition of 24hrs, the substrates coated with orange red colour CdSe on both sides are taken out from the beaker and thoroughly wash with distilled water and dried in open atmosphere. The film on the substrate surface facing the wall of the beaker during deposition is uniform and retained for further studies. The film on the other substrate surface facing towards the interior of the bath is remove with dilute acid. In the same procedure as discussed above, nanocrystalline CdSe thin films of another four sets of thin films at different reactant concentrations by keeping constant pH value 8 and deposition temperature 298K are prepared and to study their effects optical and electrical properties. The average thickness of the film is measure by the Tolansky method [11]. The optical characteristics are studied by using Carry-300 scan UV–Visible spectrophotometer. For electrical conductivity measurement 'Al' electrodes in a coplanar configuration separated by a small gap are evaporated in vacuum on the surface of prepared CdSe thin films. A constant voltage is applied cross the sample and the current is noted by using a Keithley electrometer and temperature of the thin film is measure by Instron (IN 303) electronic temperature controller.

2.3. Reaction mechanism for the formation of nanocrystalline CdSe thin films

The deposition process is based on slow release of Cd^{+2} and Se^{-2} ions in the solution, which then condense either ion by ion or cluster by cluster on the surface of the substrate. The deposition of CdSe thin film takes place when the ionic product (IP) of Cd^{+2} and Se^{-2} ions exceeds the solubility product (SP) of CdSe (i.e IP ≥ SP). The decomposition of Sodium Selenosulfate is made possible in an aqueous alkaline medium containing ammonia as a complexing agent which controls the release of Cd^{+2} ions in the reaction bath.

The hydrolysis of Sodium Selenosulfate in solution gives Se^{-2} ions in according to the chemical reaction

$$Na_2SeSO_3 + 2OH^- \longrightarrow Na_2SO_4 + Se^{2-} + H_2O \tag{1}$$

Similarly, the hydrolysis of ammonia in water gives OH$^-$ ions

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (2)$$

When ammonia is added to the solution it forms a complex lead tetra-amine ion $\left[Cd(NH_3)^{2+}\right]$ as

$$Cd(CH_3COO)_2.3H_2O \rightarrow Cd^{2+} + 2CH_3COO^{-1} + 3H_2O \qquad (3)$$

$$Cd^{2+} + 4NH_3 \rightarrow Pb(NH_3)_4^{2+} \qquad (4)$$

Then the $\left[Cd(NH_3)^{2+}\right]$ reacts with S^{-2} ions that results in the formation of CdSe thin film as follows

$$Cd(NH_3)_4^{2+} + Se^{-2} \rightarrow CdSe + 4NH_3 \qquad (5)$$

In the initial stage, the film formation is slow which could be due to the time required for the formation of stable nuclei on the glass substrates. Once, a CdSe layer is formed then the deposition of film is fast and continued till the reactants exhausted from the deposition bath.

3. Results and discussions

3.1. Photoluminescence studies

The Photoluminescence spectra of nanocrystalline CdSe films are recorded in the wavelength range 350nm-750nm with excitation wavelength of 395nm. Photoluminescence emission spectra of five different reactant concentrations are shown in Fig. 1. The spectra for all the samples contain two emission bands i.e. higher energy band and lower energy band. The Photoluminescence spectra of all the CdSe samples display broad emission spectra in the blue region of visible spectra. For 0.5M, the maximum PL peak is 498nm and 627nm corresponding to the band gap energy 2.5eV and 1.97eV respectively. The high energy band corresponding to the band gap energy 2.5eV is due to the band to band transition and the low energy band corresponding to 1.97eV is due to the defects levels present within the band gap. For 0.4M, 0.3M, 0.2M and 0.1M the maximum PL peaks are 506nm, 516nm, 522nm and 527nm corresponding to the band gap energy 2.45eV, 240eV, 2.37eV and 2.35eV respectively. The emission peaks for all the CdSe films at 498nm-527nm are attributed to transitions from conduction band to valence band. It is clearly shown from the Fig. 1 that the increase of band gap from 2.35eV to 2.5eV with increase of reactant concentration from 0.1M to 0.5M and the emission peaks shifted towards the lower wavelength due to quantum confinement effect [12]. The intensities of the peaks increases with increase in reactant concentrations, and also shifted the peaks position towards the lower wavelength [13].

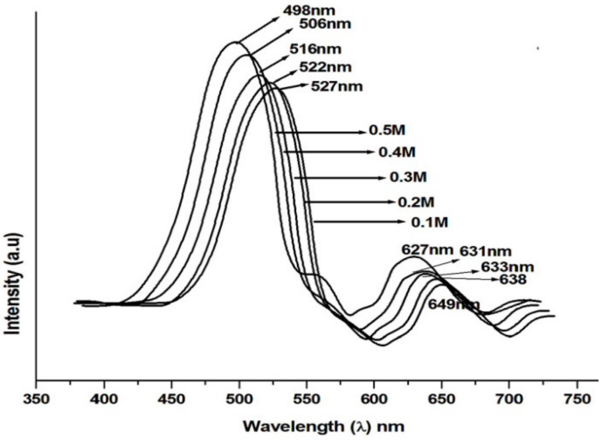

Fig. 1. PL Spectra of PVA-Capped CdSe thin films prepared at different molarities.

The high-energy band, which is close to the band edge, is sharper and better defined than the second band seen at the lower energies. The long wavelength band is weak in intensity and does not show any systematic dependence on particle size. Emission bands shifted towards the longer wavelength are observed in almost all of the semiconductors clusters studied so far and are generally assigned to defects states. These redshifted emissions are usually associated with trapped states such as vacancies, interstitials, impurities and surface defects [14].

3.2. Optical properties of the undoped PVA-capped CdSe thin films

Optical absorption spectra provides some characteristics of the band structure of the materials. In the present investigation, the optical absorbance spectra of PVA-capped CdSe thin films prepared at different concentrations are shown in Fig. 2. The spectra show that the CdSe films have high absorption in the shorter wavelength. It is clearly evident from the spectra that the optical absorption of the films decreases with increase in concentration. This may be attributed to the decrease in films thickness leading to decrease in crystallite size and causes more lattice defects. Fig.2, shows a shift of absorption edge towards lower wavelength with increase in concentration. This blue shift is indicative of the decrease of crystallite size and increase in band gap. The band gap of the films is calculated by plotting (αhν)2 vs hν using the relation

$$\alpha = \frac{a\left(h\nu - E_g\right)^n}{h\nu} \tag{1}$$

where a = a constant and $n = 1/2$ for allowed direct transition and $n = 2$ for allowed indirect transitions. The value of 'α' is obtained from the relation

$$\alpha = 2.303\frac{A}{t} \tag{2}$$

where A= absorbance and t = thickness of the film. The value of n is 1/2 or 2 depending on the presence of the allowed direct and indirect transitions.

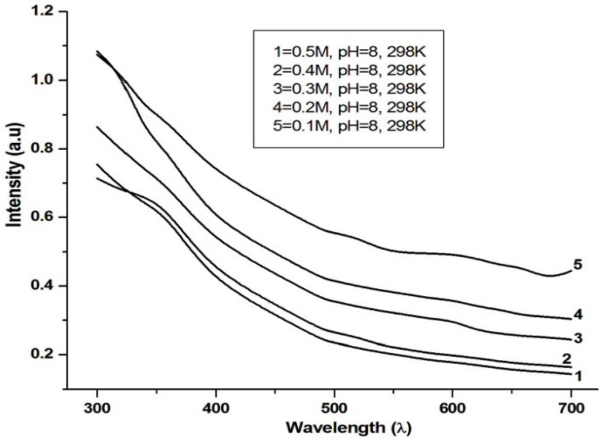

Fig. 2. Absorption spectra of PVA-capped CdSe thin films prepared at different molarities.

Fig. 3 shows the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ for the CdSe films prepared at different concentrations.

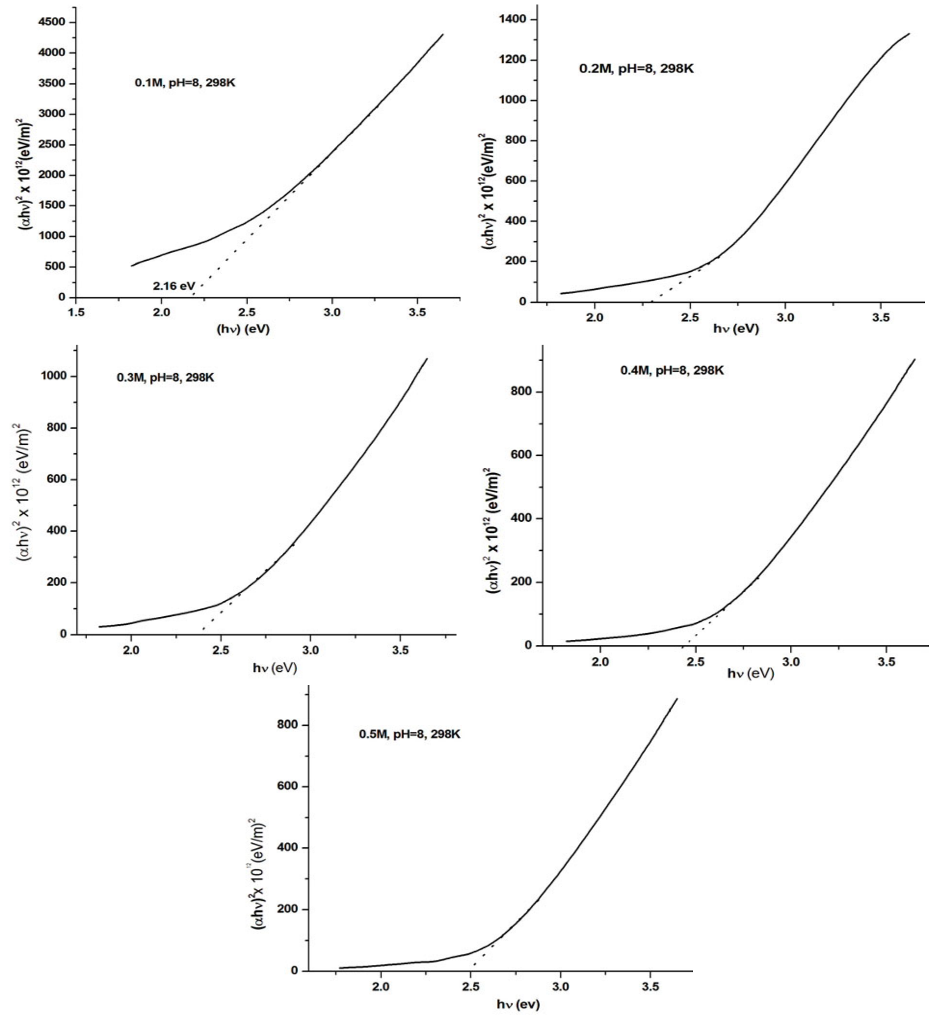

Fig. 3. $(\alpha h\nu)^2$ vs $(h\nu)$ plots of PVA-capped CdSe thin films prepared at different molarities.

The nature of the plot is linear indicating that the transition is a direct band gap. The estimated band gap obtained from the extrapolation of the straight portion to zero of the CdSe thin film prepared at different concentration as given in Table 1. The optical band gap is found to increase with increase in concentrations and the observed values of E_g (2.16 eV to 2.49 eV) are higher than the value of bulk band gap value of CdSe (1.7 eV). The optical band gap of semiconductors can affected by charged impurities, disorder at the grain boundaries and stoichiometry and other defects, which could increase the energy band gap with the decrease of particle size. The presence of defects in the nanostructure films produces discrete states in the band structure.

Table 1. Calculated values of optical band gap of PVA-capped CdSe thin films prepared at different deposition parameters.

Deposition parameters	Samples	Thickness of the films (nm)	Optical band gap (eV)
Concentration of the solution	0.1M	210	2.16
	0.2M	196	2.30
	0.3M	190	2.37
	0.4M	185	2.44
	0.5M	181	2.49

3.3. Temperature dependent electrical conductivity

The dark temperature depedent electrical conductivity of the PVA nanocrystalline CdSe thin films are measured in the temperature range 298K- 458K are shown in Fig. 4. It is evident from the Fig.2 that conductivity of all the films increases with temperature suggesting the presence of activation barriers at the grain boundaries. The increase in conductivity with increase in temperature confirms the semiconducting behaviour of the prepared CdSe films. The nature of the plots of all the CdSe samples exist two distinct regions: high temperature region and low temperature region~~.~~ The room temperature electrical conductivity are found to be in the order of $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The thermal activation energy are calculated using the relation

$$\sigma = \sigma_0 \exp\left(\frac{-E_g}{2k_b T}\right)$$

where σ_o is a constant, E_g is the activation energy, k is the Boltzman's constant and T is the absolute temperature. The calculated activation energies value are given in Table 2. In the low temperature region the activation energy for the conduction is found to be 0.148 eV to 0.295 eV. In the high temperature region the energy is found to be 1.081 eV to 1.384 eV. The calculated activation energy values of the two regions are much smaller than the corresponding band gap values. These energy levels are thought to be associated with defect levels within the band gap. Electrical conductivity of a semiconductor is controlled by the number of charge carriers available for conduction. As the temperature increases from absolute zero, transitions are taking place between the defects level and the conduction band and valence band.

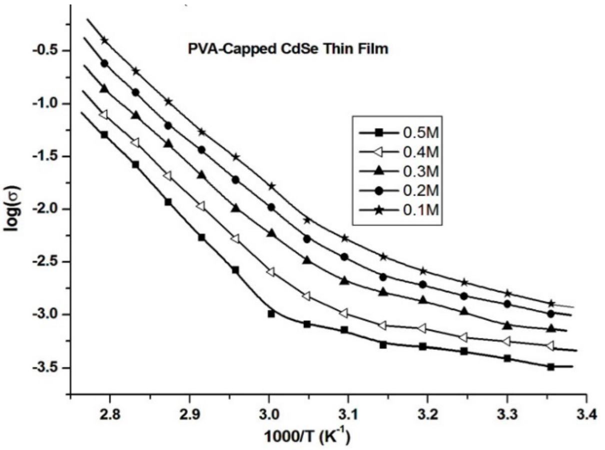

Fig. 4. Plot of log(σ) vs 1000/T of PVA-capped CdSe thin films prepared at different molarities.

Table 2. Calculated activation energy of PVA capped CdSe thin films prepared at different molarities.

Deposition parameters		Samples	Thickness of the films (nm)	Activation Energy (eV)	
				Low temperature Region	High Temperature Region
Undoped PVA-Capped CdSe films	Concentration of the solution	0.1M	210	0.148	1.081
		0.2M	196	0.190	1.109
		0.3M	190	0.219	1.121
		0.4M	185	0.266	1.194
		0.5M	181	0.295	1.384

4. Conclusions

The Photoluminescence spectra of nanocrystalline CdSe films are recorded in the wavelength range 350nm-750nm with excitation wavelength of 395nm. The spectra for all the samples contain two emission bands i.e. higher energy band and lower energy band. The Photoluminescence spectra of all the CdSe samples display broad emission spectra in the blue region of visible spectra.The curves shows similar trend, although the peaks position are different for the different molarities. The intensities of the peaks increases with increase in molarities. The high energy band which is close to the band edge is sharper and better defined than the second band seen at the lower energies. The long wavelength band is weak in intensity and does not show any systematic dependence on particle size. Emission bands shifted towards the longer wavelength are observed in almost all of the semiconductors clusters studied so far and are generally assigned to defects states. The redshifted emissions are usually associated with trapped states such as vacancies, interstitials, impurities and surface defects. The chemically prepared doped and undoped nanocrystalline CdSe have high absorbance in the UV-visible region. The linear nature of $(\alpha h\nu)^2$ vs $(h\nu)$ plots of CdSe thin films confirmed that the transition is direct and the optical band gap energy of CdSe films is found to increase from 2.16 eV to 2.49 eV which is higher than the bulk value. The temperature dependent electrical conductivity of the prepared CdSe films are to be of the order of $10^{-4}\Omega^{-1}cm^{-1}$.

Acknowledgments

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