Original Research Paper

Deposition and Characterization of CdS Nano Thin Film with Complexing Agent Triethanolamine

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Abstract: The equimolar concentration thin films of Cadmium Sulfide (Cd_xS_x) with the complexing agent TEA were deposited on a glass substrate by the SILAR technique. The crystalline nature with face centered cubic crystal system of the CdS films is determined from X-ray diffraction analysis. The broadened diffraction peaks indicated nano sized particles of the film materials. The surface morphology of the films was studied by SEM analysis. The Energy Dispersive Analysis of X-ray (EDAX) plot confirms the equimolar composition of Cd and S ions in the film materials. Surface topography of the film was studied by AFM. The optical characteristic of absorbance, transmittance and band gap was analyzed by UV-visible spectra. The band gap energy of the material was observed as 2.18 eV and chemical bonding was studied by FT-IR spectral analysis.

Keywords: Optical Material, Semiconductors, Surfaces, Thin Films

Introduction

The cadmium sulfide thin films are preferentially used in opto electronic devices their wide range of optical properties, their simple coating capacity and easy fabrication process according to Rabinovich and Hode (2013). The CdS films are also considered in the fabrication of the solar cells as alternatives to the silicon and other semiconductor based photovoltaic devices. The CdS sensitized solar cells are attracting the researches for exploring the materials elaborately (Yan *et al*., 2013; Senthamilselvi *et al*., 2013). The noticeable efficiency of the CdS makes it to be useful as a window layer in solar cell materials with several other semiconductor materials such as ZnS (Hwang *et al*., 2012), Cu_2S (Lindroos *et al*., 2000), FeS (Manikandan *et al*., 2014a), ZnSe (Raj *et al*., 2012), CdTe (Girish Kumar and Koteswara Rao, 2014) and CdSe (Deshpande *et al*., 2013). The CdS films is deposited by several coating techniques viz., chemical bath deposition (Rusu *et al*., 2003; Obaid *et al*., 2013; Oliva-Aviles *et al*., 2010), spray pyrolysis (Ikhmayies *et al*., 2013), spin coating (Seon *et al*., 2009), MOCVD (Yoon *et al*., 2006). However, all these techniques require sophisticated facilities like precise temperature control, high pressure, vacuum etc., In this

regard; the Successive Ionic Layer Adsorption and Reaction (SILAR) technique is preferred due to its significantly low cost, simple, room temperature, without sulfuration and atmosphere preparative conditions (Manikandan *et al*., 2014b). In the SILAR process; the CdS films are deposited by sequentially dipping in into aqueous cationic and anionic precursor solutions of the reactants. The quantity of deposition and the thickness of the film can be easily modified over a wide range by changing the deposition cycles and concentration of solution. Moreover, it is relatively inexpensive, simple and convenient for large area deposition. Hence, the present research work is focused on the preparation of ultra thin films of CdS with the addition of the complexing TEA. The structural, elemental, morphological and optical properties are evaluated.

Experimental Techniques

Preparation of CdS Thin Film with TEA

The SILAR is an extension of the Chemical Bath Deposition (CBD). The SILAR method is having sequential reactions at the substrate surface. Rinsing

is an important phase at each stage of the reaction, which enables the heterogeneous reaction between the solid phase and the insoluble ions in the solution. The glass plates were degreased with acetone and cleaned by conc. HNO_3 washed with a detergent solution, rinsed in distilled water and dried in hot air. The cadmium sulfide thin films were prepared from equimolar (0.10 M) and equivolume aqueous solutions of cadmium nitrate (Cd $(NO_3)_2 \cdot 9H_2O$) and Sodium Sulfide (Na_2S), 4 drops of the complexing agent TEA was added to the cationic precursor solution. The complexing agent TEA is added to produce, ultrathin and uniform growth of thin films by the way of reducing the quantity of free metal ions in the films. The CdS thin film deposition process was carried out by following the procedure given in Table 1.

The pre-cleaned glass plates were immersed in cationic precursor (cadmium nitrate) for 30 s, so that the Cd^{2+} ions can be adsorbed on the glass plates. Then, the substrate is rinsed in distilled water for 30 s, so that, the excessively adsorbed Cd^{2+} ions can be rinsed away from the deposited layer which may result in saturated adsorbed layer of (Cd^{2+}) cationic ions on the glass plate. The cation coated films were immersed in anionic precursor for 30 s leading to adsorption so that, the anions (S^{2-}) from the anionic sodium sulfide solution are introduced to the system and a solid thin film is formed on the interface. Hence, the cationic Cd^{2+} ions can react with the newly introduced anionic S^{2-} ions. The un-reacted sulfide ions were removed by rinsing them in distilled water for 30 s. Thus, a SILAR cycle is comprised of these four parts. These operations were repeated for 20 SILAR cycles in order to get an adherent thick film. The resulted cadmium sulfide thin film was annealed at 100°C for two hours in a hot air oven.

Material Characterization

The films were coated by a SILAR controller model No.HO-TH-03. The structural characterization of CdS thin films deposited on glass substrates was carried out by analyzing the XRD patterns which were obtained using Ultima3 theta-theta gonio X-ray diffractometer with Cu Kα radiation (λ = 1.540 Å) with a scanning rate of 0.02° from 2θ~10° to 80°. The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by JCPDS file. The surface morphology studies of the film deposited on glass substrate were studied by Scanning Electron Microscopy (SEM) technique. The films were loaded in the sample holder of the VEGA3 TESCAN unit for SEM analysis. The surface topography was analyzed using atomic force microscopic (Park XE100 model, Hallmark). Optical absorption studies were carried out using a UV-Visible spectrophotometer (Jasco V650 Ultraviolet Spectrum) in the wavelength range of 300-800 nm. Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) of CdS film were studied in the frequency range of 400-4000 cm^{-1}.

Results and Discussion

XRD Analysis

The X-ray diffraction patterns of the annealed film are shown in Fig. 1. Three major diffraction peaks are appearing at 2θ~26.6°, 43.98° and 52.23° which are assigned to the (111), (200) and (311) reflections of cubic CdS. The X-ray diffraction profiles clearly shown that the intensity of the (111) peak is higher than other crystalline phases. The deposited CdS films grow with Face Centered Cubic (FCC) structure and this crystalline property is enhanced due to the addition of the complexing agent TEA. The diffraction patterns of the films are found to be matched well with the JCPDS card No. 10-0454. The intense diffraction peak appearing approximately at 2θ = 26.6° corresponds to the (111) plane of the cubic CdS (Senthamilselvi *et al.*, 2013; Oladeji *et al.*, 2000; Cortes *et al.*, 2004).

Table 1. General Settings in SILAR Deposition for CdS thin films

Parameters	Cadmium nitrate	Distilled water	Sodium sulfide	Distilled water
Volume	100 mL	100 mL	100 mL	100 mL
Start position	0	0	0	0
Dip length	75 mm	75 mm	75 mm	75 mm
Dip speed	5 mm sec^{-1}	5 mm sec^{-1}	5 mm sec^{-1}	5 mm sec^{-1}
Retrieval speed	4 mm sec^{-1}	4 mm sec^{-1}	4 mm sec^{-1}	4 mm sec^{-1}
Dip duration	30 sec	30 sec	30 sec	30 Sec
Ex dip duration	4 sec	4 sec	4 sec	4 Sec
No of cycles	20	20	20	20
Soluble	Distilled water		Distilled water	
Precursor of ions	Cd^{2+}		S^{2-}	
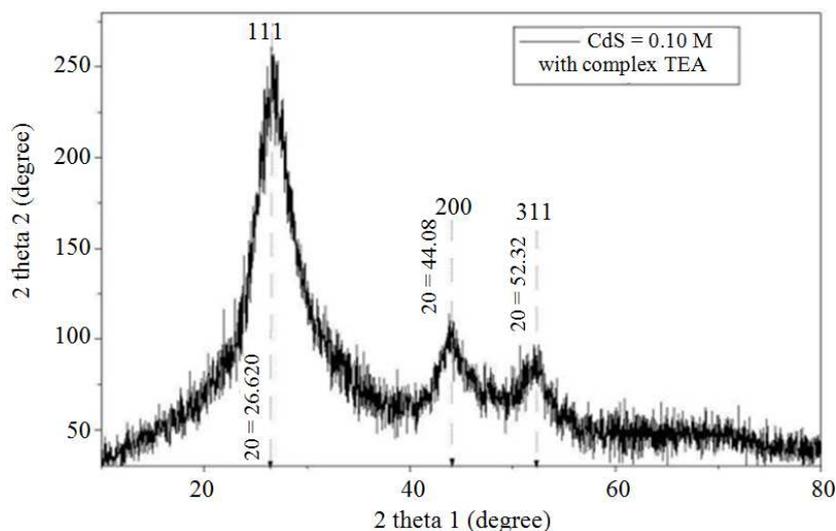
Fig. 1. XRD patterns of CdS thin film with complexing agent

The lattice constant (a) of the cubic structure of CdS films is calculated using the following formula:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{1}$$

The calculated lattice constant values are presented in Table 2. The value of the lattice constants is found to be very close to the standard value (5.818 Å - JCPDS card no. 10-0454). The slight increases of the lattice constant for the reported values were observed (Martinez *et al.*, 1988).

The average value of the crystallite size (D) can be obtained from the Debye-Scherer's Equation 2:

$$D = \frac{0.9 \times \lambda}{\beta \cos \theta} \tag{2}$$

Where:
λ = The X-ray wavelength of Cu-Kα radiation (1.5406Å)
β = The broadening of a diffraction peak measured at full width and half of the maximum intensity
θ = The Bragg diffraction angle

The crystallite size is found to be 1.84, 2.67 and 3.07 nm for (111), (200) and (311) reflection plane, respectively (Table 2).

SEM Analysis

Figure 2 shows the SEM images of the CdS film prepared with the addition of complexing TEA. The image shows that the film material is completely covered over the substrate surface by nano sized particles with an average grain size of 20 nm. From the SEM image it could be observed that the surface of the substrate is completely covered with the film particles. The surface morphology of the crystalline film is coarse and the granules in the films are uniformly distributed.

EDX Analysis

The Elemental analysis of the deposited film is carried out by EDX spectral analysis Fig. 3. The results of EDX Spectrum confirmed the presence of expected elements such as Cd and S in the films. As well, the S/Cd ratio is about 0.8 for the reported CdS thin films (Martinez *et al.*, 1988; Schaffner *et al.*, 2011; Raut *et al.*, 2013). The Cd/S ratio of the present is 1.202. The average atomic percentage of Cd:S is found to be 38.28:31.84, which confirms the formation of CdS. From the above mentioned observations, it is concluded that the Complexing agent assisted the improvement of the stoichiometry ratio of the film materials (Table 3).

AFM Analysis

The Atomic Force Microscopy (AFM) measurements were performed to evaluate the topographical characteristics of the CdS thin films. Figure 4 and 5 shows the 3D and 2D AFM images of the CdS film with a scanning area of 1×1 μm respectively. The particles are uniformly sized and randomly focused in all the directions. Average surface roughness (R_a), height and particle sizes of the deposits were observed and the results are displayed in Table 4. The CdS particles were randomly distributed on the surface of the films and their surfaces were homogeneous and the films are uniformly deposited.

Table 2. Miller indices and lattice constant properties of CdS thin film with complexing agent

Sample	2-theta (deg) Observed	JCPDS data	hkl	d(Å) observed	Lattice constant (a) (Å)	Rel.I (a.u) Observed	JCPDS data	phase CdS
Cd$_x$S$_y$	26.16	26.547	111	3.403	5.895	100.00	100.00	Cubic
(x = 0.10 M;	43.69	44.040	220	2.070	5.854	10.21	76.00	
y = 0.10 M)	52.31	52.163	311	1.747	5.794	7.45	64.00	

Table 3. EDX spectrum in chemical analysis of CdS thin film for 0.10M concentration

Molar concentration (M)		S-K	Cd-L	Total	S/Cd	Cd/S
Cd$_x$S$_y$	Mass (%)	17.60	74.16	91.76	0.2373	4.210
(x = 0.10 M; y = 0.10 M)	Atomic weight (%)	31.84	38.28	70.12	0.8317	1.202

Table 4. Surface roughness and particle size of CdS thin film for 0.10M concentration

Concentration	Roughness (Ra); (nm)	Height (Rz); (nm)	Grain size (Δx); (nm)
0.10 M	13.35	45	33
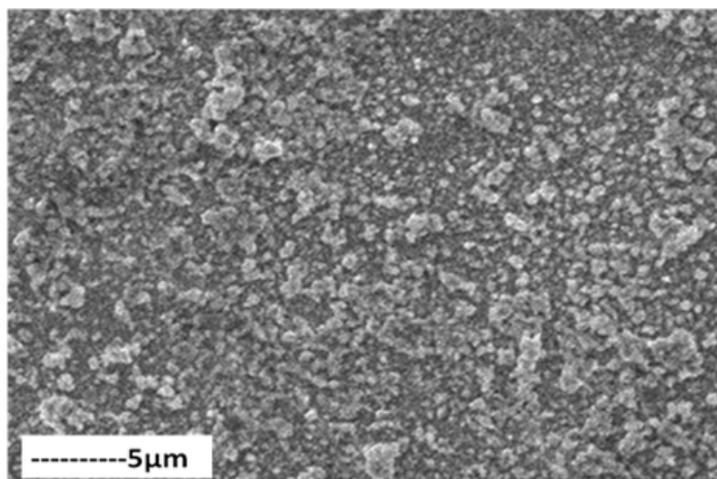
Fig. 2. SEM images of CdS thin film with complexing agent
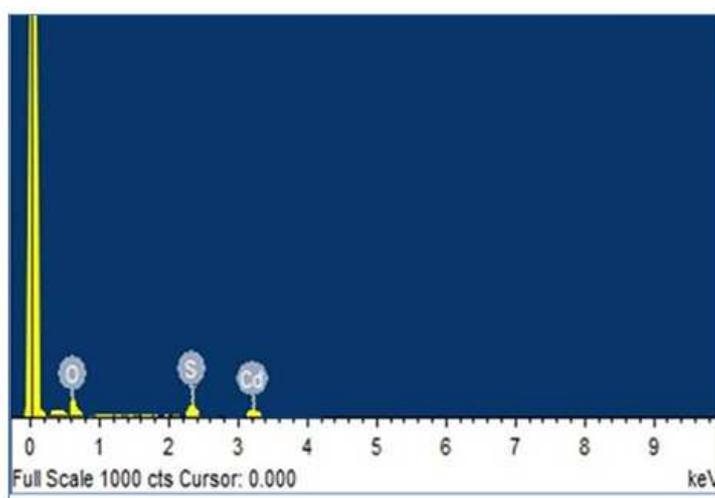
Fig. 3. EDX spectrum of CdS thin film with complexing agent
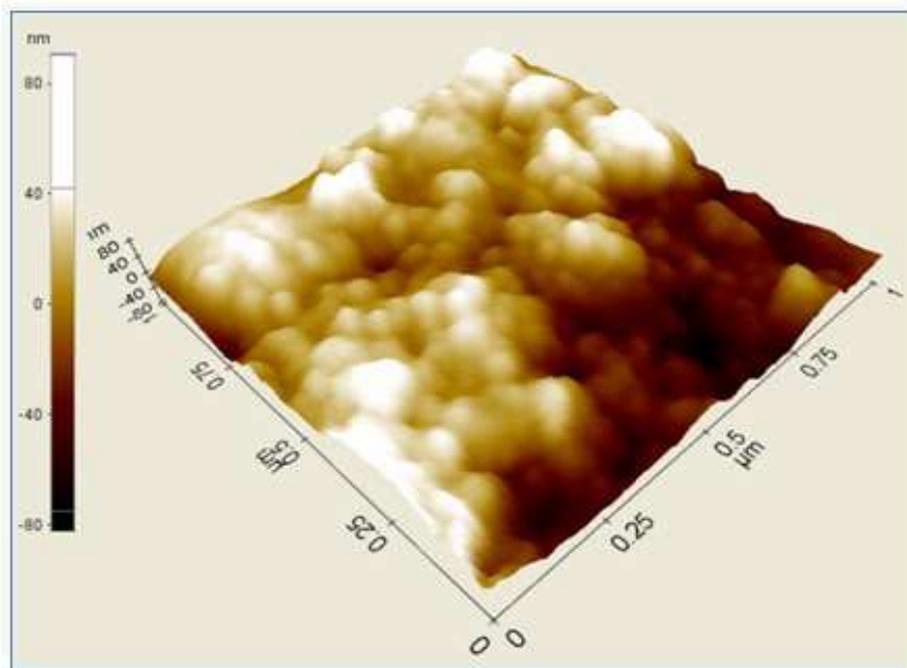
Fig. 4. AFM 3D images of CdS thin film with complexing agent
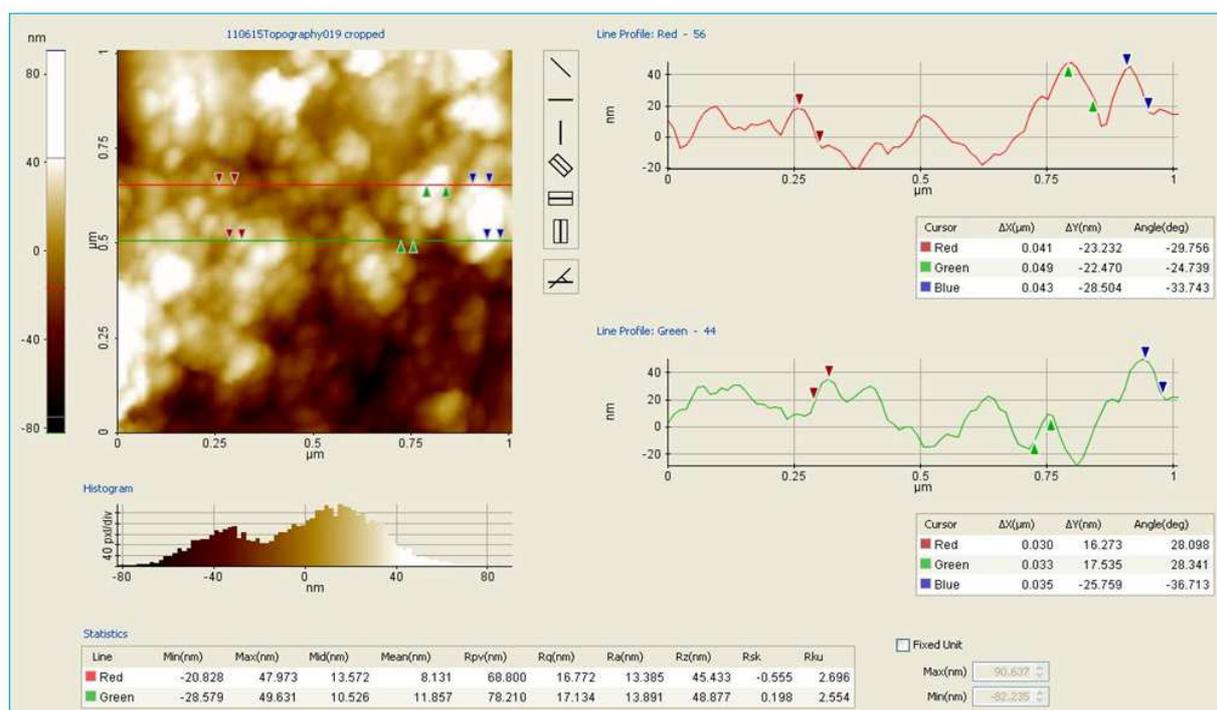
Fig. 5. AFM 2D images of CdS thin film with complexing agent

UV-Visible Spectra Analysis

The optical absorption and transmittance spectrum of the TEA added CdS thin films are shown in Fig. 6 and 7, respectively. The spectrum illustrates that the films are having a higher absorption in the UV region and the lower absorbance in the visible and near-IR regions. The spectrum exhibits a well defined absorption peak at

479 nm which is considerably blue shifted to the absorption peak of the bulk CdS material indicating due to the quantum size effect (Yogamalar and Bose, 2011; Tang *et al.*, 2005). The defined maximum observed at 479 nm is assigned to the optical transition of the first exitonic state. This wavelength of the maximum exciton absorption is lower while compared to the bulk material. While, the particle size decreases, the photo generated electron-hole pairs of the excitonic energy increases due to the quantum confinement. The excitonic peak and the cut-off wavelength were derived using the formula (3) (Ozer *et al.*, 2010):

$$E_g = \frac{hc}{\lambda}; eV \qquad (3)$$

The optical transmittance spectrum of CdS thin film illustrated the low transmittance in the UV and visible while high transmittance NIR-region of the transmittance spectrum. In a semiconductor material, the relation connecting the absorption coefficient α, the incident photon energy hv with optical band gap E_g is:

$$\alpha = \frac{1}{t} \ln \left[\frac{I_0}{I} \right] \qquad (4)$$

where, it is film thickness of the investigated films:

$$\alpha hv = A(hv - E_g)^n \qquad (5)$$

where, v is the frequency, h is Planck's constant, A is a constant related to the effective mass associated with the bands and n = 1/2 for a direct band gap material, 2 for an indirect band gap material. Since better linearity was obtained in the $(\alpha hv)^2$ versus hv plot, which is shown in Fig. 8, the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis. The estimated E_g values are found to be 2.18 eV, which is close to the literature results (Table 5) (Thangadurai *et al.*, 2008). As well as, the grain size also decreases with the influence of Complexing agent TEA. This observation is coherent with the data obtained from XRD and AFM analysis.

FT-IR Analysis

The FT-IR spectrum is used to understand and analyze more elegantly the structure and molecular arrangements of thin films. Type of functional groups present in the substance is indicated by the absorption that occurs at various frequencies. Figure 9, shows the FT-IR spectra of CdS thin films in the range of 400-4000 cm^{-1}. The presence of broad band range of 3300 cm^{-1} is attributed to hydrated water and the hydroxyl group in the spectra results from the hygroscopic nature of CdS. The transmission band at 3752 and 3313 cm^{-1} is due to O-H stretching vibrations of water molecules. CdS film showed weak intensities stretching band transmission at 2950-3313 cm^{-1}, associating with C-H stretching (Liu *et al.*, 2011).
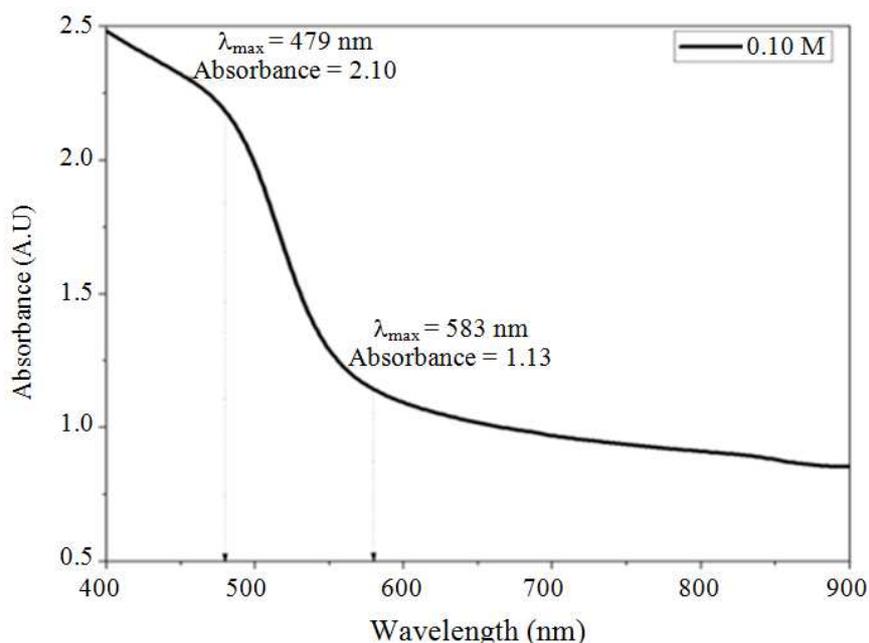
Fig. 6. Optical absorbance of CdS thin film with complexing agent

Table 5. Optical properties of CdS thin film by UV-Visible spectral analysis

Concentration 0.10 M	Max. peak λ_{max}	Cut off λ_{cut}	Concentration 0.10 M	Cut off	Max. T
Absorbance	2.14	1.13	Transmittance (%)	8.00	15.00
Wavelength (nm)	479.00	583.00	Wavelength (nm)	583.00	900.00
Band gap E_g (eV)	2.58	2.12	Band gap E_g (eV)	2.12	1.37
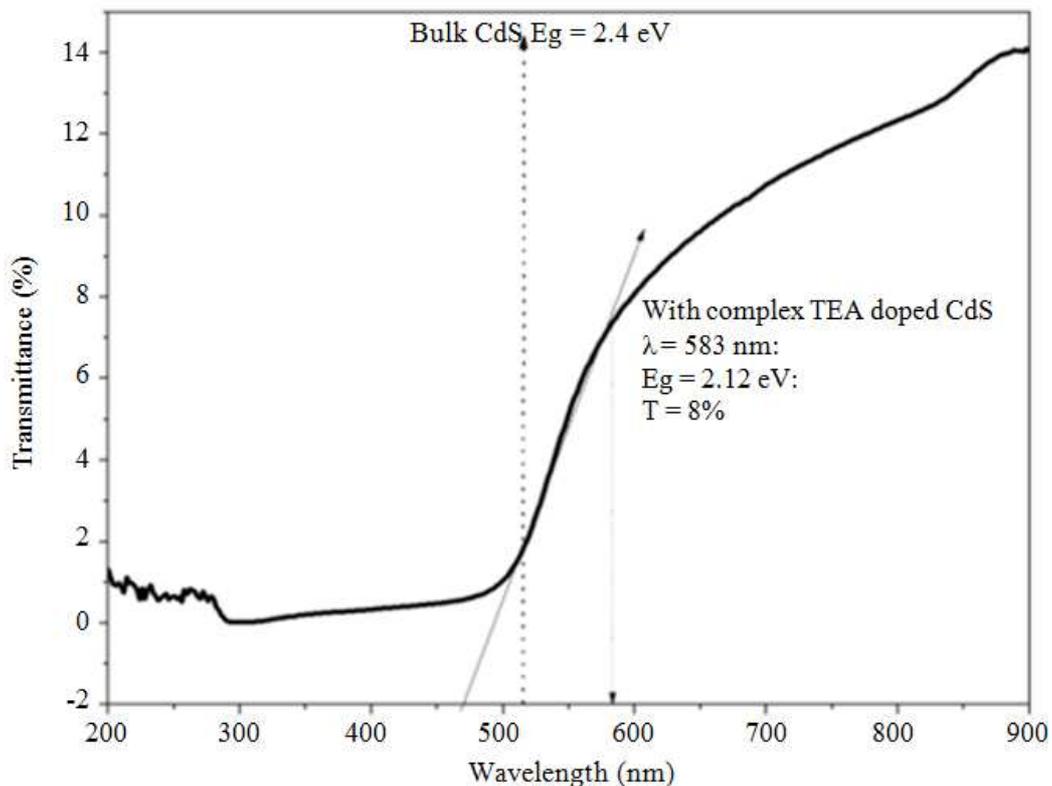
Fig. 7. Transmittance spectrum of the CdS thin film with complexing agent
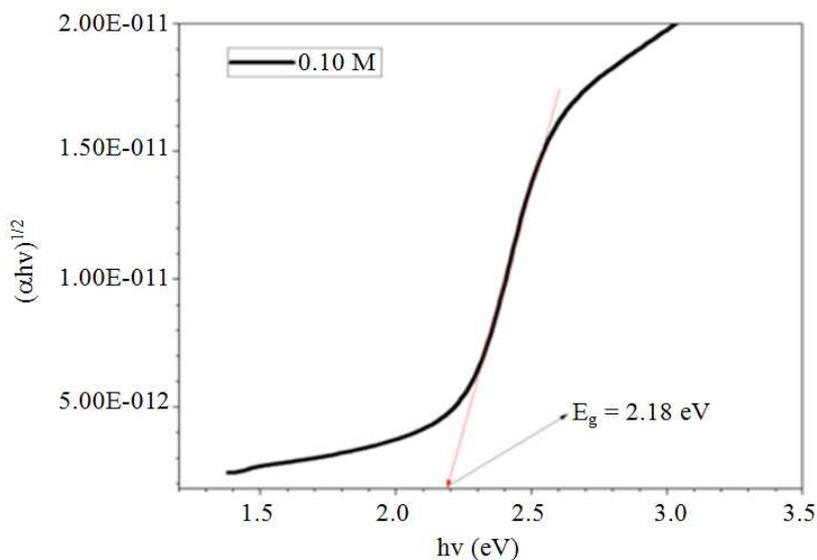
Fig. 8. The plot of $(\alpha h \nu)2$ versus $h \nu$ of CdS thin film complexing agent
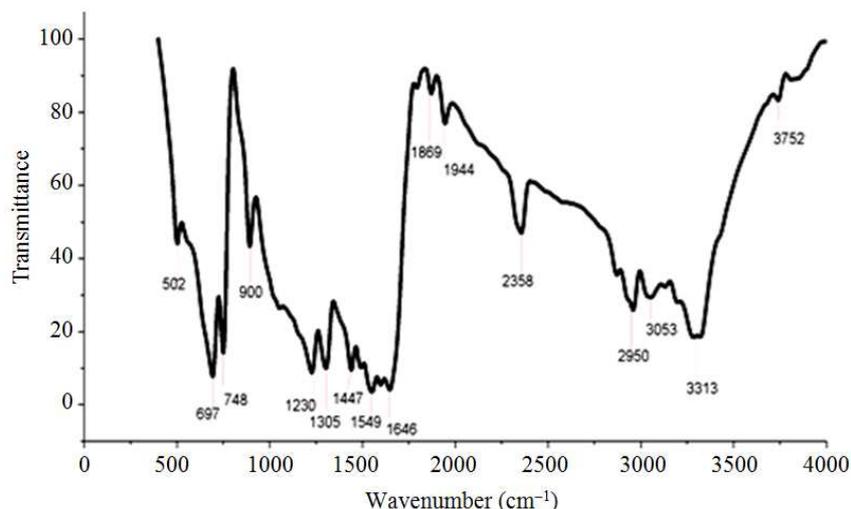
Fig. 9. FTIR as a function of the CdS thin film with with complexing agent

The bending vibrations of water molecules appeared in 2358, 1944 and 1869 cm^{-1}. The bands at 1646 cm^{-1} are assigned to the C-N bond stretching vibration of C-N (Aksay *et al*., 2011) and the frequency at 891-1051 cm^{-1} corresponds to the C-O stretching mode, at 502 and 697 cm^{-1}, there is medium to strong bands which have been assigned to cards stretching these results will be matched with the reported values (Khaorapapong *et al*., 2008).

Conclusion

CdS films were deposited by the SILAR technique using the equimolar and equivolume solutions of cadmium nitrate and sodium sulfide. The direct band gap value was found as 2.18 eV. The CdS films are cubic phase and non homogeneous CdS film were observed. These films have good optical properties and hence suitable for solar cell applications. The optical observation is coherent with the data obtained from XRD and AFM analysis.

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Author's Contributions

K. Manikandan: Participated in all experiment cording the data analysis and contributed the writing of the manuscript.

C. Surendra Dilip: Coordinated the writing of the good manuscript based on the changing background.

P. Mani: The correction of the writing manuscript.

J. Joseph Prince: Designed the research plan and motivated and organized the study.

Ethics

The authors confirm that this article is original and contains previously unpublished material. The corresponding author verifies that other authors have read and approved the manuscript and no ethical issues are violated.

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