Original Article

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Effect of Substrate Temperature on the Structure, Optical and Photoelectric Properties of CdS thin Films prepared by Spray Pyrolysis Technique Based on Photo Sensor

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Abstract

Cadmium Sulfide thin films were successfully deposited on glass substrates by spray pyrolysis method. The films were grown at different substrate temperatures in the range, (250-400) ^{o}C. The effects of substrate temperature on the structural, optical, and electrical properties were studied. The X-ray patterns and morphological studies of CdS thin films indicated that the films are crystalline in nature with a hexagonal crystal structure. The grain size calculated and found to be 13.96 to 47.02 nm. The optical spectra exhibited high transmittance and band gap varied from 2.435 eV to 2.465 eV. The present device (Al-CdS) show high sensitivity and fast responsivity in visible light of region of electromagnetic wave and providing a simple and economical way to fabricate high-performance visible detectors. The thermo-electric measurements have been measured with two probe method. It was found that CdS thin films were semiconducting in nature with n-type.

Keywords: Thin Films, CdS, Spray Pyrolysis, Photo Detector.

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Introduction

CdS is yellow compound and can be found in nature as the mineral Greenockeite. It is formed by introducing hydrogen sulfide (H_2S) into the alkaline cadmium salt solution [1]. And is one of the most studied compounds with a direct band gap of about 2.42 eV at 25 ^{o}C [2]. Thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cell and other optoelectronic devices. It is an ideal band gap high optical absorption, and relative ease of deposition have made CdS, especially attractive for preparation of thin film solar cells [3].It is used as a buffer layer present high electrical resistivity, high band energy and act as an optical window when they are deposited with certain thickness as a partner of CdTe [4]. Such as thin film FET, X-ray detector, photodiodes for solar meter, photo catalytical solar energy stocking [3].

Material and Methods

Cadmium sulfide thin films were prepared on glass substrate from aqueous solution containing cadmium chloride ($CdCl_2.H_2O$) and thiourea [$CS(NH_2)_2$] in concentration ratio of (0.1:0.1)M. The solution was sprayed as a fine mist at an angle of 90^{o} on to the preheated glass substrate kept at a distance of 29 cm from the spray nozzle. Prior to a deposition, the substrate was cleaned with acetone and double distillation water. Nitrogen (N_2) is used as a carrier gas with a pressure of 2.5 bar and the spray rate of the solution was maintained at 2 ml/mint. To avoid thermal shock and excessive cooling of the substrates, the spraying time is fixed as 9 sec with the time interval between successive spraying is maintained within 50 sec to control the substrate temperature and to ensure the complete evaporation of the residue of starting material. Substrate temperature was controlled by K-type thermocouple fed to a temperature controller with an accurate of ±2 ^{o}C. The system was kept in an aluminum and glass chamber, the chamber box is fitted with a fan to remove the toxic gases produced during the decomposition of the spray solution. The thickness of the films was determined by weight method, and kept constant for all the films for about (216±20) nm.

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The structure, composition, and morphological analysis of the films were studied by an X-ray diffract meter (6000 Shimadzu company) with Cu Ka radiation (λ = 1.540 A°) and a LeoSupra 50VP field emission scanning electron microscope. Optical measurements were carried out using Shimadzu UV-VIS mini 1240 spectrophotometer in the wavelength range (200-1100 nm). The current-voltage at dark- and photo of the samples were measured using two probes connected to (picometer, voltage source model Keithley 6487). A 117 W. m^{-2} tungsten–halogen lamp is used to illuminate the sample as show in Fig 1. Electrical contacts are made using thermal evaporation coating system type (JEE-4B/4C) the metal Al deposited on CdS films using thermal evaporation technique under a high vacuum. The as-prepared films are n-type, which is confirmed by the thermo-electric probe measurement.

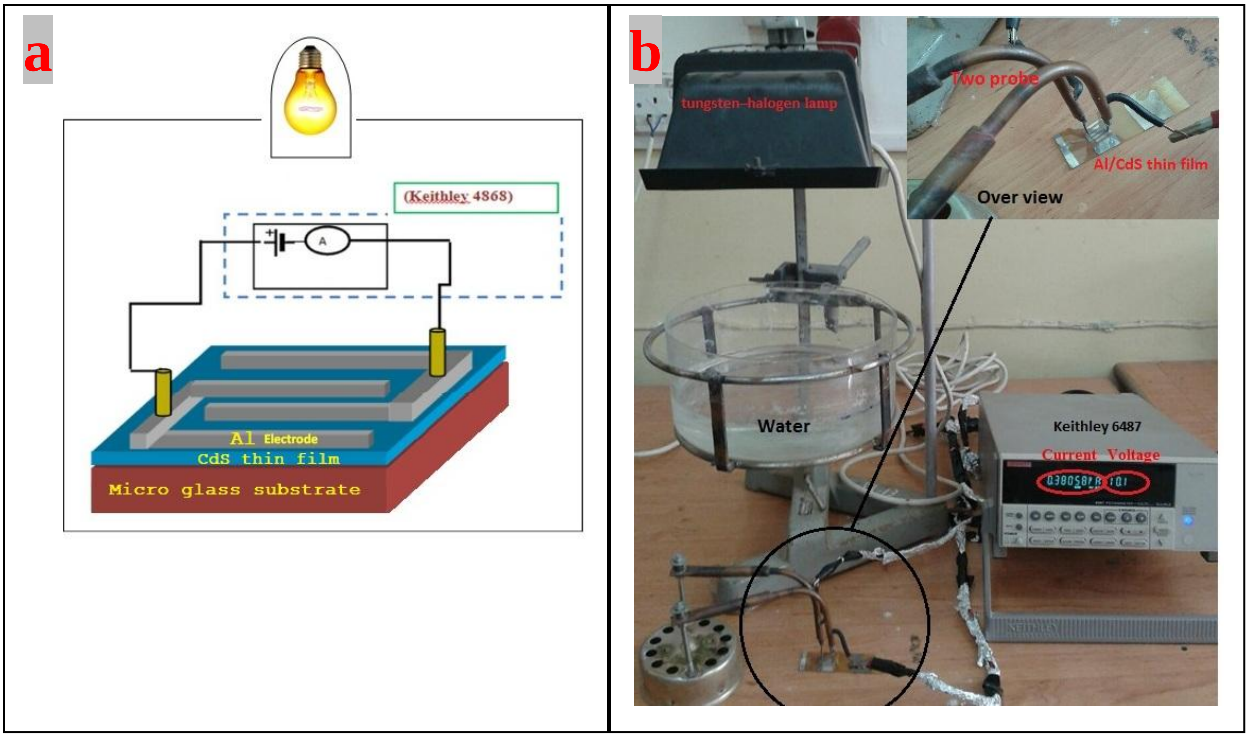


Figure 1. (a) Electric circuit for measurement dark and light I-V of Al-CdS device, (b) Photograph.

Results and Discussion

Structural Analysis

Figure 2. shows the X-ray diffraction (XRD) patterns of CdS thin films prepared at different substrate temperatures (250°C - 400°C).

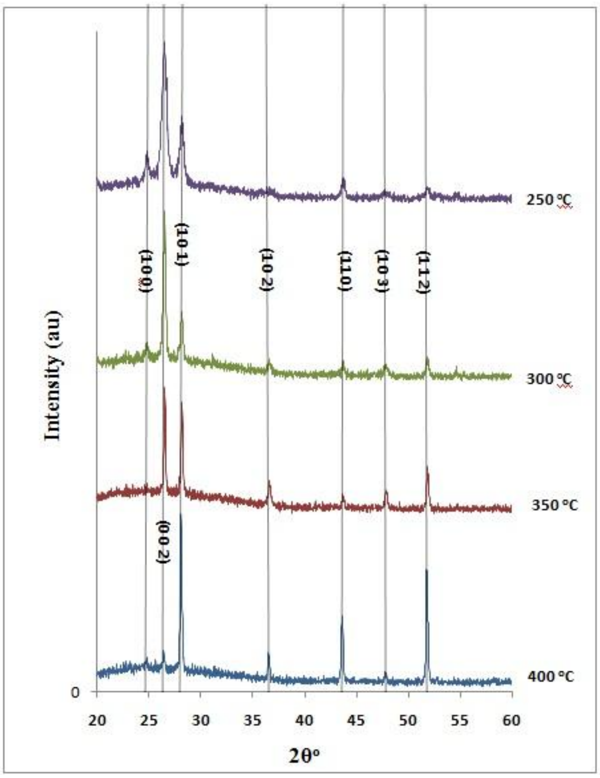


Figure 2. XRD patterns of CdS films deposited at different substrate temperatures.

The films deposited at low substrate temperatures 250 °C show poor crystalline and the dominate peak at a position 2θ = 26.49° with preferential orientation along (0 0 2) plane of the hexagonal CdS structure, with six other small peaks (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) matched with the Inorganic Crystal Structure Database (ICSD- Reference code: 03-065-3414, and 01-075-1545). An increase in the deposition temperature from (250 to 400) °C resulted in increase intensity of the most XRD peaks indicating an improvement of the film crystalline.

The lattice parameter, (a) and (c) of the unit cell in the hexagonal crystal structure was evaluated according to the relation [5]:

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2+kh+k^2}{a^2} + \frac{l^2}{c^2} \quad \text{……….. (3.1)}$$

Where **d** is inter planer spacing. The grain size of the crystallites (D) is calculated using the Scherrer formula [6]:

$$D = \frac{K\lambda}{B*\cos\theta} \quad \text{……………. (3.2)}$$

Where K is the shape factor equal to 0.9 for the unknown shape of grain size, **λ** is the wavelength of the x-ray used (1.5460A°), B is the full-width at half maximum of the peak which has maximum intensity and **θ** is the incident angle of X-ray. The results shown in the table I.

Table I. XRD results identify the determined structure parameters for dominating peak of CdS films deposited at different substrate temperatures.

T_s (°C)	Lattice constant (A°)	Gain size (nm)
250	a=4.1361 c=6.7240	13.96
300	a=4.1306 c=6.7810	30.28
350	a=4.1396 c=6.7100	47.49
400	a=4.1460 c=6.7503	47.02

Generally, the increase of the deposition temperature from 250 °C to 400 °C leads to narrower diffraction peaks as seen in the FWHM values which decrease for the most peaks, indicating better crystalline and subsequently increase in the crystallite size as shown in Figure 3.

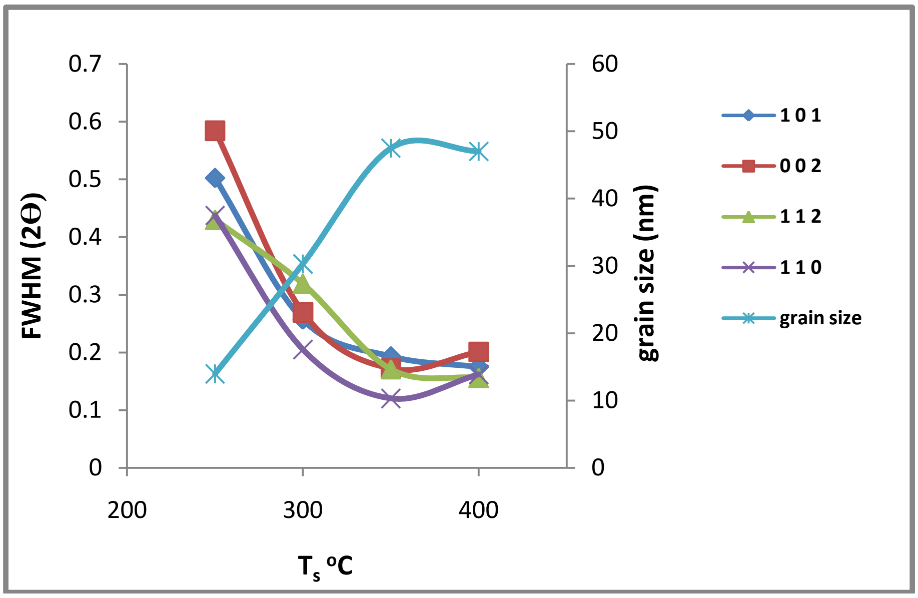
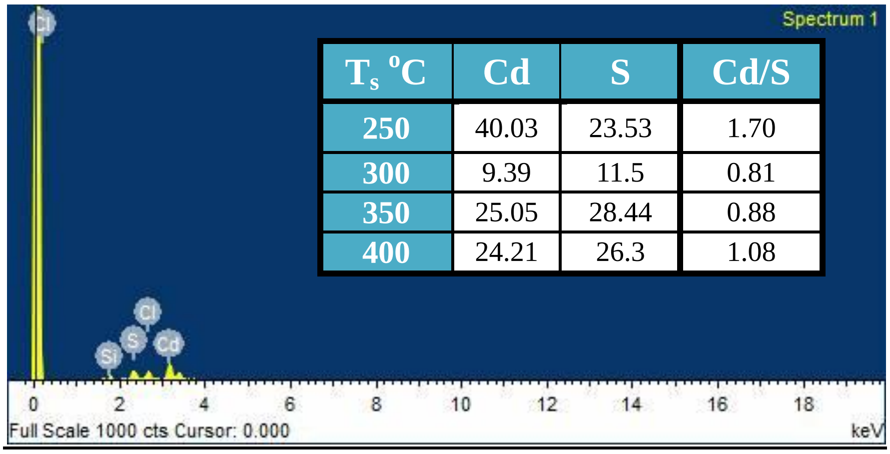


Figure 3. FWHM and Grain size for strongest peak of CdS films deposited at different substrate temperature.

Compositional analysis

For the compositional characteristics, (EDX) analysis was done on each of the prepared CdS thin films, EDX spectrum of CdS thin film prepared at the substrate temperature 250 °C has been shown in Fig 4.



T_s °C	Cd	S	Cd/S
250	40.03	23.53	1.70
300	9.39	11.5	0.81
350	25.05	28.44	0.88
400	24.21	26.3	1.08

Figure 4. EDX spectrum of CdS film deposited at substrate temperature 250 °C.

The table inset in the Fig. (4) gives the elements present in the CdS thin films prepared at a different substrate temperature. The EDX result revealed that the films are nearly stoichometric, and the better stoichometric was observed at higher substrate temperature 350, and 400 °C.

Morphology analysis

The surface morphology of the samples examined by using SEM showed noticeable changes in morphology of films, when the substrate temperature was changed from 250 °C to 350 °C. It is evident from SEM image shown in Fig. (5, a), that for the sample prepared at T_s = 250 °C the surface was smooth and no clear particulate morphology is found on the surface indicated the poor crystal structure, while Fig. (5,b) shows that the sample prepared at substrate temperature 350 °C, had a spherical grains indicated polycrystalline growth of the films.

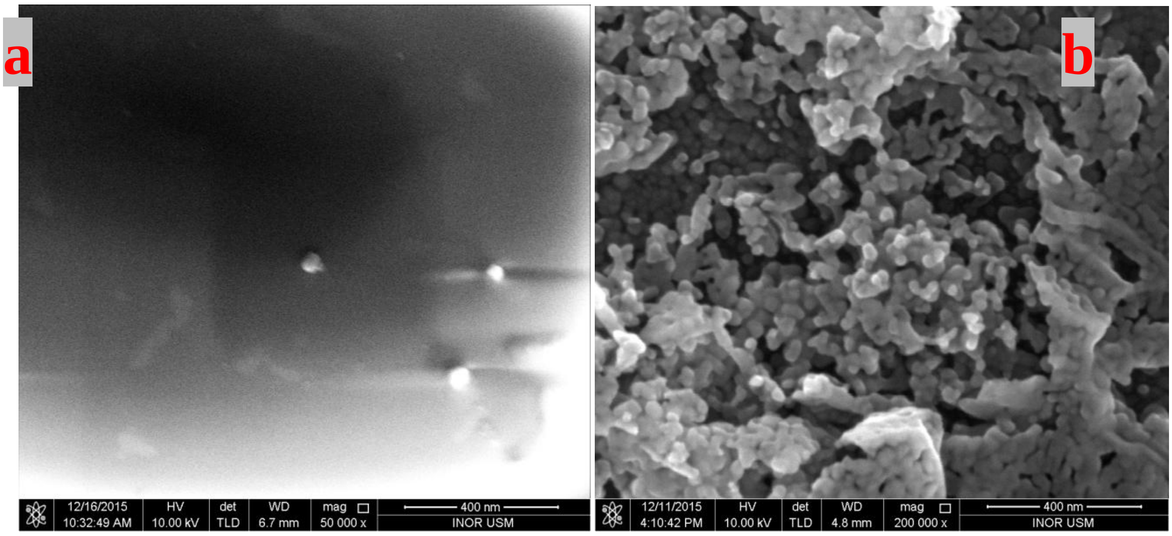


Figure 5. SEM image of CdS thin films at (200 000)x magnification prepared at substrate temperature a) 250 °C b) 350 °C.

Optical properties

The optical transmittance and absorbance spectra of CdS thin films prepared at different substrate temperatures were measured at room temperature in the wavelength range of (200-1100) nm, as shown in Fig (6).

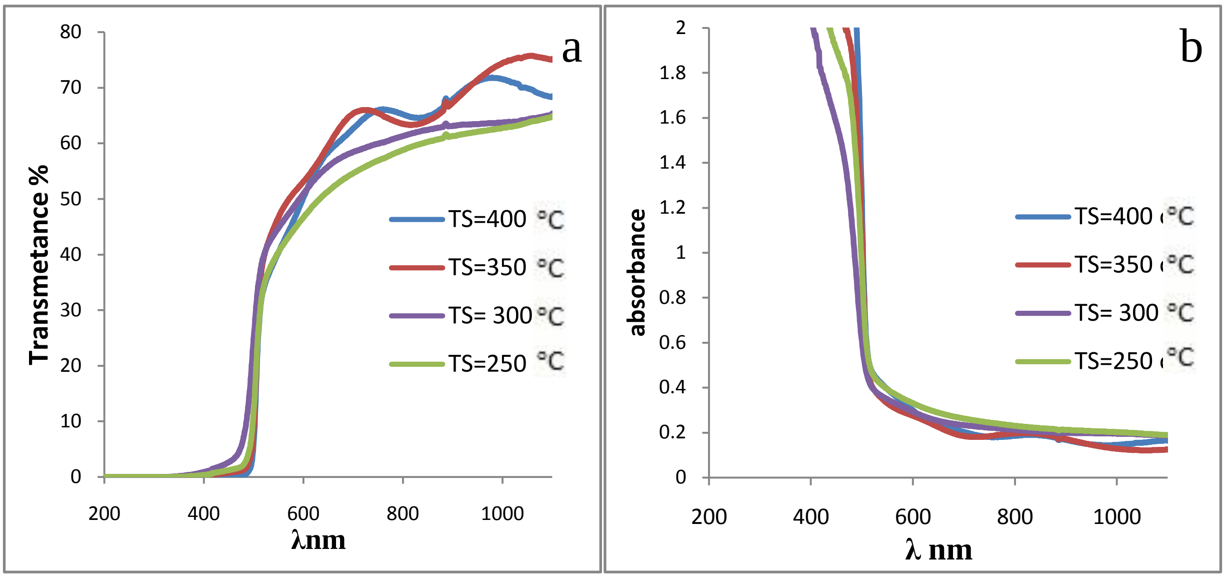


Figure 6. a) Transmittance, and b) absorbance spectrum as a function of wavelength for different substrate temperature.

It can be observed that, in general, the percentage of optical transmission increase with increase the substrate temperature in the low absorption region, this is attributed to improvement in the perfection and stoichometery of the films. The sharp decrease in the optical transmission at shorter wavelengths resulted from the excitation of the charge carriers across the optical band gap. From absorbance spectra it was observed that all films have low absorbance in the visible-near infrared region; however observance is high in the ultraviolet region. The following steps can be used to calculate the optical energy band gap:

The absorption coefficient α was estimated from the absorbance spectrum (**A**) using the formula [7]:

$$\boldsymbol{\alpha = 2.303(\frac{A}{t})} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

Where (t) is the thickness of the thin film.

The photon energy (hν) as a function of wavelength can be calculated by [8]:

$$\boldsymbol{h\nu(eV) = \frac{1240}{\lambda(nm)}} \quad \ldots\ldots\ldots\ \ldots\ldots\ldots\ldots\ldots \text{(3.4)}$$

Where (λ) is the wavelength of the incident light.

The general band gap formula is given as [9]:

$$\alpha(h\nu) = B\,(h\nu - Eg)^{\gamma} \ldots\ldots\ldots\ldots\ldots\ldots\text{(3.5)}$$

Where B is an energy-independent proportionality constant, and γ = 1/2, 3/2, 2, 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions respectively. Eg is the optical band gap energy.

The optical band gap energy (Eg) can be obtained by extrapolating the linear portion of $[\alpha(h\nu)]^2$ vs. photon energy (hν) curve to zero absorption [9].

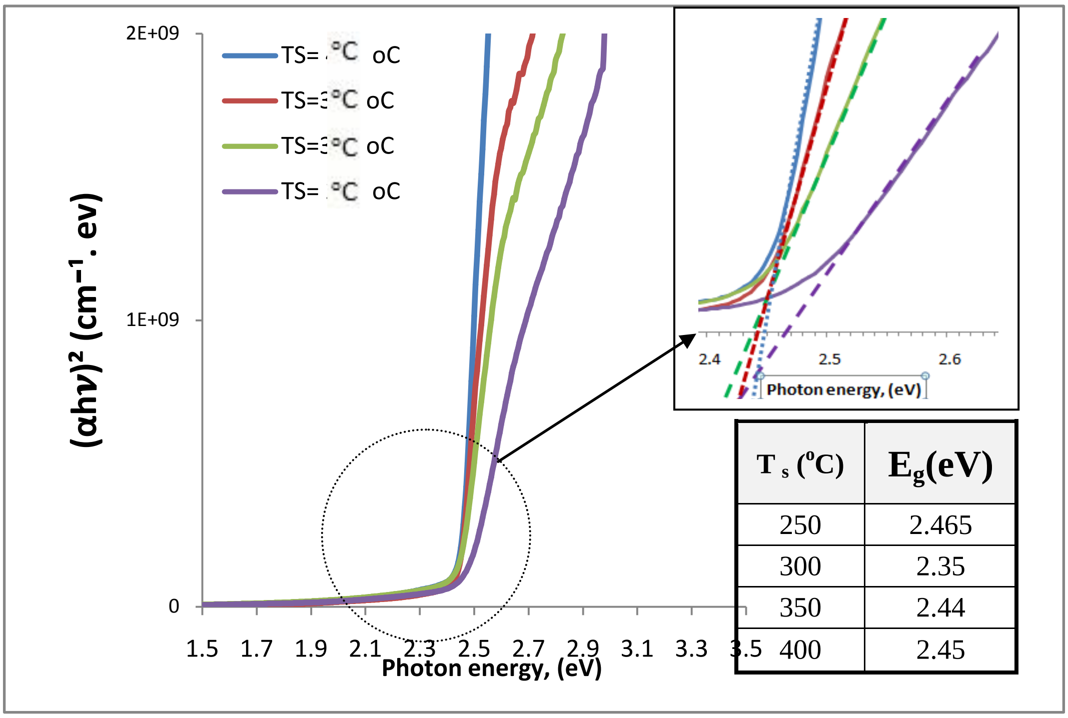


Figure 7. Variation of $(\alpha h\nu)^2$ with photon energy for CdS thin films at three different substrate temperature.

The linearity of the plots near the absorption edge indicates that CdS is a direct band gap nature. From the table inset in the Fig. (7), it is observed that the determined band gap values decreased with increasing of substrate temperature, and then the value of the band gap started to increase for the film prepared at high substrate temperature. The large band gap values may be due to the poor crystalline of the films prepared at a substrate temperature 250 ^{o}C, while the lower band gap values for the film prepared at high substrate temperature of 350 ^{o}C indicated that the film is polycrystalline in nature [10].

Ohmic contact

The current - voltage characteristic was carried out to investigate the electrical properties of the Al-CdS contact. In electronics, the relation between the d.c. current through an electronic device and the d.c. voltage across its terminals is called a current-voltage characteristic of the device. Fig. (8) shows the relation between the current and the voltage of Al-CdS contact for CdS films deposited at different substrate temperature are linear in both directions, and its coefficient of determination, equal to $R^2 \geq 0.99$ indicated that it has an excellent Ohmic behavior for all CdS films [12]. The measurement was performed in the dark and at room temperature under the sweep of voltage from (-10 to +10) voltage.

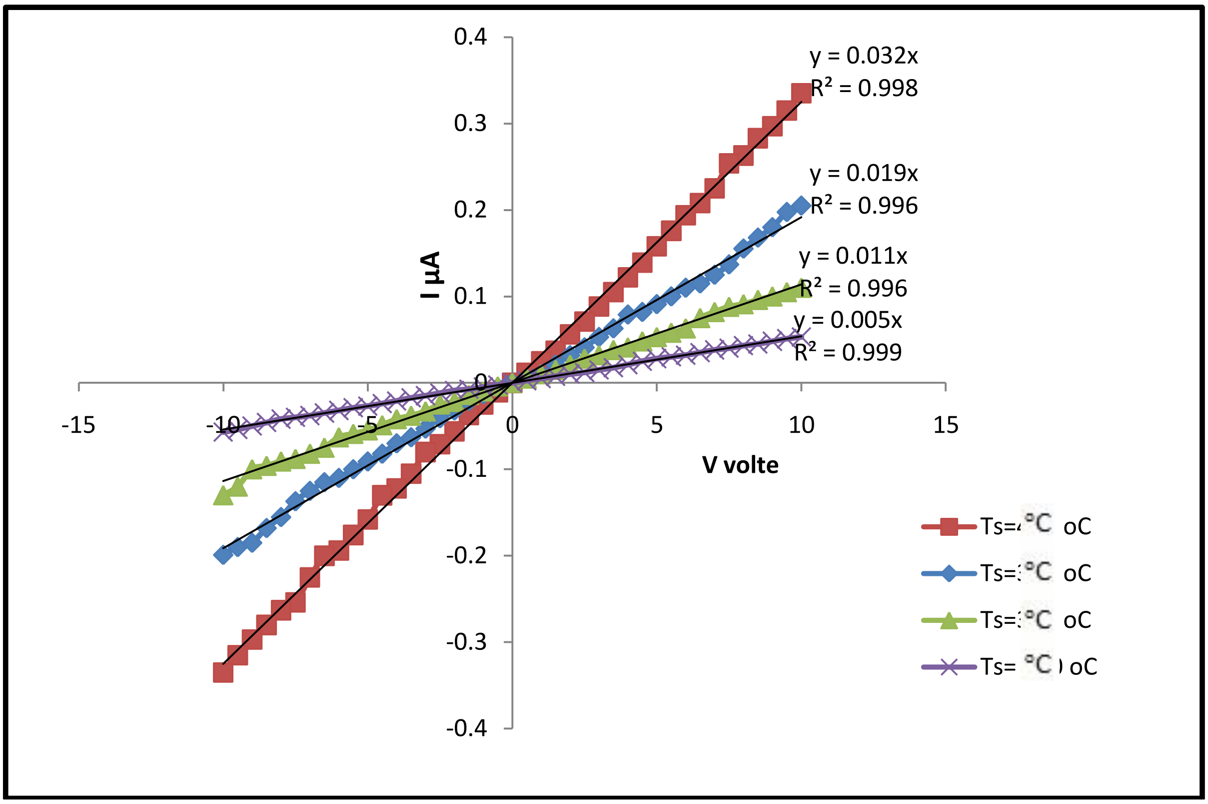
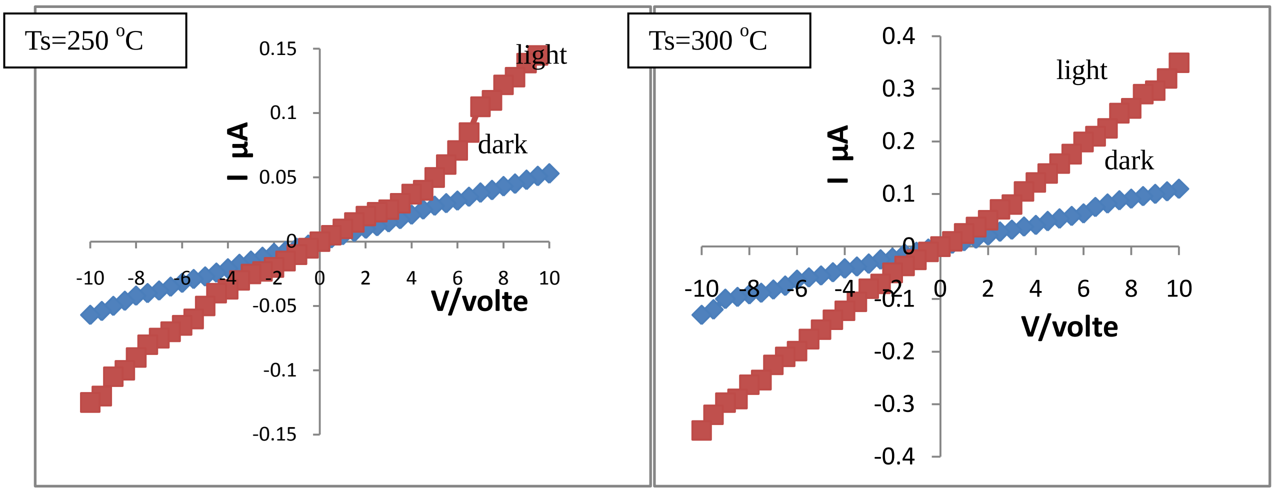


Figure 8. I-V characteristic of Al-CdS contact for CdS films deposited at different substrate temperature at dark and at room temperature

Photo detectors

Photodetectors are basically semiconductor devices that convert the incident optical signal into an electrical signal which is usually revealed as photocurrent. The photodetectors can detect the optical signals over a range of the electromagnetic spectrum that is usually predominantly defined based on the material properties [12].

Figure 9 shows I-V curves of Al-CdS device for CdS deposited at different temperature measure under a 117W.m^{-2} tungsten–halogen lamp with that of the dark current at the bias voltage (-10V to +10V). Under the bias voltage of +5V, the dark current and photocurrent of the Al-CdS for CdS growth at different substrate temperature equal to (0.028μA, and 0.05μA for T_s=250°C), (0.053μA, and 0.158μA for Ts=300°C), (0.091μA, and 2.2μA for Ts=350°C), and (0.159μA, and 3.42μA for Ts=400°C), respectively. Its appear that the photocurrent about (2, 3, 24, 22) time larger than dark current at T_s=250, 300, 350, and 400 °C, respectively.



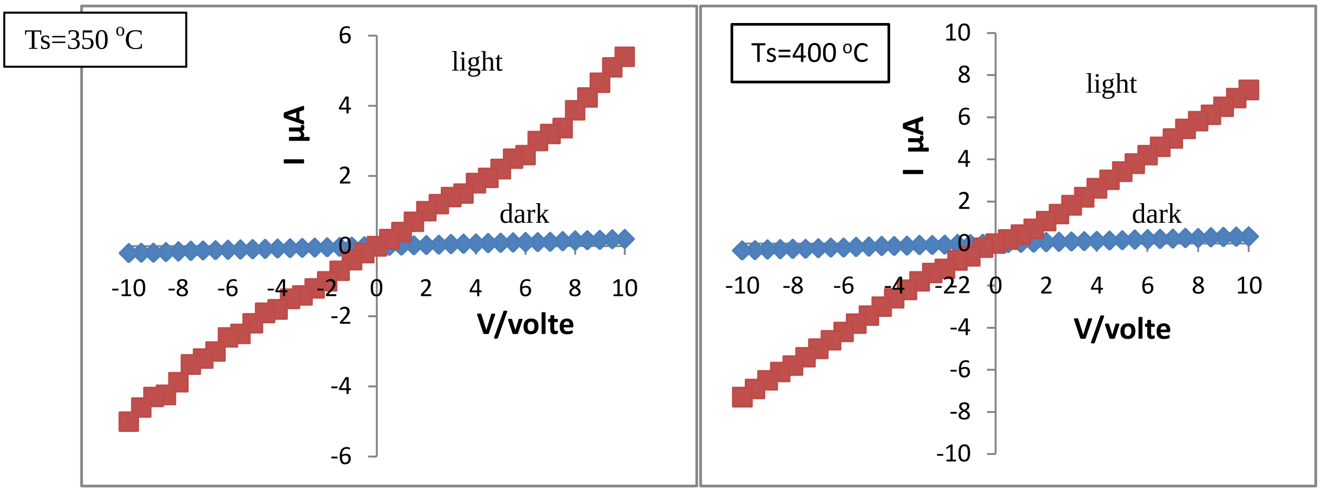


Figure 9. Forward and reveres bias Dark and light I-V characteristics of Al-CdS device for CdS films deposited at different substrate temperature**.**

Details the Parameter, sensitivity and responsivity are as follows;

Sensitivity (S):

The sensitivity of the photodetector based is obtained by using the equation [13, 14]:

$$S=I_{ph}/I_{dark}$$

Where, $I_{ph}= I_{light}-I_{dark}$

Figure 10. Shows the forward bias photo sensitivity for Al-CdS under a voltage range (0-10) V.

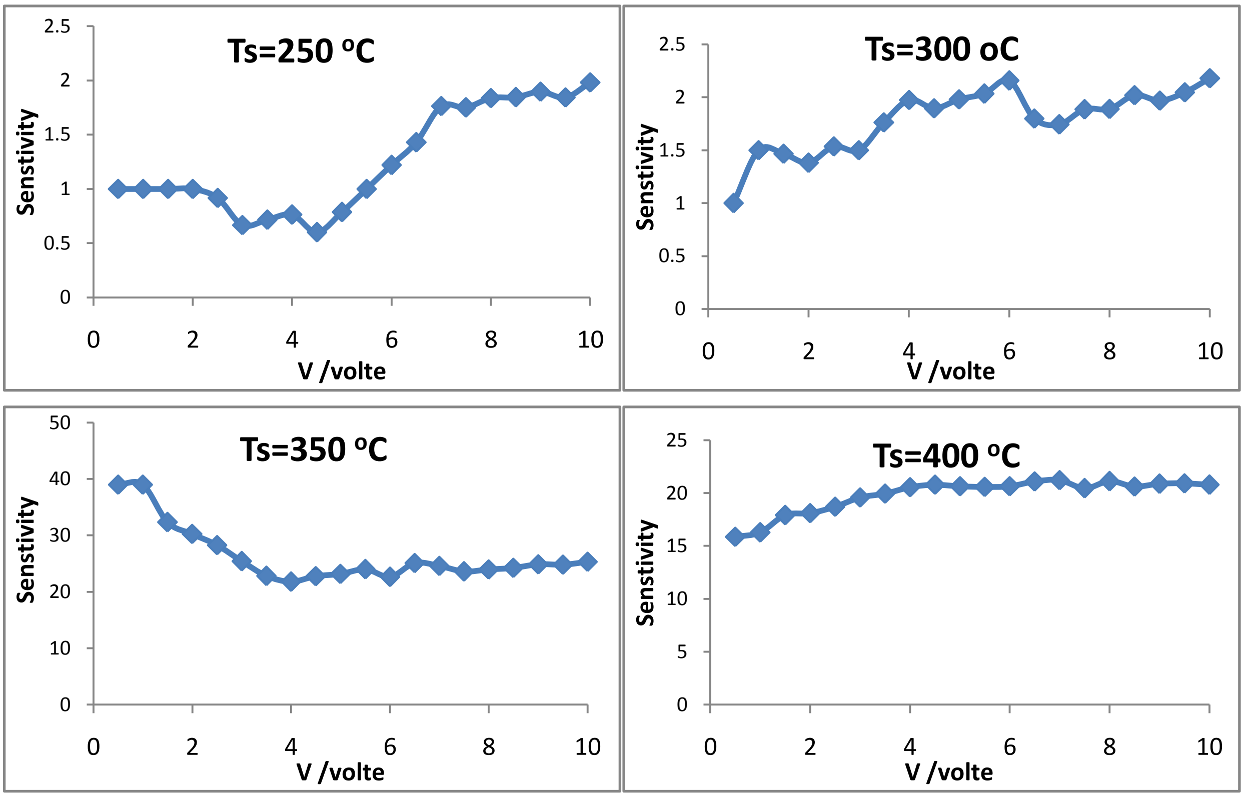


Figure 10. Sensitivity of CdS thin film prepared at different substrate temperature as a function of applied voltage under light illumination.

Responsivity ($\Re$):

It is an important parameter that is usually specified by the manufacturer. The responsivity of a photodetector is defined as the ratio of the output current to the optical power input and is quoted in amperes per watt (A/W). Therefore, responsivity is the measure of effectiveness of the detector for converting electromagnetic radiation to the electrical current. The responsivity depends on wavelength, bias voltage, and temperature. This is the most important characteristic when considering the biasing of the detector, then $\Re$ is [15];

$$\Re = \frac{I_{ph}}{P_{op}}$$

Where P_{op} is the absorbed power by (active material). Table (II) shows the calculated sensitivity and responsivity of Al-CdS device for CdS films deposited at different substrate temperature with their bias voltages. It was observed that the photo sensitivity of Al-CdS device increase as the substrate temperature increase, this increase may be attributed to the growth of the grain size and the improvement in the film stoichiometry.

Table II. Sensitivity and Responsivity of CdS photo detector deposited at different substrate temperature.

Al-CdS				
Ts °C	**Voltage**	**Sensitivity**	**Responsivity (A/W)**	**Reference**
250	1,5,10	1, 0.78, 1.98	1.19*10^(-6), 5.23*10^(-6), 0.25*10^(-4)	**This work**
300	1,5,10	1.5, 1.98, 2.18	3.57*10^(-6),0.25*10^(-4), 5.7*10^(-5)	**This work**
350	1,5,10	39,23.17, 25.34	9.2*10^(-5), 5.02*10^(-4), 1.23*10^(-3)	**This work**
400	1,5,10	16.28, 20.64,20.79	9.6*10^(-5), 0.77*10^(-3), 1.65*10^(-3)	**This work**

Conclusion

Role of substrate temperatures on CdS thin films were studied successfully by spray pyrolysis technique. XRD studies showed that the sharpness of the peaks were a function of substrate temperatures and suggested that as deposited CdS films were crystalline in nature. The optical prosperities showed films were smooth, free from pin hole with around 70% transmittance. The optical band gap varied in the range of 2.435 - 2.465 eV due to change in grain size with respect to substrate temperatures. The electrical studies revealed that the sensitivity and responsivity of Al-CdS device increases with substrate temperatures. Finally, it is concluded that 350°C found to be the optimum temperature to prepare CdS film by spray pyrolysis technique.

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