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STRUCTURAL, COMPOSITIONAL AND OPTICAL PROPERTIES OF PVA-CAPPED NANOCRYSTALLINE CdSe THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION

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Nanocrystalline CdSe thin films are prepared by chemical bath deposition method using Cadmium acetate [$Cd(CH_3COO)_2.3H_2O$] and Sodium Selenosulfate (Na_2SeSO_3) as Cd^{2+} and Se^{2-} ions sources respectively. Characterization of the prepared films are carried out using X-ray diffraction (XRD), Scanning electron microscopy (SEM), optical absorption and Energy dispersive X-ray analysis (EDAX). Average crystallites sizes are calculated from the XRD spectra by using the Debye Scherrer's formula are found in between 9.1nm-3.1nm. Surface morphology of the films is obtained from Scanning electron microscopy. EDAX gave the composition ratio of the prepared film. The band gap energy obtained from the absorption spectra are found to change from 2.16 eV to 2.49 eV on changing the grain size from 9.1nm to 3.1nm.

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1. Introduction

In the last two decades, synthesis and characterization of nanocrystalline semiconductor compounds occupied an important place in research work due to their interesting properties and potential applications in solar cells, photoelectronic and photovoltaics devices. The properties of these materials changes on changing the crystalline size and thickness of the film. So, it offers the possibility of materials enhancement device characteristics [1]. Cadmium Selenide (CdSe) belongs to group II-VI semiconductor compound with energy gap in the range (1.65-1.84 eV) which lies in the visible region of the spectra [2-3] and also one of the most promising materials that have been studied for future applications in electronics devices [4]. CdSe thin films have been reported to be synthesis by different techniques such as spray pyrolysis [5], chemical deposition [6-9], electrochemical [10], Electron beam deposition [11], laser ablation [12], SILAR method [13] etc. Among the various deposition techniques, chemical bath deposition method is a promising technique because of its simplicity, inexpensive and convenient for large area deposition. With this technique, size of the particles can be easily controlled by changing deposition parameters such as the concentration of the solution, pH, deposition temperature and deposition time etc. In this paper, we report the preparation of nanocrystalline PVA- capped CdSe thin films and studied their structural, surface morphological and optical properties.

2. Experimental details

Nanocrystalline CdSe thin films are deposited on glass substrates by 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) is used as capping agent. For the preparation of nanocrystalline CdSe thin films in PVA matrix involves in three steps. First steps,

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Preparation of 2wt% PVA matrix solution. For this, 2gm of PVA dissolve in 100ml of double distilled water and stirred with the help of a magnetic stirrer at constant temperature (348K) until a transparent solution is formed. Different concentrations of Cadmium acetate [$Cd(CH_3COO)_2.3H_2O$] are used to get different matrix solution. Second steps, 0.25M of Sodium Selenosulfate (Na_2SeSO_3) is 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°C in N_2 atmosphere for 6 hrs and filtered. The filtrate solution is used as stock solution of Se^{-2} source. Finally step, equal amount of PVA matrix solution and Se^{-2} source are mixed together. The pH value of the solution is adjusted by drop wise addition of aqueous ammonia (NH_3). The cleaned glass substrates are vertically immersed 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 resulting to the formation of nanocrystalline CdSe films. After deposition of 5 hrs, the substrates coated with orange red colour on both sides are taken out, thoroughly washed with distilled water and dried in open atmosphere. The CdSe 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 surface facing the interior of the bath is removed with dilute acid. In the same procedure, nanocrystalline CdSe thin films of five different concentrations (0.1M, 0.2M, 0.3M, 0.4M and 0.5M) at constant pH value and deposition temperature are prepared and to study their structural, morphological and optical properties.

3. Reaction mechanisms

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

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

Similarly the hydrolysis of ammonia in ammonia gives OH^-

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

When ammonia is added to the cadmium acetate solution it forms tetraamine complex ion as $\left[Cd\left(NH_3\right)_4\right]^{2+}$

$$Cd\left(CH_3COO\right)_2.3H_2O \rightarrow Cd^{2+} + 2CH_3COO^- + 3H_2O \tag{3}$$

$$Cd^{2+} + 4NH_3 \rightarrow \left[Cd(NH_3)_4\right]^{2+} \tag{4}$$

Then the $\left[Cd\left(NH_3\right)_4\right]^{2+}$ reacts with Se^{2-} ions that results in the formation of CdSe thin film as follows

$$\left[Cd\left(NH_3\right)_4\right]^{2+} + Se^{2-} \rightarrow CdSe + 4NH_3 \tag{5}$$

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.

4. Results and discussion

4.1. X-ray diffraction studies

The X-ray diffractograms of CdSe thin films deposited on glass substrates at different reactant concentrations keeping constant pH value 8 and deposition temperature 298K are shown in Fig.1 (a-e). The main feature of the diffraction patterns of the films prepared at different reactant concentrations are the same but only the peak intensity and broadening varies. The observed‘d’ spacing and the respective prominent peaks correspond to reflection (111), (220), and (311) planes which are in good agreement with the JCPDS data card (ASTM data file No. 19-0191). Therefore, it has been concluded that the chemically deposited CdSe thin films at different reactant concentrations are polycrystalline in nature with cubic structure. The XRD results are well agreement with the earlier report [14-15]. As we see from X-ray diffraction patterns that the CdSe thin films deposited with lower molarities are of polycrystalline nature while films prepared with higher molarities are found to be amorphous nature. The broadening of the peaks in the diffraction pattern is found to increase with increase in reactant concentration of the solution. This suggests that increase in reactant concentration decrease in nucleation and growth of grains. Since the deposition of CdSe thin films occurs when ionic product of Cd^{2+} and Se^{-2} ions exceeds the solubility product of CdSe. The availability of Cd^{2+} and Se^{-2} ions in the solution controls the rate of CdSe formation. At higher reactant concentration, the rate of release of free Cd^{+2} ions from Cadmium acetate and free Se^{-2} ions from Sodium Selenosulfate is more and fasten the reaction however all the ions did not get the chance to stick on the glass substrate hence settle down at the bottom of the container [16]. The intensities of (220) and (311) peaks are low in comparison with the (111). This indicates that the orientation of the grain growth is preferably along (111) direction. The preferential orientation in the (111) direction has also earlier reported by [17]. The average crystallite sizes of the CdSe films are calculated from the full width at half maximum (FWHM) of X-ray diffraction peaks using Scherrer’s formula

$$d = \frac{0.94\lambda}{\beta \cos\theta} \tag{5}$$

where λ is the wavelength of X-ray used, β is the full width at half maxima in radian and θ is the Bragg’s diffraction angle.The calculated crystallite size is found to decrease from 9nm to 3nm as the reactant concentration increased from 0.1M to 0.5M. Moreover, the increase in molarities results in the broadening of the diffraction peaks suggestion the formation of small crystallite and presence of strain. The lattice parameter ‘a’ is calculated using the equation

$$a = d(h^2 + k^2 + l^2)^{1/2} \tag{6}$$

for cubic structure and the calculated values are given in Table 1. The observed lattice parameter ‘a’ is within the range from 5.983 Å to 6.040 Å which are slightly different from the bulk value 6.007 Å. The deviation in the values of the lattice constant of the CdSe films from the bulk value indicates the presence of strain in the films. The misfit stress is one of the most important factor adversely affecting the structural properties which is resulted from geometric mismatch at inter phase boundaries between crystalline lattices of films and substrates [18]. These stresses can cause microstrain in the films. The microstrain and dislocation density of the CdSe films deposited at different reactant concentration are calculated using equation (7) and (8) respectively

$$\varepsilon = \frac{\beta \cot \theta}{4} \tag{7}$$

$$\delta = \frac{n}{d^2} \tag{8}$$

The calculated values are represented in the Table 1 and we see grain size decreases with concentration whereas microstrain and dislocation density increase with increase in reactant concentration.

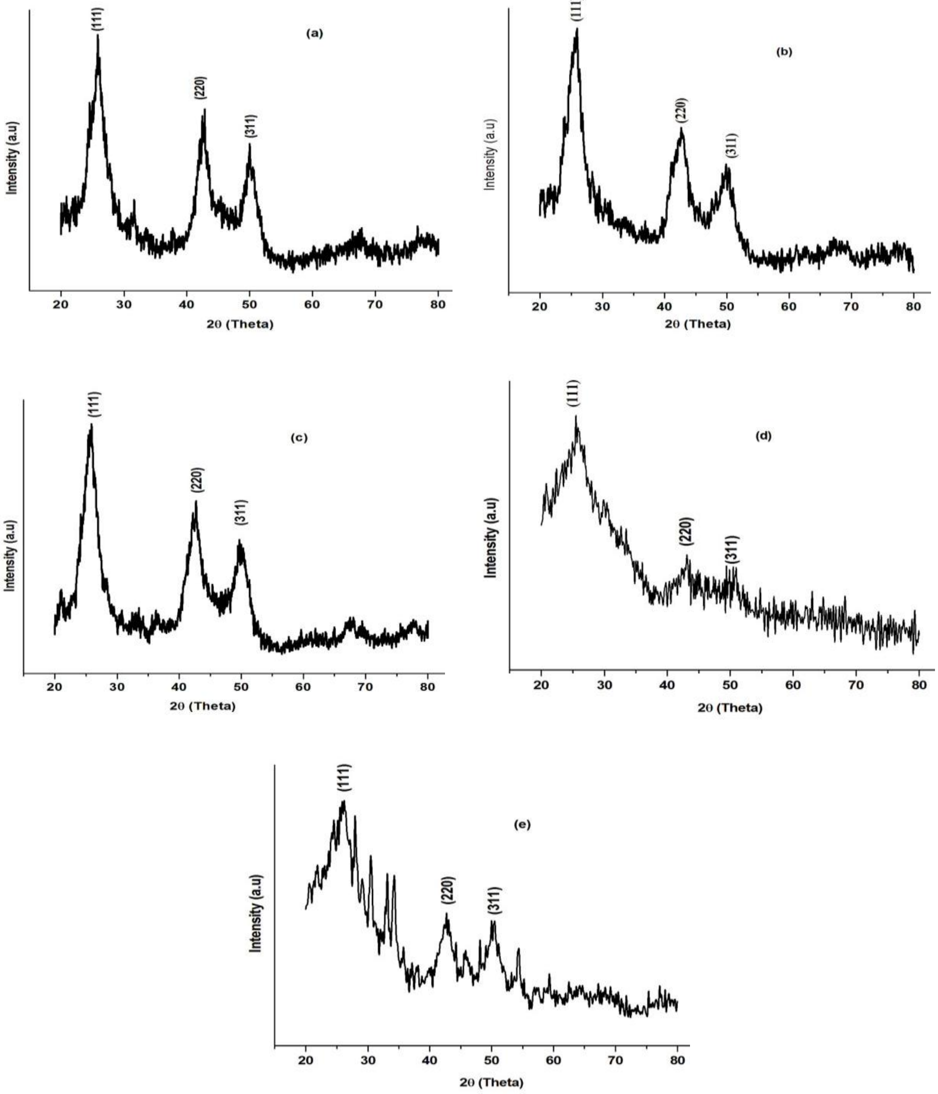

Fig. 1. XRD spectra of PVA capped CdSe thin films of different concentration (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M at constant bath temperature 298K and pH value 8.

Table 1. Various structural parameters calculated from the XRD spectra of PVA-capped CdSe films prepared at different reactant concentration.

Concentration of the solution	Average crystallite size (nm)	Standard d-value (Å)	Calculated d-value (Å)	Plane (hkl)	Calculated lattice constant (a) (Å)	Average Microstrain (ε) 10^{-3}	Dislocation density (δ) 10^{15} (lines/m^2)
0.1M	9.1	3.5087 2.1486 1.8334	3.4451 2.1299 1.8218	(111) (220) (311)	5.966 6.003 6.040	12.93	16.99
0.2M	7.6	3.5087 2.1486 1.8334	3.5031 2.1080 1.8186	(111) (220) (311)	6.067 5.963 6.030	16.166	18.41
0.3M	6	3.5087 2.1486 1.8334	3.4253 2.1150 1.8153	(111) (220) (311)	5.932 5.981 6.019	20.63	29.11
0.4M	5.64	3.5087 2.1486 1.8334	3.4548 2.1242 1.8255	(111) (220) (311)	5.983 6.007 6.053	20.36	42.20
0.5M	3.12	3.5087 2.1486 1.8334	3.4707 2.1184 1.8313	(111) (220) (311)	6.011 5.990 6.072	38.33	107

4.2. Surface morphology studies

The surface morphology of the CdSe films deposited on the glass substrates have been investigated by scanning electron microscope (SEM) operating with an accelerating voltage 20kV. Fig. 2(a-e) show the SEM photographs of the nanocrystalline CdSe thin films deposited at five different reactant concentrations (0.1M-0.5M) keeping constant pH value 8 and deposition temperature 298K. It is seen that the surfaces are compact and well covered with smooth, irregular shaped grains of random sizes. These irregular shaped nanograins are interconnected with each other to form clusters. Agglomeration of small crystallites in the films are also evident from the photographs. Such agglomeration makes it difficult to evaluate the grain size from SEM images. The estimated grain sizes of the films are found to vary from 30 nm to 80 nm which is larger than the XRD results. This larger value of grain sizes may be due to the agglomeration of smaller grains. It is clear from these images that a common characteristics of the grains is their spherical shapes.

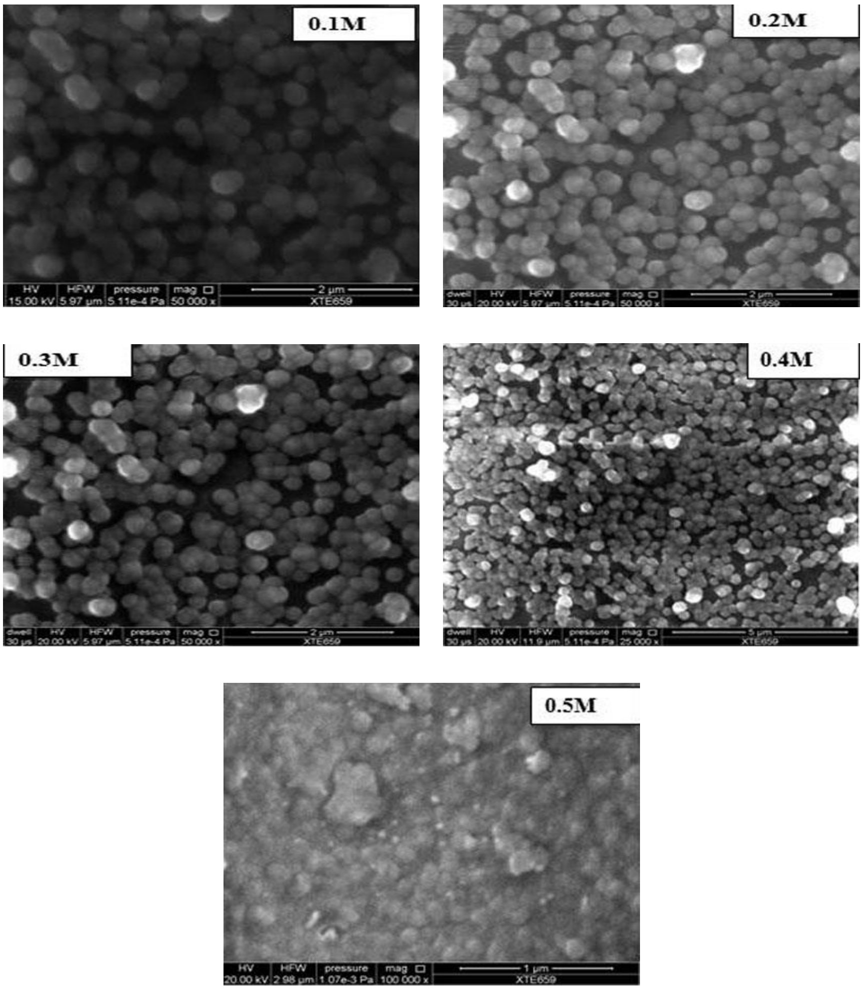

Fig. 2. SEM photographs of PVA capped CdSe thin films different concentration (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M at constant bath temperature 298K and pH value 8.

4.3. Edax studies

The chemical compositions of the prepared CdSe films are determined by the energy dispersive analysis by X-ray (EDAX). The analysis of the EDAX spectrum of undoped CdSe film Fig.3 confirms the presence of Cd and Se in the deposited film with Cd ≈ 48.20% and Se ≈ 51.80%. It also confirms that the prepared film is selenium (Se) rich. As it can be seen from Fig. 3, the Cd:Se atomic ratio is 0.93 suggesting the presence of Cadmium vacancies (excess of sulphur) in the deposited films.

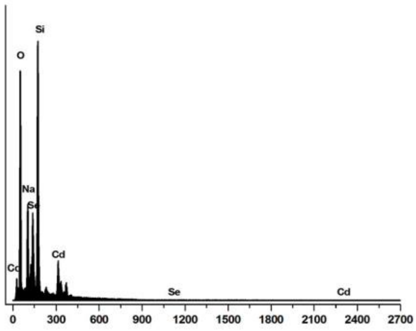

Fig. 3. EDAX spectra of PVA Capped CdSe thin film prepared at 0.3M, pH value 9 and 298K.

4.4. Transmission electron microscopy (TEM) studies

Transmission electron microscopy (TEM) images of the nanostructures CdSe thin films for two reactant concentrations of 0.1M and 0.5M are shown in Fig. 4 and Fig. 5, respectively. It shows that larger grains constituted by smaller grains. The particles in dark colour shown in Fig. 4 (a) and Fig. 5 (a) are the nanocrystalline CdSe particles. The estimated particle sizes of Fig. 4.(a) are found to be in the range of 6 nm-11 nm and that of Fig. 5(a) is 4nm-9nm which are in good agreement with the X-ray diffraction results. Fig. 5 (b) and Fig. 6 (b) images had shown the multiple diffractions ring with missing periodicity which is due to the random orientation of the polycrystalline particles. In both the films observed nearly spherical CdSe nanoparticles.

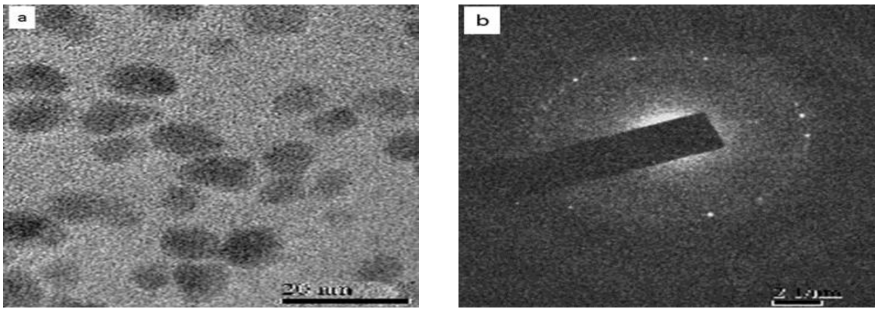

Fig. 4. TEM image of nanocryatalline CdSe thin film of 0.1M concentration at constant pH value 8 and deposition temperature 298K.

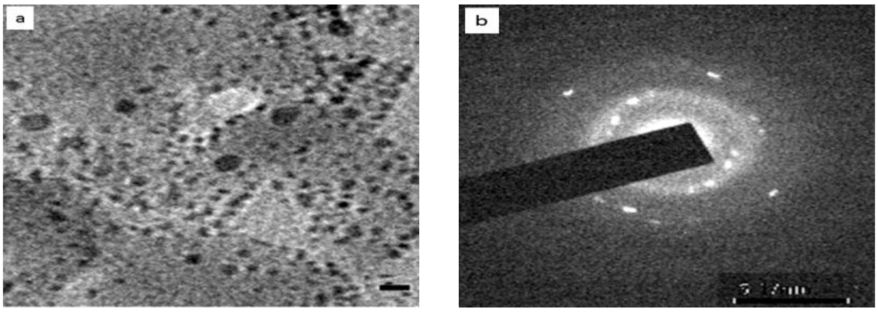

Fig. 5. TEM image of nanocryatalline CdSe thin film of 0.5M concentration at constant pH value 8 and deposition temperature 298K.

4.5. Optical properties studies

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 at constant pH value 8 and deposition temperature 298K are recorded as a function of wavelength in the range 360-800 nm and are shown in Fig. 6. The spectra shows that the CdSe films have high absorption in the shorter wavelength and also clearly evident from the spectra that the optical absorption of the films decreases with increase in concentration of the solutions. This may be attributed to the decrease in films thickness leading to decrease in crystallite size and causes more lattice defects. This blue shift is indicative of the decrease of crystallite size and increase in band gap. The band gap of the films are calculated by plotting $(\alpha h\nu)^2$ vs $h\nu$ using the relation

$$\alpha = \frac{a\left(h\nu - E_g\right)^n}{h\nu} \tag{9}$$

where ‘a’ is 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

$$\alpha = 2.303\,\frac{A}{t} \tag{10}$$

where ‘A’ is the absorbance and ‘t’ is the 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. 7(a-e) shows the plots of $(\alpha h\nu)^2$ vs hν for the CdSe films prepared at different concentrations. The nature of the plots is linear indicating that the transition is a direct band gap. The band gap is determined by extrapolating the straight line portion of the plot to the energy axis. The intercept on energy axis gives the value of band gap energy for all the films. The optical band gap is found to increase with increase in concentrations and the observed values of E_g is in between 2.16 eV to 2.49 eV which are higher than the bulk band gap value of CdSe 1.7 eV as given in Table 2. The optical band gap of semiconductors can be 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 [19]. The presence of defects in the nanostructure films produces discrete states in the band structure.

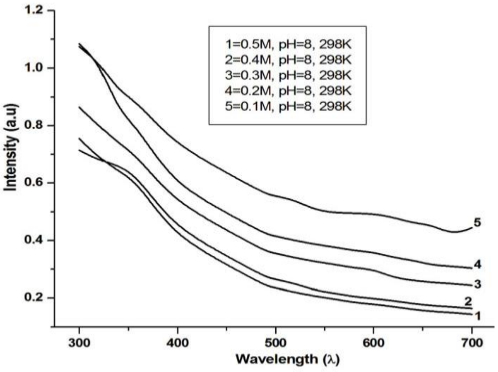

Fig. 6. Absorption spectra of CdSe thin films prepared at different concentration (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M at constant bath temperature 298K and pH value 8.

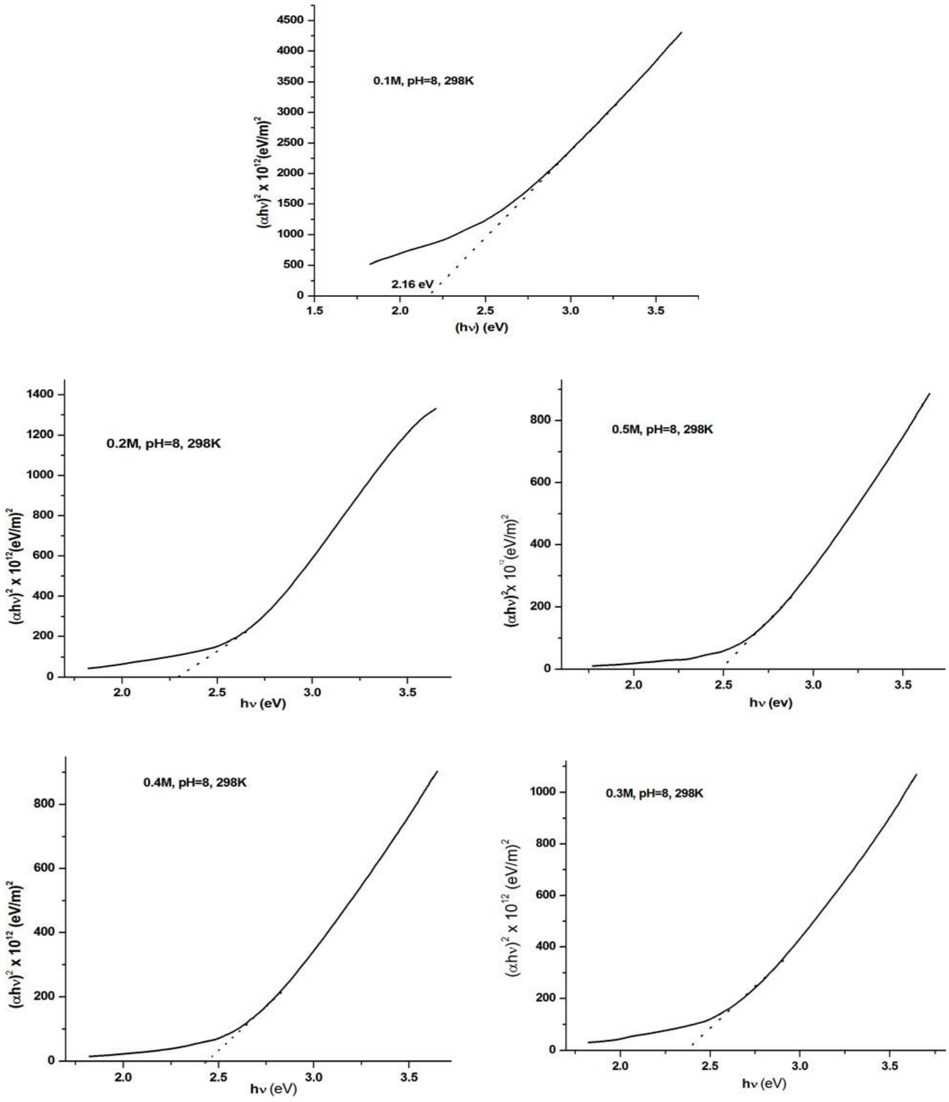

Fig. 7. $(\alpha h\nu)^2$ vs (hν) plots of CdSe thin films prepared at different concentration (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.4M (e) 0.5M at constant bath temperature 298K and pH value 8.

Table 2. Calculated values of optical band gap of PVA-capped CdSe thin films prepared at different concentrations.

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

5. Conclusions

Nanocrystalline CdSe thin films are successfully deposited on glass substrates by chemical bath deposition technique using PVA as a capping agent. The structural, compositional and morphological, properties of chemically prepared nanocrystalline CdSe films have been investigated. X-ray diffraction observation of all the films is found to be polycrystalline in nature with cubic structure. The preferred orientations for these thin films are along (111) direction. The crystallite size is within the range of 3nm to 9 nm. The crystallite size has been observed to decrease whereas microstrain and dislocation density increase with increase in reactant concentration. The chemical compositional analyses of the CdSe films by EDAX show that the average atomic percentage of Cd and Se is 48.20 and 51.80 respectively showing that the films are cadmium deficient. Surface morphology studies of the CdSe films by Scanning electron microscopy (SEM) reveals that the prepared films at different concentration have uniform surface morphology and well covered over the entire glass substrate without any voids.

Transmission electron microscopy (TEM) studies have confirmed the formation of polycrystalline CdSe with grain sizes in the range 6 nm-11 nm and 4 nm-9 nm for 0.1M and 0.5M of CdSe film respectively which are good agreement with the XRD results. The optical absorption of all the films decreases with increase in concentration. The optical band gap energy of CdSe films is found to increase from 2.16 eV to 2.49 eV with decreasing crystallite size from 9nm to 3nm and these obtained band gap values are higher than the bulk value.

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