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ARTICLE

Effect of Substrate Temperature on Optical Properties of Spray Pyrolytic Cadmium Sulphide Thin Films

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Abstract: Cadmium sulphide (CdS) thin films were prepared by chemical spray pyrolysis technique on micro-slide glasses using cadmium acetate and thiourea as precursors. The substrate temperature was varied in the range of 250°C- 350°C. The prepared films were annealed at 500°C for 1hour. The effects of substrate temperature and annealing on the optical properties of the films were investigated. The films were characterized using UV-Visible Spectrophotometer. The absorption and transmission spectra revealed that the transmission increases with wavelength, while the absorbance reduces as the wavelength increases in the visible region. The optical band gaps of the films were found to be 2.26eV, 2.07eV and 1.88eV with deposition temperature of 250°C, 300°C and 350°C, respectively. It was observed that the refractive index of the thin film obtained reduces as the substrate temperature increases and that annealing reduces the refractive index of the cadmium sulphide thin film. These findings show that cadmium sulphide is one of the most promising materials to be used as a window layer in hetero-junction thin film solar cells. It is also of good interest for its applications in some optoelectronic devices, like photoresistor and photodiode.

Keywords: Cadmium sulphide, Spray pyrolysis, Thin film, Annealing, Optical properties.

Introduction

Cadmium sulphide (CdS) is known as a II-VI semiconductor compound with wide band gap; 2.42 eV at room temperature [1]. It has been used in making hetero-junction thin film solar cells. A layer of material having thickness of the order of a few nanometers is generally referred to as ‘thin film’ [2]. The use of thin film has been growing at an increasing rate because of its potential applications in various fields of science and technology. The deposition of CdS films has been explored by different techniques: thermal evaporation, chemical bath deposition (CBD), molecular beam epitaxy and spray pyrolysis [3]. Spray pyrolysis technique gives opportunity to vary several deposition parameters; like flow rate, air pressure, substrate temperature, spray nozzle-to-substrate distance, … etc. Structural and optical properties of CdS deposited by spray pyrolysis technique depend on the parameters of relative concentration of the reactants for

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chemical reaction, thickness of the film, substrate temperature and even annealing [4].

Apart from the afore-mentioned merits of spray pyrolysis technique for depositing thin films, it was also reported that it is simple, faster and provides uniform deposition of thin films [5].

The investigation of the basic properties of CdS thin films is of paramount importance in understanding and developing modern CdS solar cells [6].

Other schemes for power generation *via* solar cells include thin film solar cells and multi-junction solar cells. Multi-junction solar cells, although more efficient, have higher fabrication cost. Polycrystalline thin film solar cells are among the important candidates for large-scale photovoltaic applications because of their low cost, high efficiency and stable performance.

The influence of substrate temperature and annealing on the properties of cadmium sulphide thin films prepared by spray pyrolysis technique is reported in this study.

Experimental Details

Cadmium sulphide (CdS) was synthesized using spray pyrolysis technique. 0.1M of cadmium acetate dihydrate [Cd $(CH_3COO)_2$. $2H_2O$] ≥ 98.0 % (Sigma-Aldrich product) and 0.1M of thiourea [NH_2CSNH_2] (Sigma-Aldrich) were used as source of cadmium and Sulphur, respectively. The precursors, having been mixed with distilled water of required volume, were stirred by the magnetic stirrer (ARGO LAB M2-A). Micro-slide glasses were used as substrate for the thin films. The substrates were pre-cleaned with detergent and distilled water as well as with methanol in an ultrasonic cleaner (VWR ultrasonic cleaner).

The substrate temperatures were varied between 250°C and 350°C using the Proportional Integral Derivative (PID) temperature controller, in the interval of 50°C. The air pressure used was 2 bars and the distance between the nozzle and substrate was kept at 24 cm. The solution was sprayed at a rate of 10 $mlmin^{-1}$. The thickness of the films was calculated using weight difference method and it was in the range of 2.98µm – 3.39µm for the as-prepared films. The films were annealed in a furnace at 500°C for 1hour.

Results and Discussion

Transmittance and Absorption Spectra

The UV-Visible spectrophotometer was used for obtaining the optical properties of the cadmium sulphide (CdS) film produced. The chosen range is within that of the visible region of the electromagnetic spectra, which is about 400-800nm. This region is chosen because the application of the prepared thin film in solar cell is of major concern in this work.

The wavelength dependence of the optical transmittance spectra for the thin films at different substrate temperatures of 250°C, 300°C and 350°C are shown in Fig. 1.

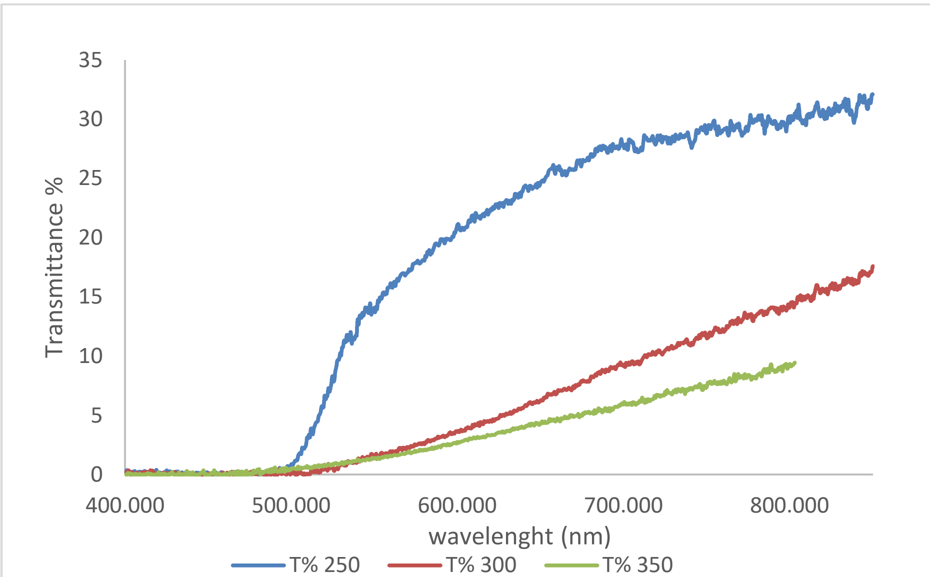


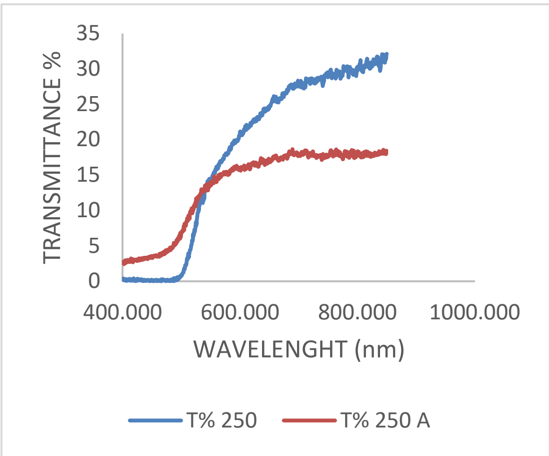
FIG. 1. Comparison of the variation in transmittance with wavelength for films sprayed at different substrate temperatures; 250°C, 300°C and 350°C.

It was observed that the transmission of visible light by the film increases as the wavelength increases in the visible region for all the films prepared at the different substrate temperatures stated above, though the transmission commenced at around 450 nm - 490 nm.

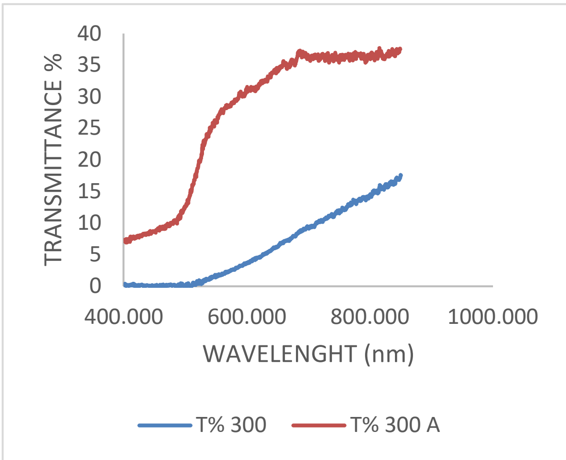
The percentage of transmission is a bit low when compared with what has been obtained by some researchers on cadmium sulphide thin film properties. This may be due to a little deviation of the composition of the material from the stoichiometric structure of the film or the thickness of the film. For a window layer in an hetero-junction thin film solar cell, the thickness of the material is expected to be very small (thinner than that of an absorber).

Figs. 2 and 3 show the comparison of the variation of transmittance with wavelength for the as-prepared films and those annealed at 500°C. From the comparison, it was observed that annealing improves the transmittance of the films prepared at 300°C and 350°C, while it reduces the transmittance of the film prepared at 250°C, though annealed films transmit earlier in the visible region than as-prepared film, (Fig. 2). This effect of thermal annealing on the transmission of CdS films may be a result of some physical effects, such as structural and/or surface irregularity, and defect density, according to Hasnat and Podder, (2012). The heat treatment (annealing) is likely to have removed the defects present in the films prepared and thereby improved the crystallinity of the material which enhances more percentage of the visible light to be transmitted through the material.

Also, it was observed that the material prepared is sensitive to electromagnetic wave near infrared region (wavelength range of 700nm – 1mm). This makes it a potential material for use as a sensor in remote control devices, likewise in a light dependent resistor (LDR) and photodiode.



(a)



(b)

FIG. 2. Transmittance spectra of the as-prepared film at (a) 250°C and (b) 300°C, annealed at 500°C.

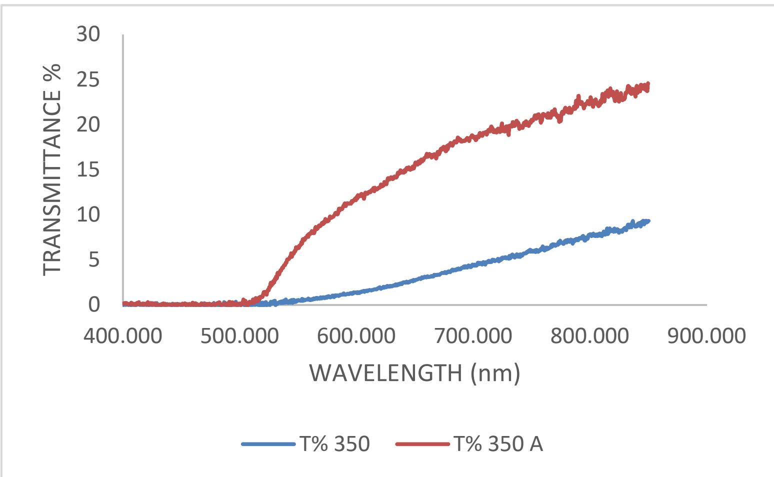


FIG. 3. Transmittance spectra of the as-prepared film at 350°C and annealed at 500°C.

The absorbance of the films deposited at the different temperatures mentioned earlier was also studied. The Absorbance **A** was obtained from the expression, $\boldsymbol{A = 2 - [Log\%T]}$, where 'T' is the transmittance value. The result in Fig. 4 shows that the absorbance of visible light by the films reduces with increase in wavelength, though the absorption was observed till around 450nm; the absorption peak, before the fall commenced. When the films were treated with heat (annealed) at 500°C, the absorbance decreases with increase in substrate temperature. Invariably, annealing reduces the optical absorbance of the film. This may be due to the fact that annealing removes likely defect that might be present in the film produced initially. Hence, it improves the property of the film for better application as a window layer in a thin film solar cell.

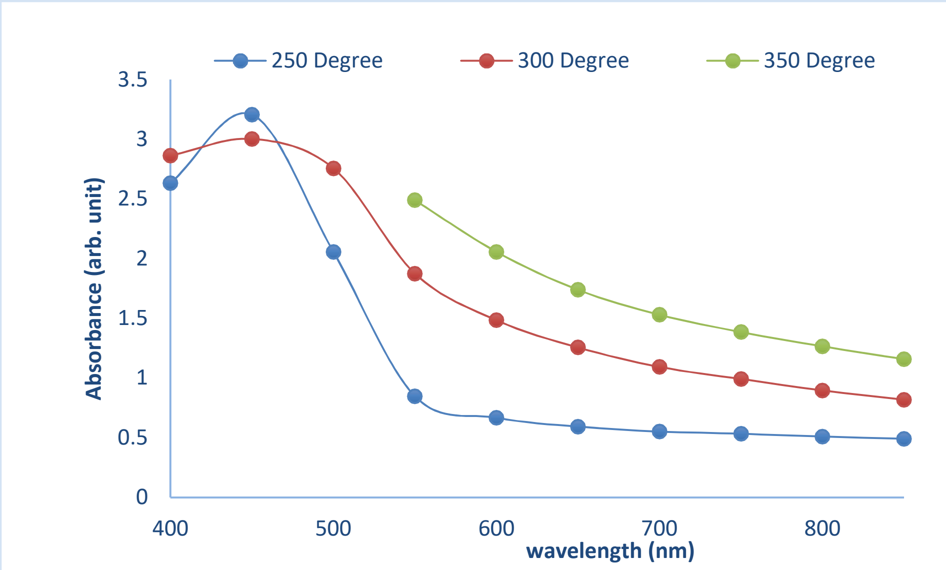


FIG. 4. Comparison of the variation of absorbance with wavelength for films sprayed at different substrate temperatures; 250°C, 300°C and 350°C.

Figs. 5, 6 and 7 show the comparison of the variation of the absorbance with wavelength for as-deposited film and the annealed films at 500°C.

It has been known that cadmium sulphide is a good window layer in a solar cell, which connotes that the absorbance will be low, with a reasonably high transmittance as compared with its absorbance in the visible region. The results shown in Figs. 1 - 4 confirmed this fact.

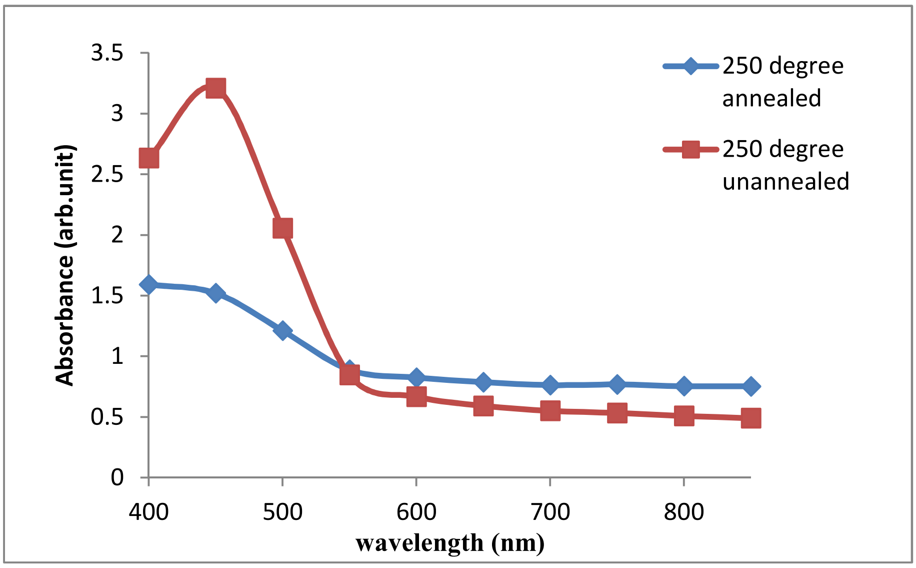


FIG. 5. Comparison of the variation of absorbance with wavelength for films sprayed at 250°C with the one annealed at 500°C.

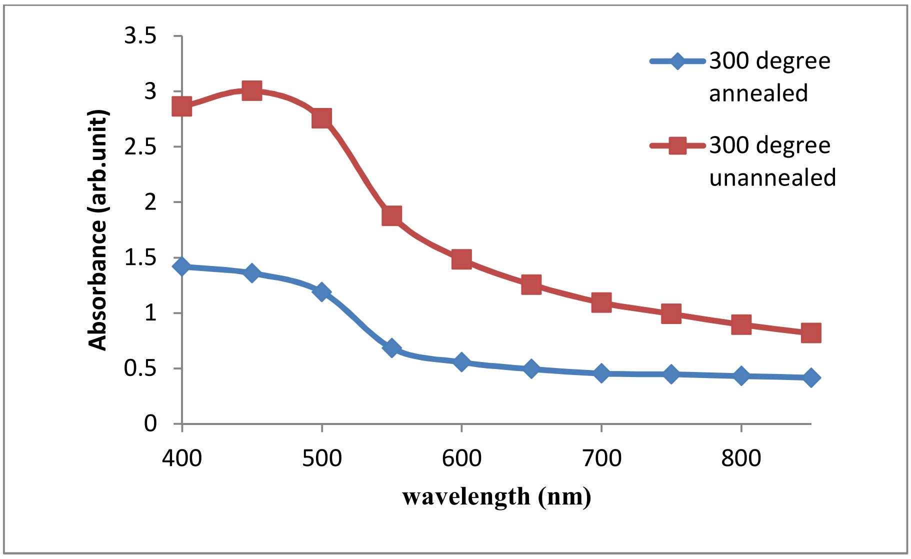


FIG. 6. Comparison of the variation of absorbance with wavelength for films sprayed at 300°C with the one annealed at 500°C.

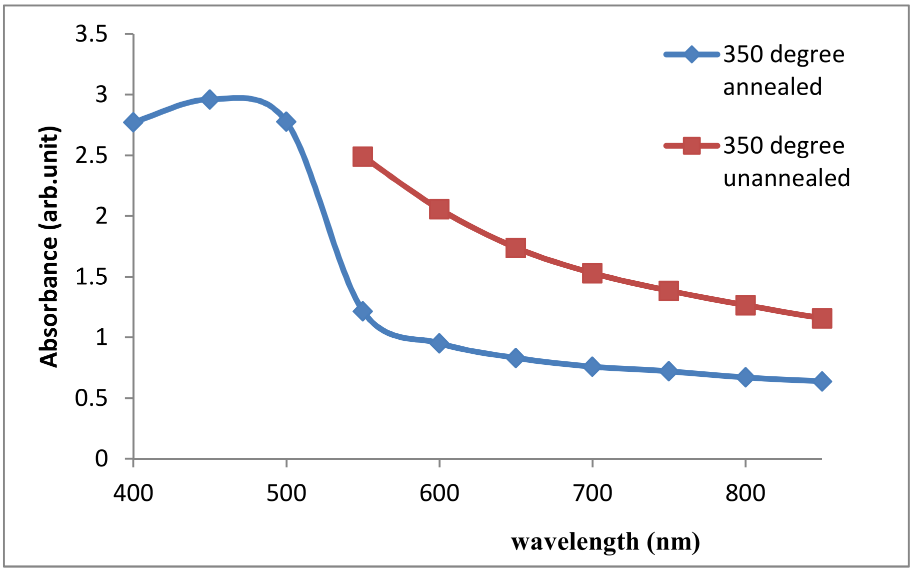
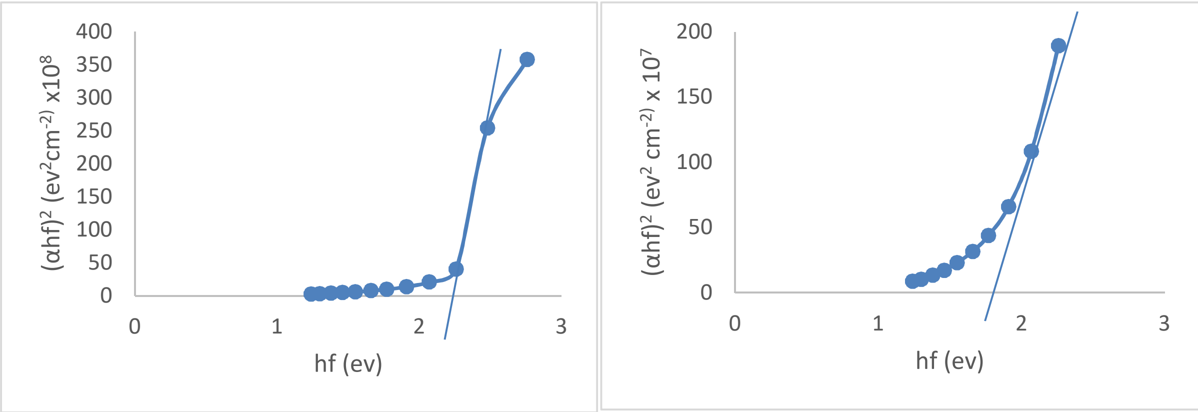


FIG. 7. Comparison of the variation of absorbance with wavelength for films sprayed at 350°C with the one annealed at 500°C.

Energy Band Gap

Moreover, the optical band gap $\boldsymbol{E_g}$ of the CdS thin film prepared was also determined from the absorption spectra using the Tauc-relation given as $\boldsymbol{\alpha hf = A\,(hf - E_g)^n}$. With n as ½ for a direct transition, since the semiconductor compound – CdS is having a direct band gap, α is the absorption coefficient, the energy band gap was obtained from the plot of $(\alpha hf)^2$ *vs*. hf, where h is Planck's constant and f is frequency. The absorption coefficient, $\boldsymbol{\alpha = \frac{2.303\,A}{t}}$, where 't' is the film thickness. This was done by extrapolating the linear portion of the plots to obtain the direct band gap of the films.

From Fig 8, the energy gap of the film as-prepared at 350°C is around 1.88 eV, while it is about 2.26eV for the same film annealed at 500°C. This shows that treating the film with heat, i.e., annealing, actually affects its optical properties. The annealed film has its band gap increased. The value of the energy band gap obtained for the annealed film is close to the bulk value for cadmium sulphide, which is 2.42eV.



(a) (b)

FIG. 8. Energy band gap of film as-prepared at (a) 350°C and (b) as-prepared at 350°C then annealed at 500°C.

A comparison of the band gaps of films prepared at different substrate temperatures is shown in Fig. 9. The band gaps at 250°C, 300°C and 350°C as-prepared are about 2.26eV, 2.07eV and 1.88eV, respectively. It was observed that the band gap decreases as the substrate temperature used to prepare the film increases. This may be due to the fact that as temperature increases, some of the covalent bonds will be broken because of the thermal energy supplied to the crystal and hence the gap between the conduction band and the valence band gradually reduces.

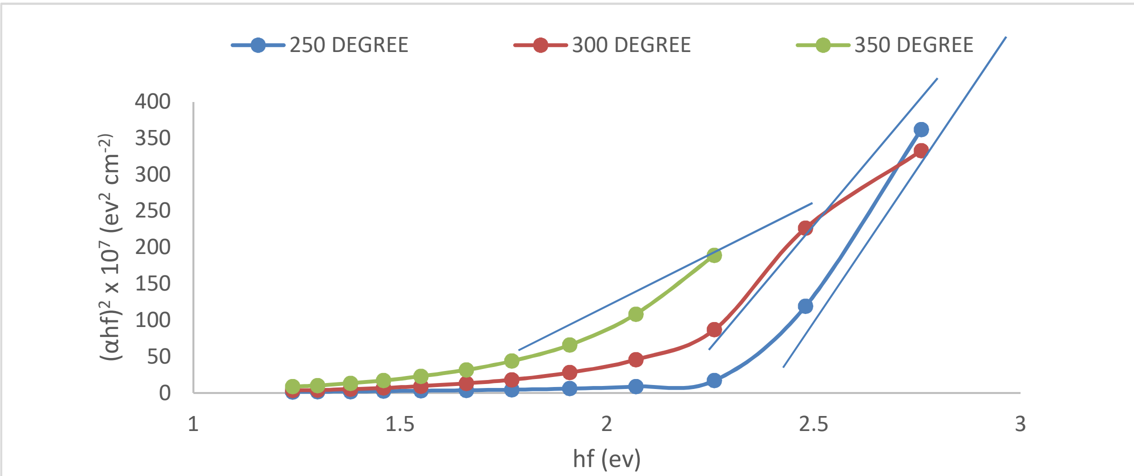


FIG. 9. Comparison of the energy band gaps of the films as-prepared at 250°C, 300°C and 350°C.

The band gap values of the CdS film prepared are around its theoretical value at room temperature given as 2.42eV and almost in agreement with previous works on CdS, especially as reported by [1].

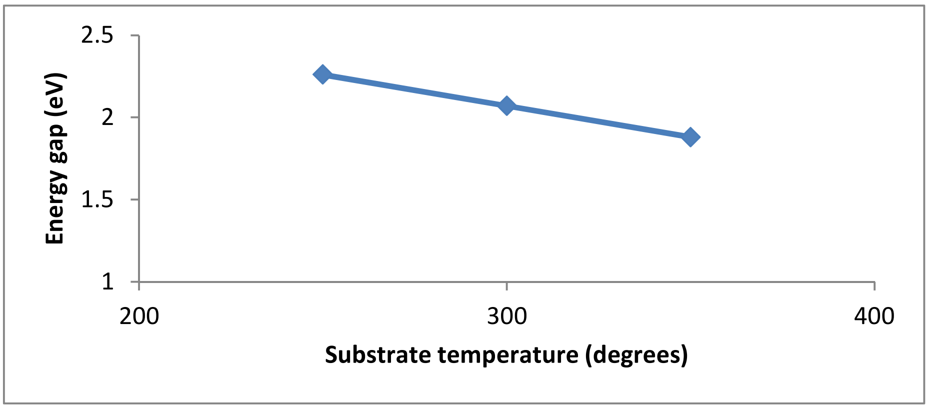


FIG. 10. Variation of energy band gap with substrate temperature of the thin films.

Refractive Index

Refractive index is a dimensionless quantity that describes how light propagates through that medium. It shows how much light is bent, or refracted, when entering a medium.

From Fig. 11, it was noticed that the refractive index reduces as the temperature used in preparing the film increases. Also, Figs. 12, 13 and 14 show that annealed films have lowered refractive indices compared to the ones not annealed. In this work, the refractive indices were calculated using the expression $n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$, where R is the reflectance values obtained from the UV-Vis spectroscopy characterization. Refractive index can also be given by the expression $n = c/v$, where n is the refractive index, c is the speed of light in vacuum and v is the speed of light in the material. Since n is inversely proportional to v, it connotes that as **n** reduces, the rate of transmission of electromagnetic wave in the material increases. This will actually result in better performance of the material as a good window layer in hetero-junction solar cells. The refractive index of a bulk CdS is about 2.52.

TABLE 1. The variation of refractive index with substrate temperature for the as-prepared films.

Substrate temperature (°C)	Average refractive index (in visible region), **n**
250	4.1
300	3.4
350	2.9

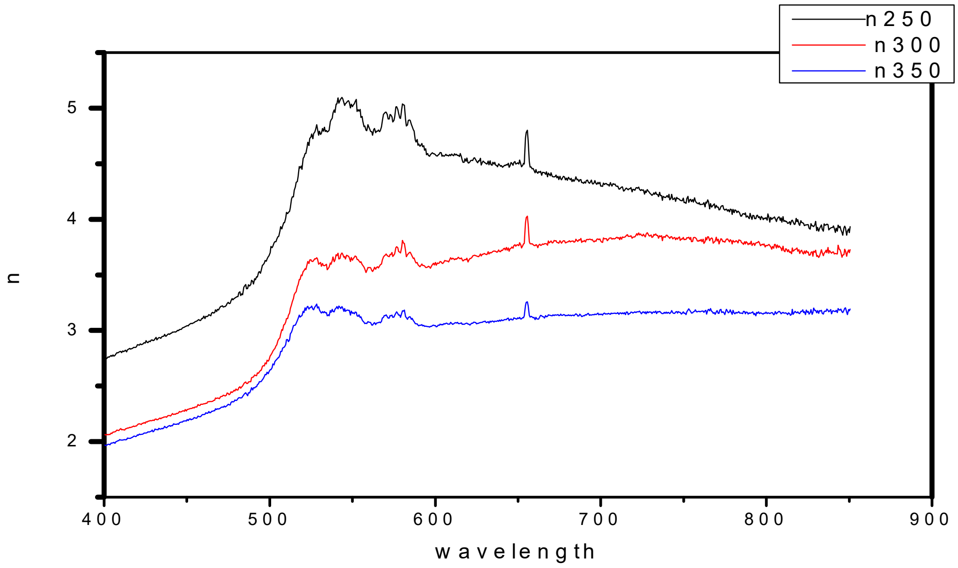


FIG. 11. Comparison of the variation of refractive indices of CdS thin films prepared at different temperatures with wavelength.

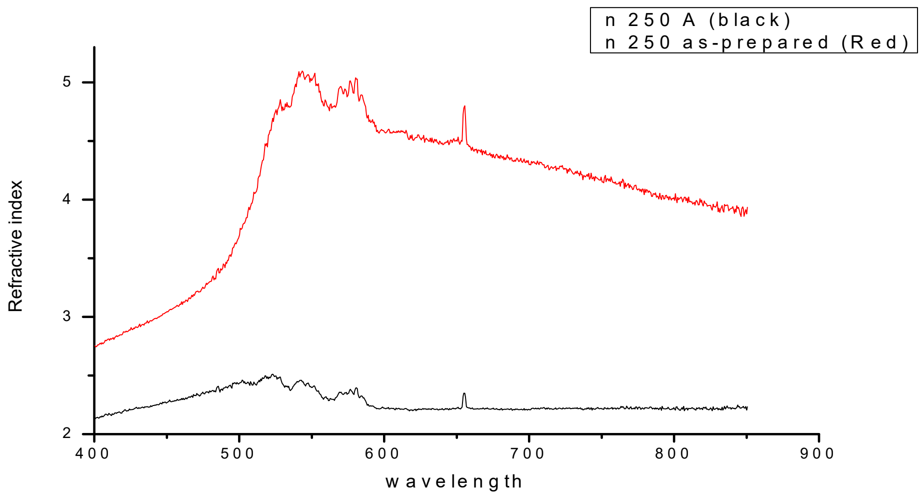


FIG. 12. Comparison of the variation of refractive indices of CdS thin films prepared at 250°C and the annealed film with wavelength.

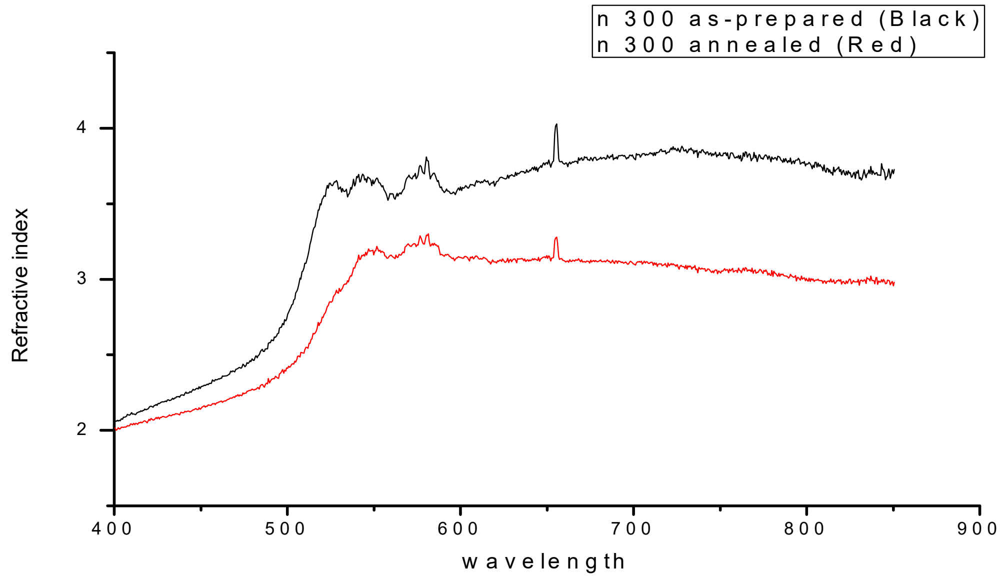


FIG. 13. Comparison of the variation of refractive indices of CdS thin films prepared at 300°C and the annealed film with wavelength.

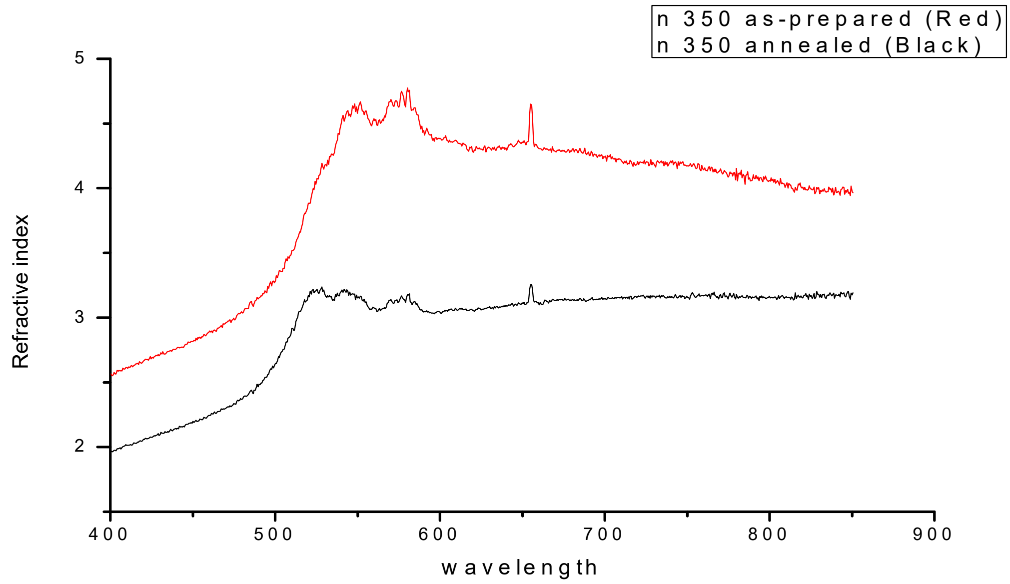


FIG. 14. Comparison of the variation of refractive indices of CdS thin films prepared at 350°C and the annealed film with wavelength.

Crystallinity of the Thin Film

The thin film was subjected to phase analysis by employing X-ray diffractometer (Model: EMPYREAN) that was equipped with CuKα as radiation source (λ = 1.5406 Angstrom). Only the film annealed at 500°C was characterized with XRD.

Fig. 15 shows the X-ray diffractometer pattern of CdS thin film obtained at an annealing temperature of 500°C and revealed the formation of cadmium sulphide (CdS) with hexagonal crystal structure, though with background noise. The peaks considered at 2Θ angles of 24.4, 26.0 and 27.2° correspond to diffraction from planes (1 0 0), (0 0 2) and (1 0 1), respectively, which are very close to the expected values from JCPDS 41-1049 for CdS. Using the X-ray diffraction data and Scherrer's equation given below, the average grain size was estimated.

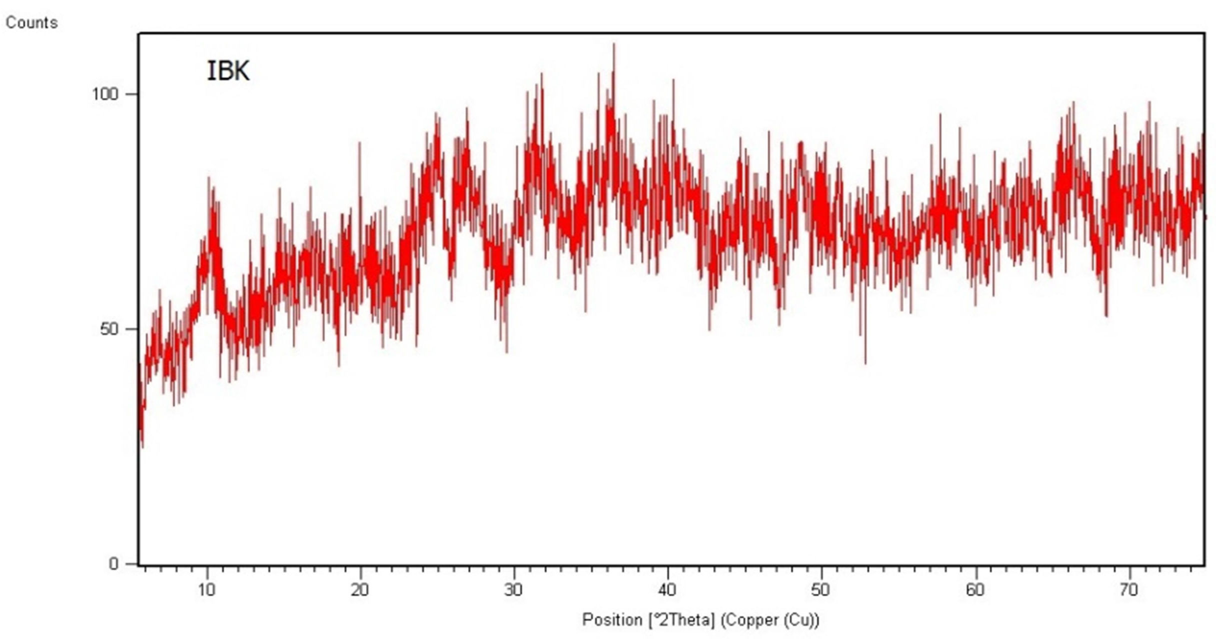


FIG. 15. XRD spectra of CdS thin film annealed at 500°C

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$$g = \frac{K\lambda}{\beta Cos\Theta} \qquad \text{(Scherrer's equation)}$$

where K = 0.94 is the shape factor, λ = wavelength of X-ray used; 1.5406 Angstrom, β = full width at half maximum (FWHM) in radians, ϴ = Bragg angle of the diffraction peak in radians and g = average grain size.

The average grain size of CdS was calculated to be 20.50 nm, which confirmed that the CdS synthesized is in nano scale. The 2ϴ peaks for CdS, even though with background noise, show crystallinity of the nanostructured thin film produced by the annealing process. The noise in the XRD pattern may be due to the presence of impurities in the synthesized compound. Although not carried out in this work, the variation of substrate temperature influences phase of CdS films according to [7].

Conclusion

Cadmium sulphide (CdS) thin films have been prepared from cadmium acetate and thiourea as sources of Cd and S, respectively, using the chemical spray pyrolysis technique on micro-slide glasses. It has been observed that the films were affected by the variation of the substrate temperatures used in preparing the thin films as well as by annealing the film. The optical band gap of the material was obtained in the range of 1.88eV – 2.26eV. Film thicknesses, transmission spectra, optical band gaps, absorption spectra and refractive indices obtained in this investigations have really confirmed that annealing and increase in substrate temperature improve the properties of CdS for application in a solar cell and in some optoelectronic devices, because of its ability to transmit electromagnetic waves even near the infrared region, its high index of refraction and high electron affinity.

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