Full Length Research Paper

Nanocrystalline Cadmium sulfide (CdS) thin film synthesized at different dip times by chemical bath deposition technique

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Nanocrystalline Cadmium sulfide (CdS) thin films were prepared by chemical bath deposition technique on a glass substrates at a temperature of 80°C and at different deposition times with composition of cadmium chloride ($CdCl_2$), thiourea ($CS(NH_2)_2$), ammonia solution (NH_4OH) and triethanolamine (TEA) solution. The characterization of thin films was carried out for the structural, morphological and optical properties using X-ray diffraction (XRD), Scanning electron microscope (SEM) and UV-VIS spectrophotometer. XRD studies show that the preferential orientation (002), analysis shows that the prepared samples have hexagonal crystal structure. Scanning electron microscopy (SEM) reveals small nanosized grains tied up in a fibrous-like porous structure uniformly distributed over the surface of the substrate for the CdS films. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocrystalline CdS thin films. The average band gap was found to be 2.25 eV, which is lower than the bulk value (2.4 eV). The increase in absorption coefficient with photon energy makes the deposited CdS thin film a suitable candidate for the fabrication of solar cells.

Key words: Nanocrystalline Cadmium sulfide (CdS), X-Ray diffraction, scanning electron microscopy, solar energy.

INTRODUCTION

The conversion of sunlight directly into electricity using the electronic properties of suitable materials appears to be an elegant energy conversion process and an ideal alternative to conventional energy sources. It has being a research laboratory interest for more than a hundred years, the solar cell technology has seen enormous development during the last four decades, initially for providing electrical power for space crafts and more recently for terrestrial applications (Mathew, 2009). Among the II-VI semiconductors, CdS polycrystalline thin films is a representative material with a wide energy gap semiconductors. This CdS thin film has experienced a fast rising mainly due to its applications in piezoelectric transducers, laser materials and photovoltaic cells, also it can be used as a window material together with several semiconductors such as CdTe, Cu_2S and $CuInSe_2$

(Selma et al., 2009; Mahdi et al., 2009). In CdS/CdTe heterojunction solar cells, where CdS acts as the n-type semiconductor for the window layer, a thicker CdS layer is believed to yield lower transmittance. In addition, as CdS films become thinner, the probability of a short circuit between the CdTe and the front contact increases. In order to prepare transparent and high resistivity CdS thin films with the good conformal coverage (Maeng et al., 2011). Ximello-Quiebras et al. (2004), deposited CdS with time variation at constant temperature from an aqueous ammoniacal solution containing cadmium ion from cadmium chloride and thiourea reported hexagonal phase with a preferential (0 0 2) orientation, dark resistivity of 10^4 Ωcm and with band gap in the range of 2.4eV. (Demir and Gode, 2015) obtained a band gap between 2.15-2.25eV with electrical conductivity of the films calculated from the current–voltage characteristic in the dark increases from 5.482×10^{-10} $(Ω\ cm)^{-1}$ to 5.304×10^{-8} $(Ω\ cm)^{-1}$. The CBD process, adapted for the preparation of CdS window layers in high efficiency solar cells, includes a cadmium salt, a complexing agent, and thiourea as Sulphur source, these precursors are mixed in an alkaline aqueous solution (Liu et al., 2010). Various deposition techniques such as electrodeposition (Bastol et al., 1985), spray pyrolysis (Chamberlain and Skarman, 1966), successive ionic layer adsorption reaction (Partha and Ayan, 2014) and a new chemical bath technique under rotation (Oliva-Avilés et al., 2010). Among these various techniques, the CBD is the most successful method used in the production of uniform, adherent, and reproducible large-area thin films for solar related application (Mane and Lokhande, 2000; Ximello-Quiebras et al., 2006). Thus, the deposition rate can be modified not only by changing the chemical reagents concentrations, or with the type of bath agitation used during deposition or by changing the bath temperature, it can also be modified by deposition time. The importance of this deposition changes can determine the thickness of the film and the bath and or substrate agitation can be directly related with the physical properties of the CdS films (Moualkia et al., 2009). In this research, the authors report a systemic investigation on the effect of deposition time on the physical properties of CBD–CdS films such as structure, surface morphology and properties using X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical transmission (UV).

EXPERIMENTAL DETAILS

Chemical reaction

The growth of CdS by CBD is given by the decomposition of the thiourea $(NH_2)_2SC$ in presence of a cadmium salt $((CdCl_2 . 2\frac{1}{2}H_2O))$ in a basic solution with ammonia (NH_3) as complexing agent. The chemical process can be described through the following chemical reactions:

$$Cd(NH_3)_4^{2+} \rightarrow 4NH_3 + Cd^{2+} \tag{1}$$

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

$$Cd(NH_2)_2 + OH^- \rightarrow SH^- + CH_2N_2 + H_2O \tag{3}$$

$$SH^- + OH^- \rightarrow + H_2O \tag{4}$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \tag{5}$$
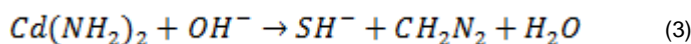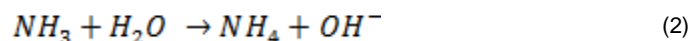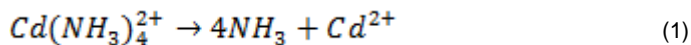
Synthesis

Thin films were deposited on glass substrate (micro slide - 75 mm L × 25 mm wide), thickness 1.45 mm (±0.1 mm). The glass substrates were first washed with detergent and rinsed thoroughly with normal water 2-3 times, subsequently soaking them in acetone for 45 min. After that the slides were thoroughly washed by deionized water several times, ultrasonicated in an ultrasonicator for 10 min. and dried in an oven at 60°C for 15 min. The chemical bath solution was prepared by 0.2 molar solution of cadmium chloride $(CdCl_2 . 2\frac{1}{2}H_2O)$ as the Cd^{2+} ion source, 0.1 molar solution of thiourea $(NH_2)_2SC$ as the S^{2-} ion source, 30% ammonium (NH_3) and triethanolamine (TEA) $(N(CH_2CH_2OH)_3)$. 10 ml of cadmium chloride was complexed with 5 ml of TEA in a 100 mls capacity of beaker, then 5 ml of ammonium solution was added to the 100 ml capacity beaker making the solution colourless, then 10 ml of thiourea was added to the already solution. The mixture was then topped to 80 ml level by addition of 40 ml of distilled water and stirred gently to ensure uniform mixture. The glass substrate was dipped vertically suspended into beaker containing the solution. The optimal deposition temperature and dip time for cadmium sulphide thin films was 80±2°C during the growth and 40, 60 and 80 min, respectively, during which the solution color changed to dip yellow as the deposition time increases. At the end of the deposition CdS thin film formed on the substrates with desired thickness, adherent, homogeneous and yellowish without any powder precipitation. The substrates were removed from the chemical bath, rinsed thoroughly in distilled water and dried in air at room temperature.

Characterization techniques

The films were structurally characterized by X-ray diffraction (XRD). X-ray diffractometer in the range of scanning angle (20° - 120°) with CuK_α radiation (45 Kv, 40 mÅ) of wavelength λ = 1.54443Å. Optical properties of Cadmium sulfide films with UV-VIS spectrophotometer to measure the absorbance of the films in the range of wavelengths 400 – 1100 nm. For the morphological properties of the thin film, the authors used the Scanning Electron Microscope (SEM) at X1000 magnification and scale bar length of 100 μm. Finally, Energy Dispersive X ray (EDAX) is used to determine the quantitative composition on the deposited thin film on the glass substrate with count up to 1000 with electron volts of range 0 – 20.

RESULTS AND DISCUSSION

Structural characteristics of the films

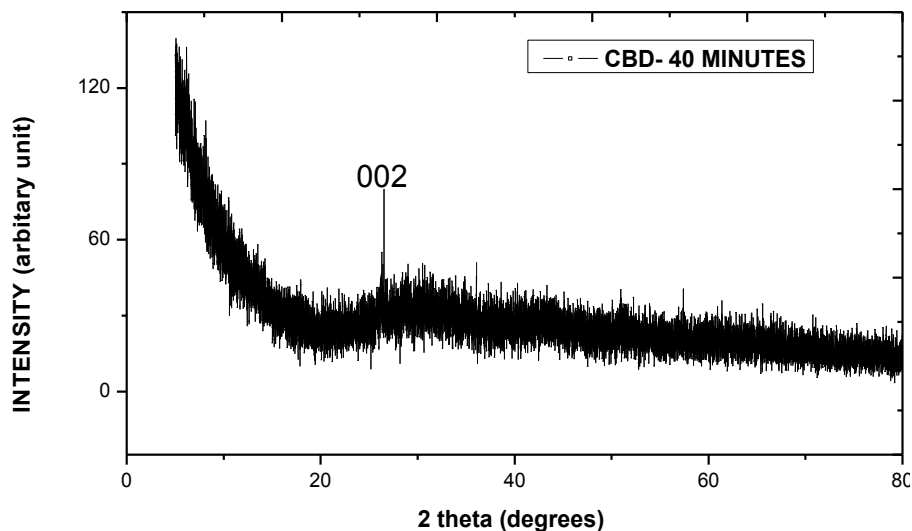CdS films, which were deposited on glass, can have either a hexagonal or a cubic structure or a mixed
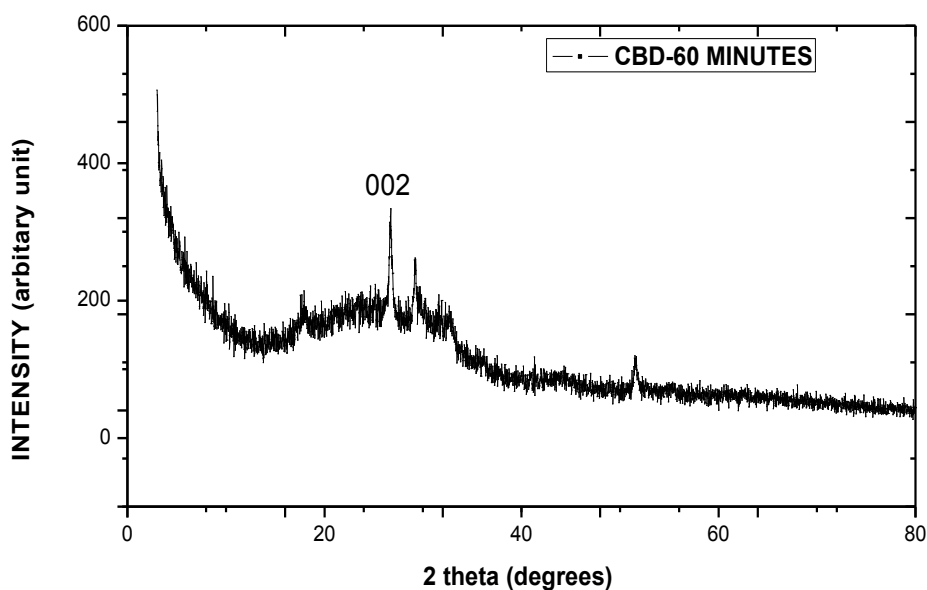
Figure 1. XRD pattern of CdS thin film – 40 min.

Figure 2. XRD pattern of CdS thin film – 60 min.

structure of the two, depending on the condition in which the film is prepared (Enriquez and Mathew, 2003). The structural analysis of CdS thin film was carried out by using X-ray diffractometer in the range of scanning angle (20° - 120°). Figures 1, 2 and 3 shows X ray diffraction patterns of CdS film deposited at different time interval at 80°C. The CdS films was found to be hexagonal crystal structure with strong orientation associated with (0 0 2) reflection according to data file reference no.01-074-9664. For the XRD pattern of CdS film at 40, 60 and 80 min all showed prominent peaks at 2θ = 26.25°, 26.67°, 26.76°,

which corresponds to the (002) lattice plane. The results of X-ray analysis are agreed with earlier investigators report (Gopinathan et al., 2011; Kodigala et al., 2001; Fangyang et al., 2010). The crystalline size of the deposited film is calculated using FWHM data and Debye-Scherer formula, $D = k\lambda/\beta\cos\theta$, where k is a Scherer's constant taken to be 0.94, λ the wavelength of X-ray used (λ = 1.54443Å), D = Grain Size, θ = is Bragg's diffraction angle at peak position and β = is Full width at half maximum of the peak in radian. Using Scherer's formula grain or particle size was found to be of the order range between 11 to 15 nm.
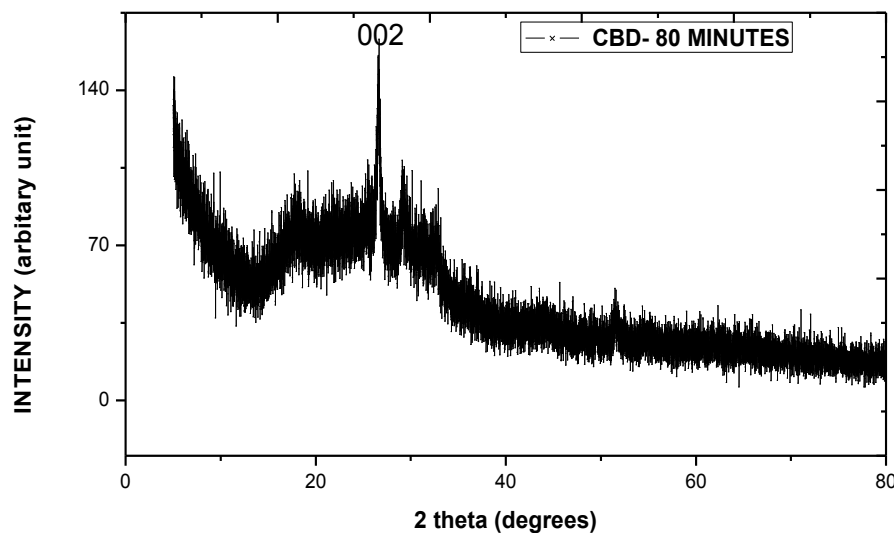
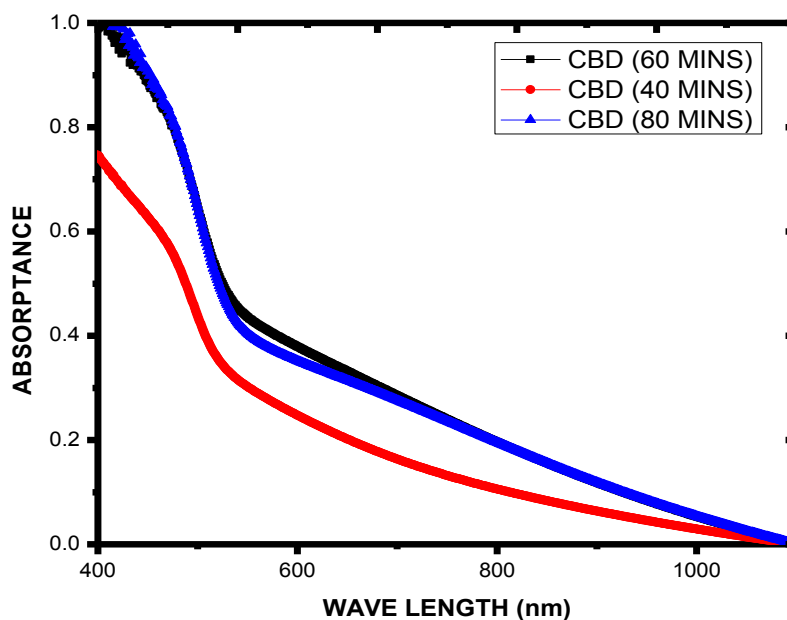**Figure 3.** XRD pattern of CdS thin film – 80 min.

Figure 4. Absorbance spectra of CBD-CdS film at 40, 60 and 80 min.

Optical properties of CdS thin films

Figure 4 shows the absorption spectra of the deposited CBD-CdS of different samples at 40, 60, and (80 min), respectively. The figure shows a high absorbance in the visible region between (400 to 520 nm) and a corresponding decrease in absorbance as the wavelength increases along the near infra-red region. The decrease in absorbance in the near infra-red region shows high transmittance near the infra-red region of the spectrum (Ezema et al., 2010) for all samples of CdS and low transmittance in the visible light region for all samples. Figure 5 shows the reflectance spectra of the deposited CBD-CdS of different samples at 40, 60, and (80 min), respectively. The figures shows a high reflectance in the wavelength range of visible light region (400 – 490) nm and a gradual fall in the reflectance in the wavelength range of 500 – 1100 nm was observed for all samples deposited by chemical bath deposition.

Figure 6 shows the variations of absorption coefficient (α) with photon energy for CdS thin films for all deposited samples CBD-CdS thin film of different samples at 40,
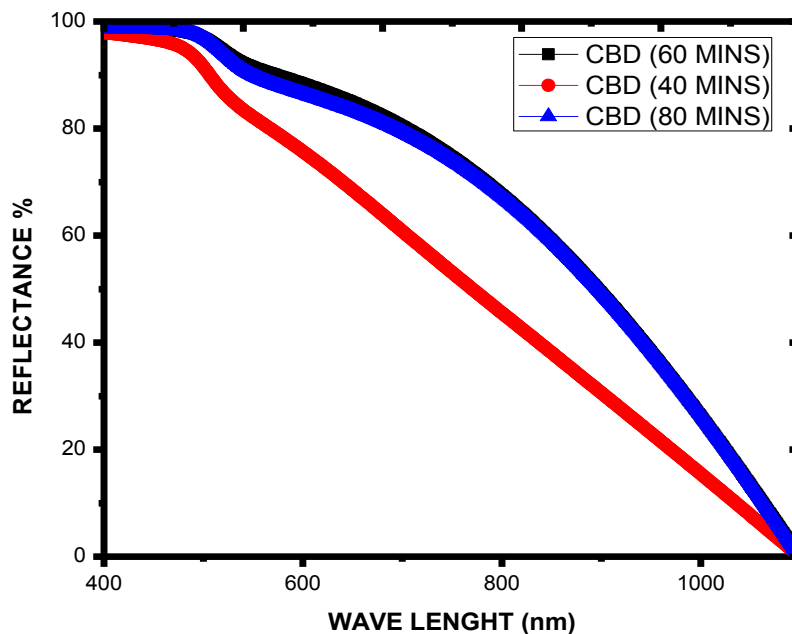
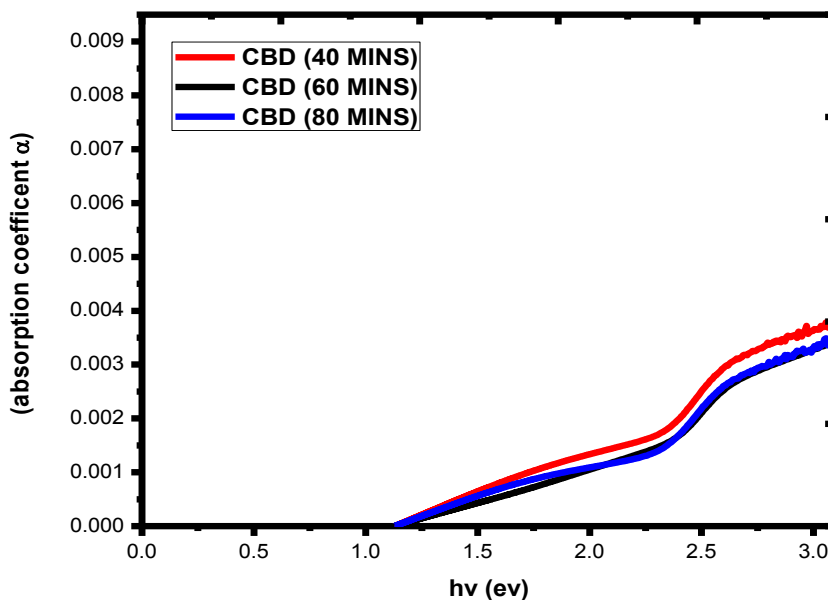**Figure 5.** Reflectance spectra of CBD-CdS film at 40, 60 and 80 min.

Figure 6. Plot of the variation of absorption coefficient (α) with photon energy (eV) of CBD-CdS at 40, 60 and 80 min.

60, and (80 min), respectively, the result reveals that there is a gradual increase in the absorption coefficient with increase photon energy for all the samples (Awodugba et al., 2012; Awodugba and Adedokun, 2011). As the photon energy increases, not just the electrons already having energy close to that of the band gap can interact with the photon. Therefore, a larger

number of electrons can interact with the photon and result in the photon being absorbed. Materials with higher absorption coefficients more readily absorb photons, which excite electrons into the conduction band. This increase in absorption coefficient of the deposited CdS thin film makes it suitable in the designing of solar cells.

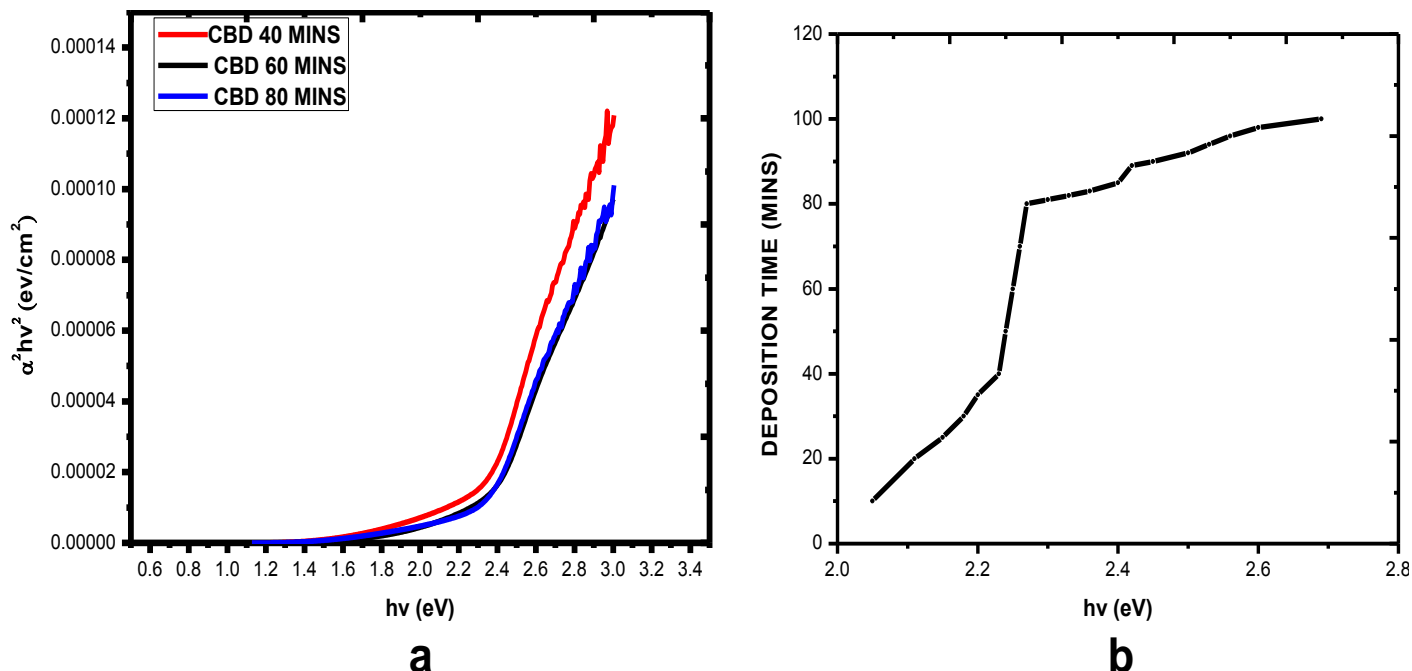The absorption coefficient α associated with the strong

Figure 7. a) Plot of Photon energy (eV) dependence on $\alpha^2 hv^2$ eV/cm^2 CBD-CdS at 40, 60 and 80 min; b) Plot of photon energy (eV) dependence on deposition time (mins).

absorption region of the film was calculated from absorbance (A) and the thin film thickness (t) using the relation (Jadhav et al., 2014; Fajinmi and Adelabu, 2009):

$$\alpha = 2.3026 \, A/t \tag{6}$$

In semiconductors, the relation connecting the absorption coefficient α, the incident photon energy (hv) and optical band gap E$_g$ takes the form (Ezema et al., 2010):

$$(\alpha hv) = K(hv - E_g)^{n/2} \tag{7}$$

where K is a constant, E_g is separation between valence and conduction bands and n is equal to 1 which makes it ½ for direct band gap semiconductor, also 2, 3/2 or 3 correspond to indirect, forbidden direct or forbidden indirect transitions, respectively. CdS as a semiconductor material has received much attention due to its direct band gap resulting in emission in the visible wavelength (Abdullah et al., 2012). The band gap of the films was determined by plotting a graph between (αhv)^2 and (hv). The band gap energy (Eg) was estimated by a linear interpolation of each curve to energy axis. Figure 7a shows optical energy band gaps of the CBD-CdS thin film for 40, 60 and 80 min. The value of band gap was found to be between 2.23 - 2.27 eV depending on deposition condition. It was observed that the band gap energy values obtained on films at different deposition time did not show any important changes; however the band gap

energy increases slowly with deposition time (Figure 7b).

Morphology properties and elemental composition of CdS thin films

Scanning electron microscope (SEM) was used for the morphological study of CdS thin films. Figure 8, 9 and 10 shows the SEM images of CBD-CdS at X1000 magnification for 40, 60 and 80 min. It is observed that the films where uniform and smooth throughout all the regions which means that the deposited film was uniform yellowish and well substrate covered. The films are without pinhole or cracks, from all samples, we clearly observe the small particles tied up in a fibrous-like porous structure, this indicates the nanocrystalline nature of CdS thin films deposited.

The elemental composition of the as-deposited CdS thin film was investigated using EDAX and the pattern is shown in Figures 11, 12 and 13 for different deposition time (40, 60 and 80 min, respectively) using chemical bath deposition method. For all samples, peaks of Cd and S exhibit the presence of these elements in the deposited thin film. Also for all samples, the ratio of Cd element is more compared to S element. The peaks of silicon originate from the glass substrate.

Conclusion

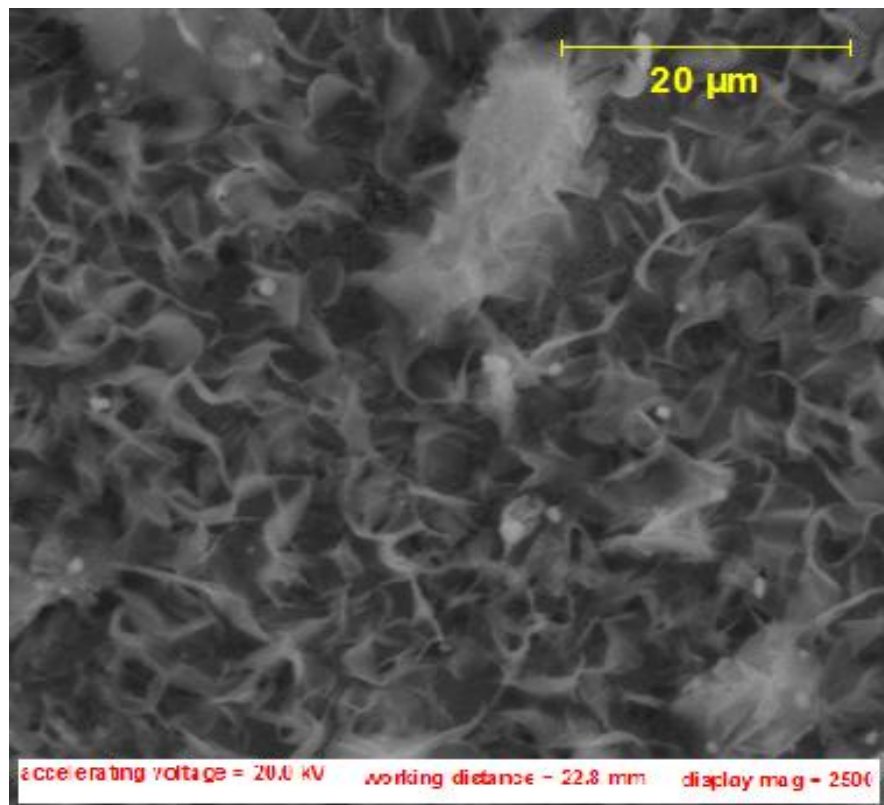The chemical bath method was successfully used to
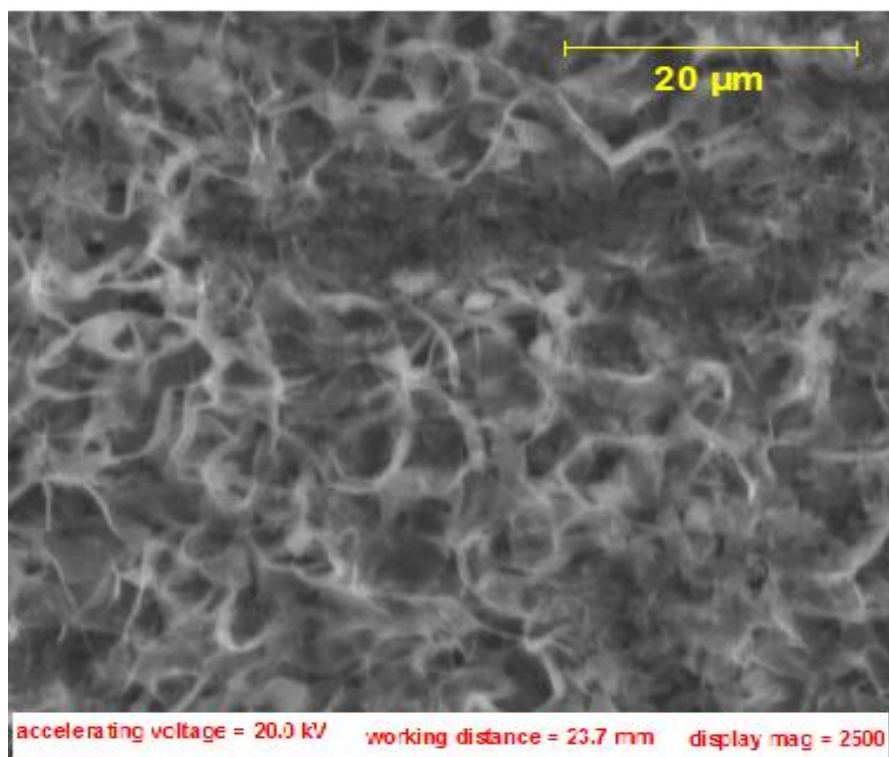
Figure 8. SEM image of CBD-CdS film 40 min.

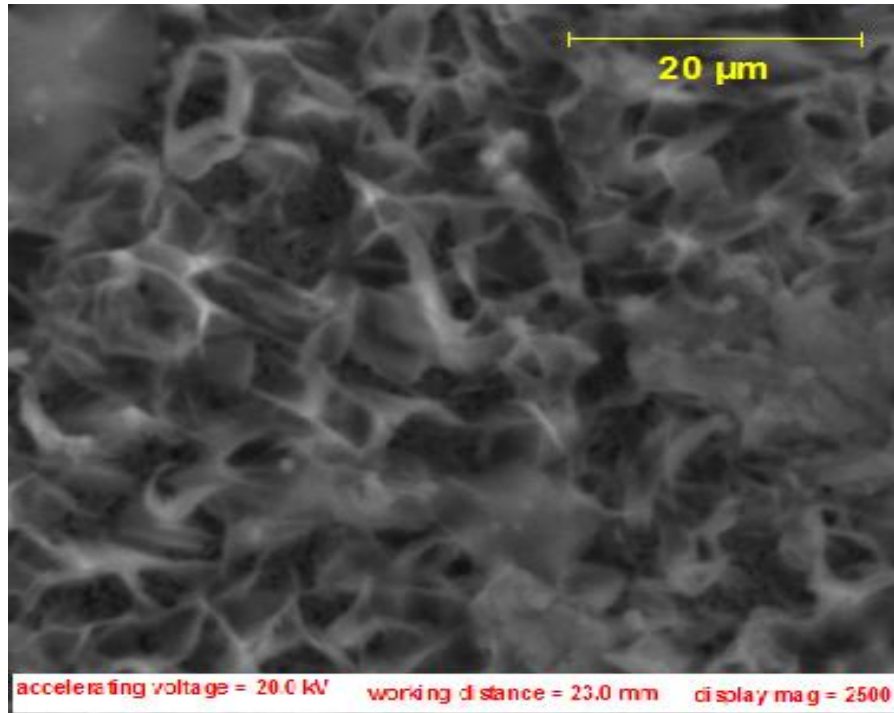**Figure 9.** SEM image of CBD-CdS film 60 min.

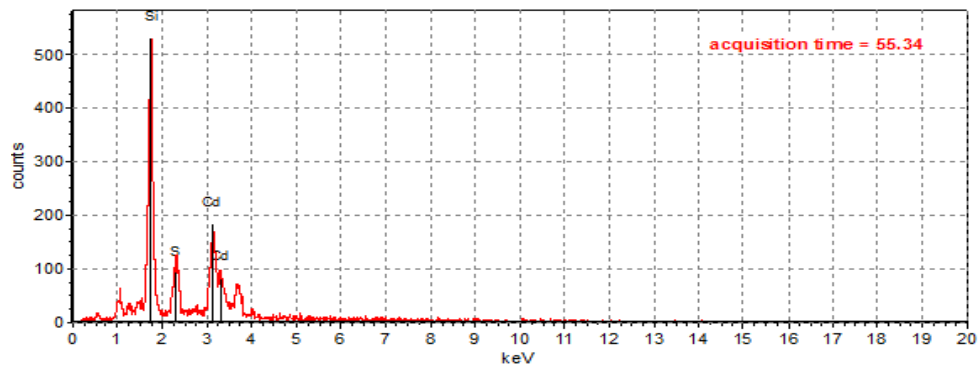**Figure 10.** SEM image of CBD-CdS film 80 min.

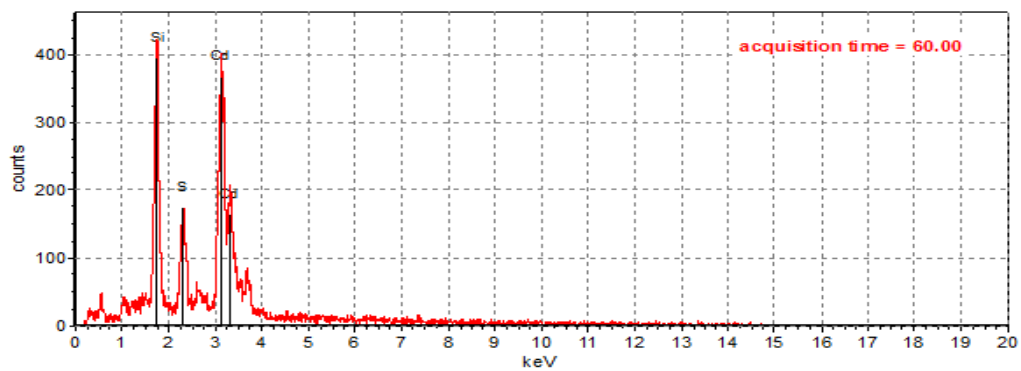**Figure 11.** EDAX pattern of CBD-CdS thin film 40 min.

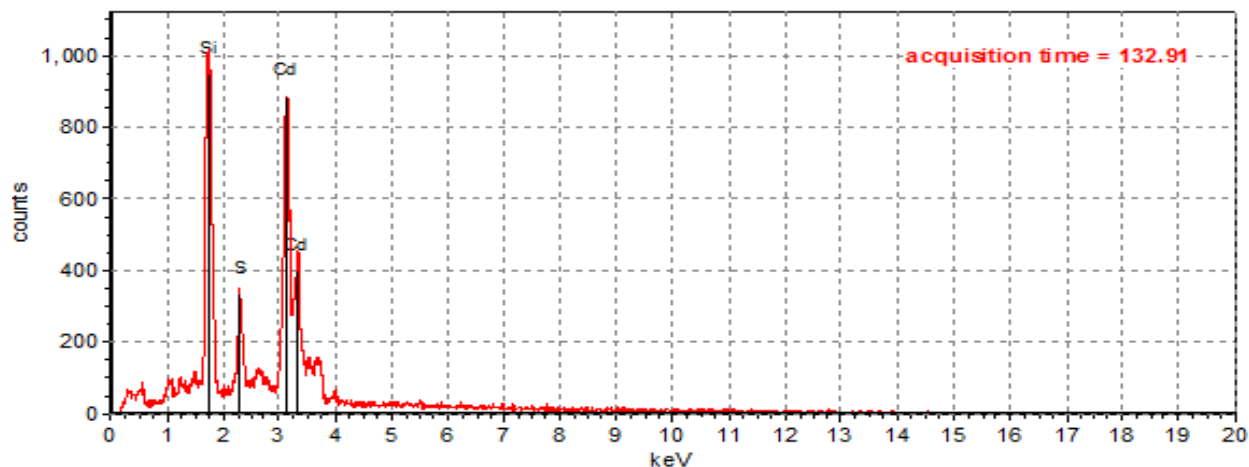**Figure 12.** EDAX pattern of CBD-CdS thin film 60 min.

Figure 13. EDAX pattern of CBD-CdS thin film 80 min.

deposit CdS thin films. The morphology of the thin films is smooth, uniform and good adherent to substrate surface for all samples. The EDAX pattern showed the presence of Cadmium and Sulfur which was the salt used in this experiment. The prepared films were found to be nanocrystalline thin films. XRD analysis reveals that CdS thin films are polycrystalline having a hexagonal structure with a preferential orientation of (002) plane for all samples. In the optical studies, the CdS thin film showed a high absorbance and high absorbance coefficient in the area of the visible region, this makes the deposited film suitable in the designing of solar cells. The energy band gap for deposited CBD - CdS thin film was in the range of 2.23 – 2.42eV which can be used in the application of thin film as window layer in solar cell fabrication.

Conflict of Interest

The authors declare no conflict of interests.

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