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The Effect of Thermal Annealing Processes on Characterization of Al/CdS/Si/Al Heterojunction

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***Abstract*—Cadmium sulphide (CdS) nano-particles have been successfully synthesized by a Thermal Evaporation Technique . CdS thin films having around 100 nm thickness annelid at (200 and 300) °C which deposited on glass substrates. The study of X-ray diffraction investigated all the exhibit polycrystalline nature .Thin film's internal structure topographical and optical properties. Furthermore, the crystallization directions of CdS (002) can be clearly observed through an X-ray diffraction analysis XRD, Atomic Force Microscope AFM (topographic image) showed that the surface Characteristics , thin films crystals grew with increases in either the annealing temperature, also , the grain size increased in range from 88.4 nm to 96.5 nm. The optical properties concerning the absorption and transmission spectra were studied for the prepared thin films. UV-Vis measurement spectra showed that Vis transmittance intensity decreased with increases annealing temperature, the energy band gap decreased from (2.2 to 2.4) eV when the annealing temperature. Heterojunction character-rization showed that the films are semiconducting and can be used in solar cell devices.**

Keywords—Thermal Annealing, XRD, SEM, Heterojunction,AFM, crystalline size,I-V,C-V

1. Introduction

In the recent years, II-VI semiconductor materials have been under intense research due to their exciting , unique properties, which are absent in bulk materials since thin films have a wide number of surface atoms than that of bulk [1-4]. In such nano-regime, nanoclusters with imperfect surfaces have interesting effects is a major challenge among the researchers. It is feasible to design materials of required optical, chemical and magnetic properties by controlling the surface and size effect, such as enhancement of photo catalytic properties and quantum size effects of the nanoparticles with decreasing crystallite size [5]. A semiconductor crystallite with an exciton Bohr diameter exhibits a blue shift in the exciton energy, which is the so-called quantum size effect [6]. It is explained that the continuous energy band of the bulk crystal transforms into a series of discrete energy states resulting in the broadening of the band gap due to the finite size of the nanocrystals. Among II-VI compounds, Cadmium sulphide (CdS) with a direct band gap, Eg=2.40 eV, is an important semiconductor with nonlinear optical properties have been extensively studied and has potential applications such as solar battery, photoelectrocatalysis, Biolog-ical sensors and photodiodes [7-11].

2.Experimental

Cadmium sulphide thin films of thickness (100 nm± 5) were deposited with rate deposition 48 nm/s at R.T and then annealed at 200°C and 300°C on chemically and ultrasonically cleaned glass substrates with the high Vacuum Coating unit at a vacuum about10^{-5}torr. The distance between source and substrate was maintained at 6.5 cm for the cases. The prepared films were annealed in vacuum at elevated temperature for 2 hours. Optical transmittance measurements for the film were carried out using UV/Vis double beam spectro-photometer (Schimadzu, 160Å, Japan Company) in the wavelength range (300-800 nm). (XRD) patterns were obtained with automatic Diffract meter using the CuKα radiations (λ=1.54059 Å) in the range of 2θ between 10° and 80° .Atomic force microscopy (AFM) measurements were carried out using (SPM model AA 3000 Angstrom Advanced Lns., USA) to determine the nanocrystalline topography and grain size of the films Cary 100 Conc plus UV-Vis spectrophotometer.

3. Results and discussion

The crystalline size and crystal structure of the Cadmium sulphide (CdS) nanocrystalline thin films were determined from X-ray diffraction pattern. CdS known to exist in either cubic or hexagonal structure or sometimes a mixture of both phases [3, 13, 14]. Figure 1 shows X-ray diffraction pattern of CdS thin films deposited on glass coated glass substrate. The XRD peaks indicate that the film is nanocrystalline in nature. The peak of Cadmium sulphide at 26.5^{o} corresponds to CdS because of the glass substrate used and corresponding to the (0 0 2) reflections of the CdS possessing hexagonal crystal structure, with lattice parameters of a = 4.15 Å and c = 6.58 Å,which agrees with standard pattern (JCPDS card no. 41-1049). Thus , from XRD studies, it is clear that Cadmium sulphide (CdS) is a mixture of cubic and hexagonal phases, which agrees with the earlier report for Cadmium sulphide (CdS) thin film [12].

The average crystallite size (D) was estimated using Scherrer formula [13];

$$D = \frac{K\lambda}{\beta\ COS\ (\theta)} \qquad (1)$$

Where K is the shape factor that was taken equal to 0.9, λ is the wavelength of X-ray source, β is the full width at half maximum (FWHM) of (002) peak corresponding to hexagonal phase of Cadmium sulphide and θ is the Bragg's diffraction angle in degrees. The average crystallite size is found to be 36 nm. The microstrain value 'ε' and the dislocation density 'σ' can be evaluated by using the following relations [13, 14]:

$$\varepsilon = \frac{\beta\cos(\theta)}{4} \qquad (2)$$

$$\sigma = \frac{1}{D^2} \qquad (3)$$

The strain and dislocation density of CdS thin films chemical reaction were around 8.5×10^{-4} ($lines^{-2}.m^{-4}$) and 7×10^{14} ($1ines/m^2$) respectively as shown at Table 1:

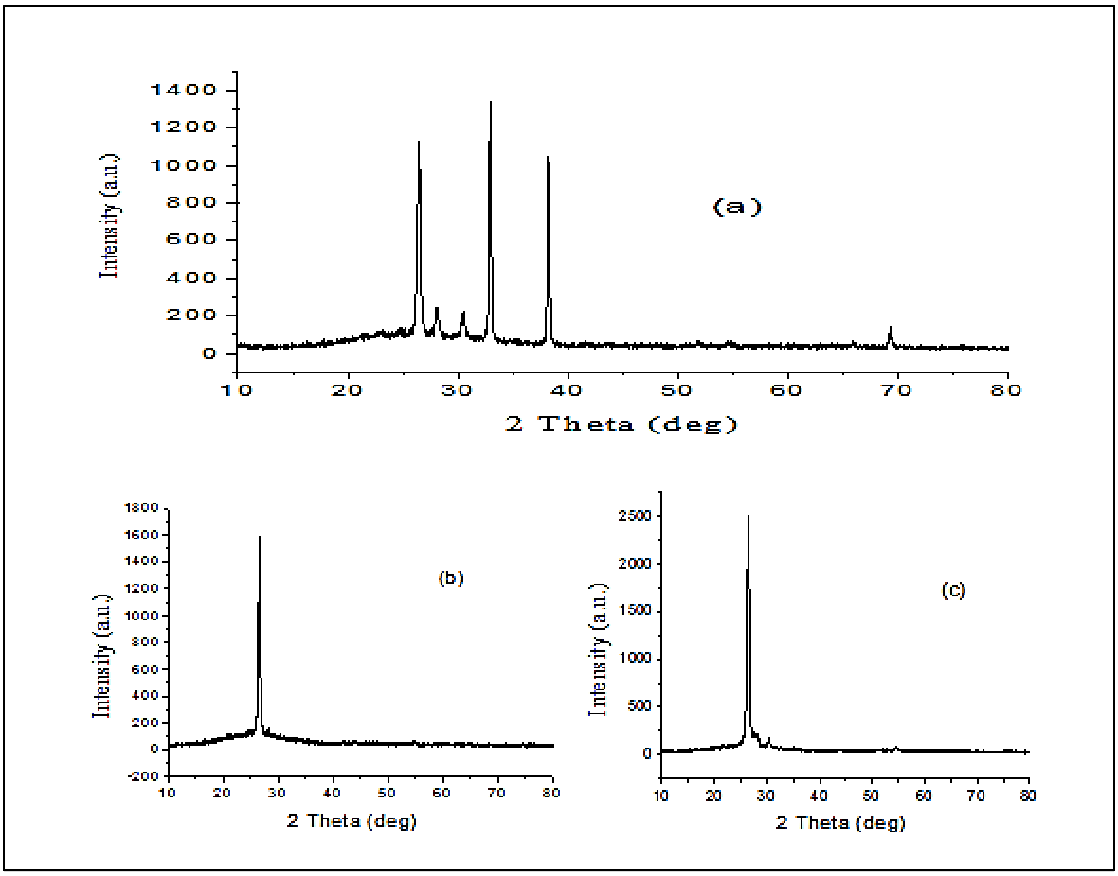

Fig. 1 X-ray diffraction (XRD) pattern of CdS thin film deposited on glass a)as-prepared at different annealing temperature: a)as-prepared ,b) 100 °C , c)200 °C .

Table 1. Powder X-ray diffraction data of CdS.

CdS Thin films	2 Theta (deg)	β (deg)	D (nm)	$\delta \times 10^{14}$ (lines.m^{-2})	$\eta \times 10^{-4}$ (lines^{-2}.m^{-4})
As-prepared	32.90	0.17	46.85	04.55	7.39
	38.19	0.18	46.47	04.63	7.45
	26.41	0.29	27.14	13.56	12.76
100 °C	26.53	0.35	22.59	19.59	15.33
	27.14	0.23	35.34	08.00	9.80
200 °C	26.50	0.20	40.59	6.06	8.53

Figure 2 shows SEM images of CdS thin films which deposited on glass substrates and annealed at 100 °C and 200 °C . SEM images confirmed that these NPs have different morphology, it can reveal that the morphology of Cadmium sulphide thin films is not uniform and consists of many small irregular nanoparticles with average size ranging from 80 nm to 100 nm depending on annealing temperature.

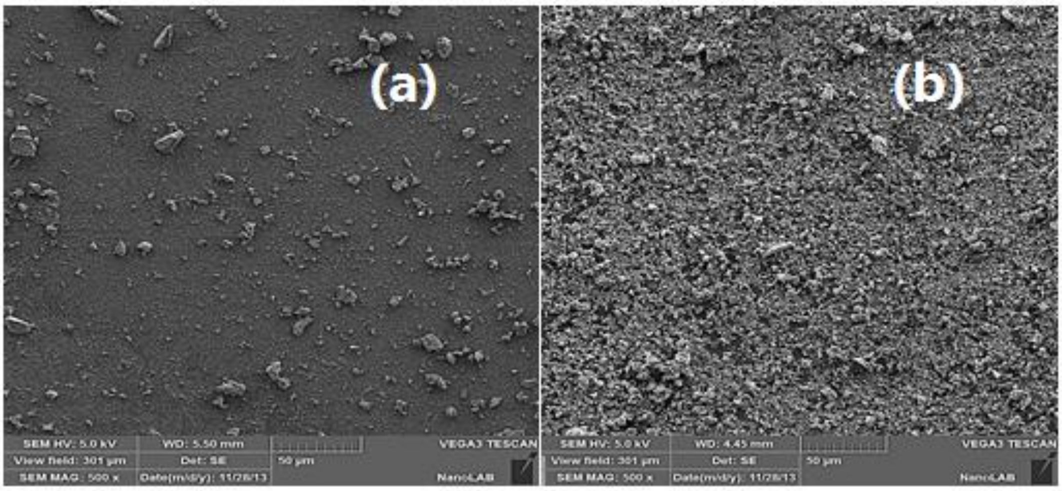

Fig. (2) SEM images of CdS thin films deposited at a) 100 ^oC and b) 200^oC

Figure 3 shows 3D AFM image of CdS thin films prepared at different annealing temperature . The surface of the substrate is well covered with Cadmium sulphide (CdS NPs) nanoparticles; distributed uniformly on the surface. It is obvious from this figure that the nanoparticles have small ordered particles with semispherical shape with the existence of some monopod rods. The average particle size of Cadmium sulphide estimated with the aid of software was about 90 nm. The value of particle size is higher than that calculated from XRD analysis. This is because XRD depends on the size-defect free volume, while AFM directly visualizes the grain without taking into account the degree of crystal defects [15].The formation of larger particles can be attributed to aggregation of small particles [16]. Higher annealing temperatures resulted in the formation of elongated particles indicating the presence of multi-armed structures.

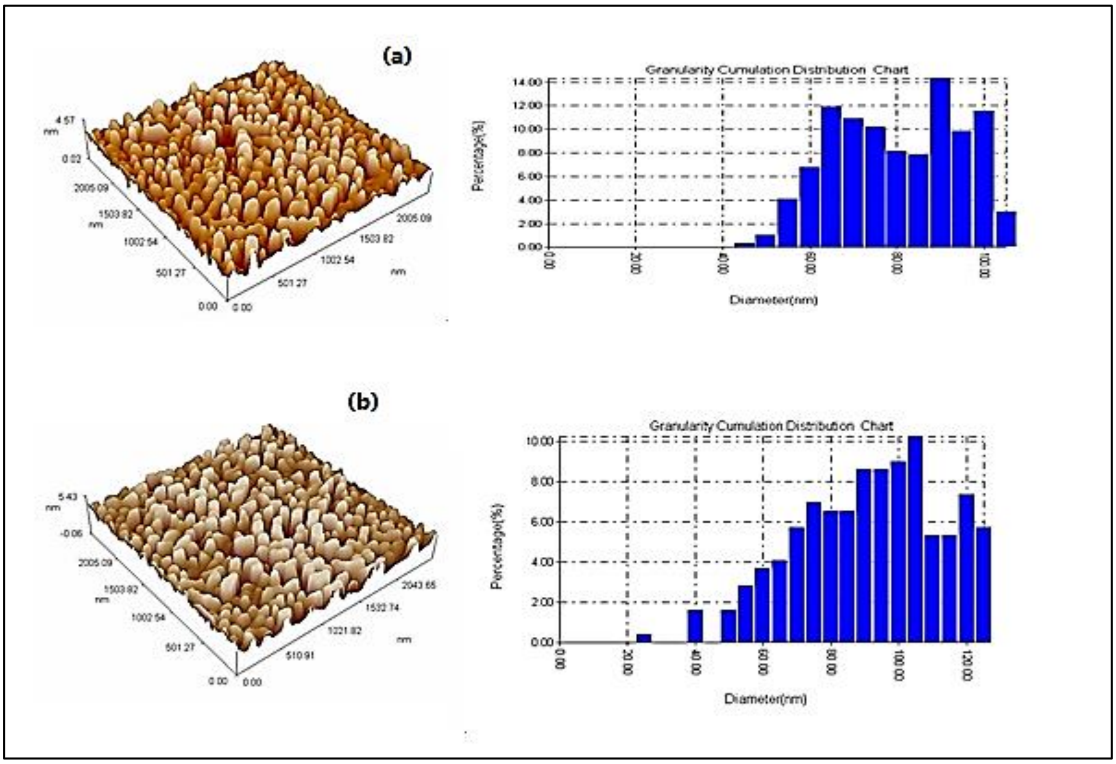

Fig. 3. 3D, 2D AFM images and Granularity accumulation distribution chart of CdS thin films with a) 100 ^{o}C and b) 200 ^{o}C annealing temperatures .

Table (2): Average grain, Roughness density and RMS of thin films which prepared at different annealing temp.

CdS Thin films at annealing temperatures	Average grain size (nm)	Roughness density (nm)	RMS (nm)
100 ^{o}C	88.4	1.1	1.37
200 ^{o}C	96.5	0.57	0.68

The transmittance spectrum of samples is taken by UV-VIS Double Beam Spectrophotometer Version 6.51 in the wavelength range 300-800 nm. The UV spectra of the material provide important information about the details related with optical band. Figure 4a shows the wavelength dependence transmittance of the films of bulk and thin films material Cadmium sulphide in the wavelength range 300nm-900nm. The optical transmittance of the film formed at 100 ^{o}C was about 2 % at wavelength ≈ below 470 nm then decreases to 20% transmittance at wavelength 700 nm and for thin film of CdS at 100 ^{o}C annealing temperature . The optical transmittance increases from 100 ^{o}C to 200 ^{o}C CdS thin films.The optical absorption coeffi-cient (α) was evaluated by Tauc relation [17]:

$$\alpha h\nu = C\left(h\nu - E_g\right)^n \qquad (4)$$

where α is constant called absorption coefficient $(\alpha = \frac{2.303\,A}{t})$, t is the film thickness, $h\nu$ is the photon energy , E_g is the band gap and n= 0.5 for allowed direct transition.Fig.4a. Transmittance Spectra of Bulk & nano CdS thin films

Fig.4b Plot between $(\alpha h\nu)^2$ and hν for different deposition conditions for band gap measurement.

Plotting the graph between $(\alpha h v)^2$ versus photon energy hv gives the value of direct band gap. The extrapolation of the straight line to$(\alpha h v)^2 = 0$, gives the value of band gap, shown in Figure 4b. From the UV spectra, it is clear that the absorbance decreases with increase in wavelength. This increase in transmittance indicates the presence of optical band gap in the material. The optical band gap of the films increases from 2.3eV to 2.42 eV from Cadmium sulphide thin films. The difference in the optical band values achieved was mainly due to the difference in the deposition techniques employed and the process parameter maintained during the growth of the films.The refractive of the film has been calculated by knowing reflectance that can be determine by formula [18]:

$$n = \frac{1 + R^{1/2}}{1 - R^{1/2}} \qquad (5)$$

Where, R is the normal reflectance.

Using this relation refractive index n can be determined by the formula

Fig.4d shows the variation in the refractive index with the incident wavelength. The refractive index of the bulk Cadmium sulphide thin film initially increases with increase in photon energy to 2.48 eV (≈ 500nm) after that it decreases with increase in photon energy due to increase in reflectance. The refractive index of Cadmium sulphide thin film deposited at 200 °C increases exponentially with increase in photon energy, whereas the refractive index of the CdS thin film deposited at (100 and 200) °C initially decreases then increases and finally decreases with increase up 500 nm wavelength due to change in reflectance of the film.

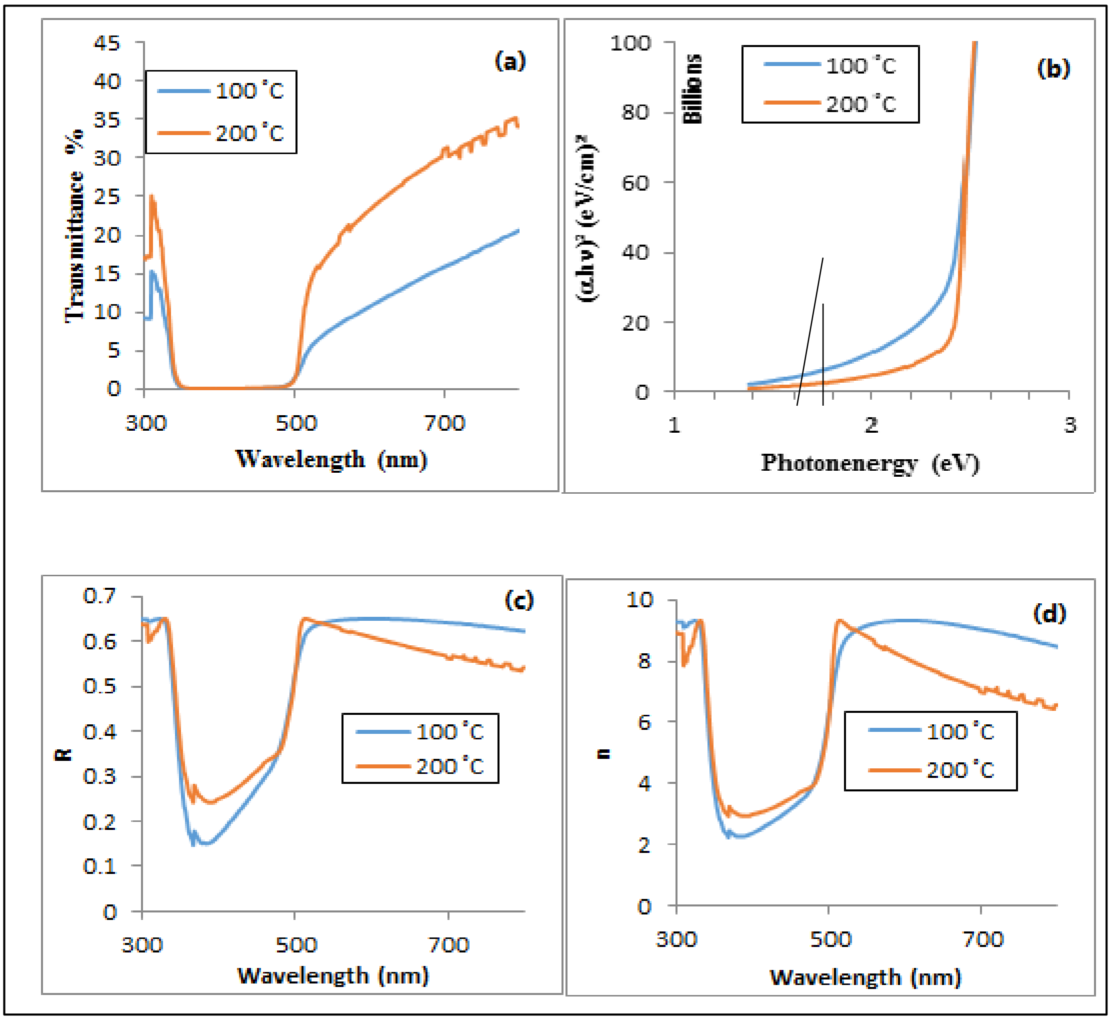

Fig.(4) a: Transmittance Spectra of Cadmium sulphide thin films .b: Plot between $(\alpha hv)^2$ and hv for different deposition conditions for band gap. c: Reflectance Spectra CdS Thin films. d: Change in Refractive Index with wavelength of Cadmium sulphide thin films.

Figure 5 shows the I-V dark characteristics in forward and reverse direction of Al/CdS/p-Si/Al Heterojunction prepared with different annealing temperatures . The forward current of Photodetector is very small at voltages less than 2 V. This current is known as *recombination current* which occurs at low voltages only. It is generated when each electron excited form valence band to conductive band. The second region at high voltage represented the diffusion or bending region, which depending on serried resistance .In this region; the bias voltage can deliver electrons with enough energy to penetrate the barrier between the two sides of the junction.

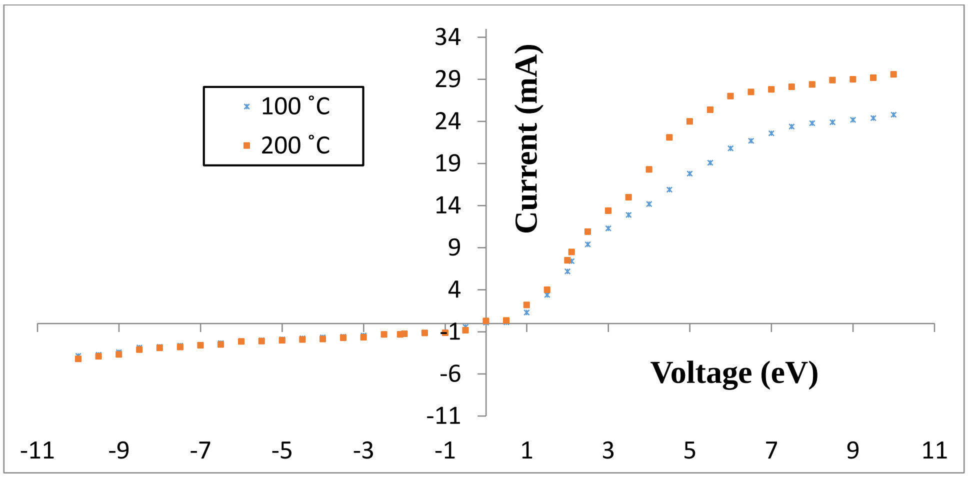

Fig.5 : I-V characteristic under forward reverse bias of the CdS/ p-Si.

Figure 6 shows that the variation of ln (I_f) with a bias voltage of CdS/ p-Si heterojunction prepared with different annealing temperatures . The ideality factors of heterojunctions are estimated Ideality factor was found to be around 2.1 for CdS/p-Si hetrojunction at 100 ^oC and 1.9 at 200 ^oC depending annealing temperatures . When the structure has a series resistance and interface states, ideality factor becomes higher than unity; most practical Schottky diodes shows deviation from the ideal the moronic theory. The fact that such recombination currents are flowing not homogeneously in the structure, but always at local sites.

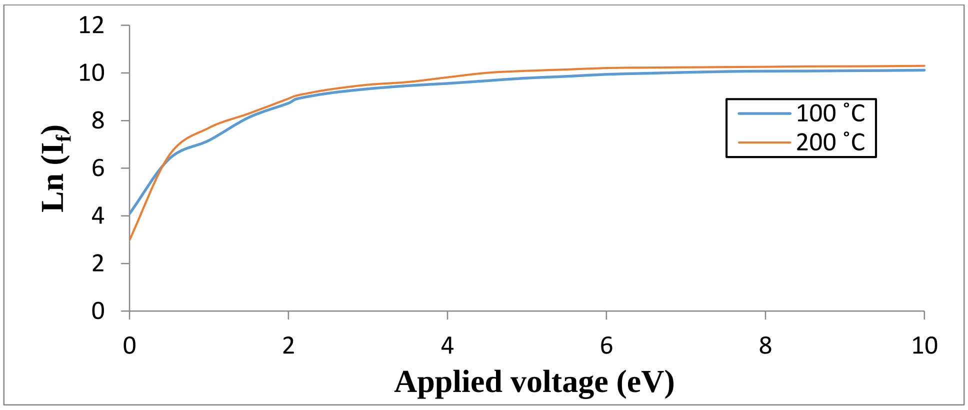

Fig.6 : Variation of ln (Ip) with bias voltage of CdS/p -Si heterojunction.

From the figure 7 which shown the relation between current (l) and applied voltage (v), that the value of current value Al/CdS/Si/Al thin film with 200 ^oC annealing temperature higher than that value of CdS/Si thin film with 100 ^oC due to defects. It can be noticed that the forward dark current is generated due to the flow of majority carriers and the applied voltage injects majority carriers that leads to the decrease of the build-in potential in addition to the reduced of the depletion layer.

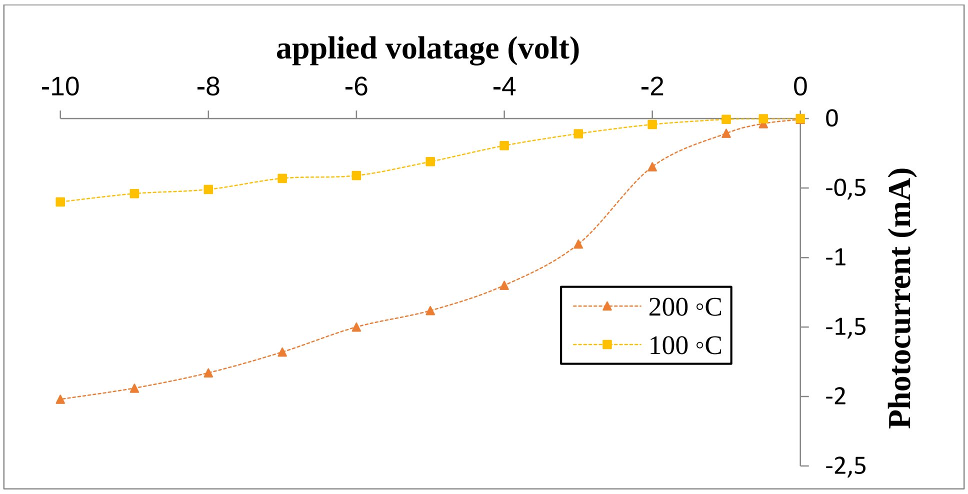

Fig.7: illuminated (I-V) characteristic of Al/CdS/ Si/Al thin films at different annealing temperature.

Figure 8 shows that a linear relationship between $1/C^2$ and reverse bias voltage was obtained for the structure. The values of the built-in potential have been obtained and it has been found 1.1 volt at 100 °C and 0.6 volt at 200 °C depending on the annealing tempreature. It represents the energy required by the electron to transfer from the CdS to Si .

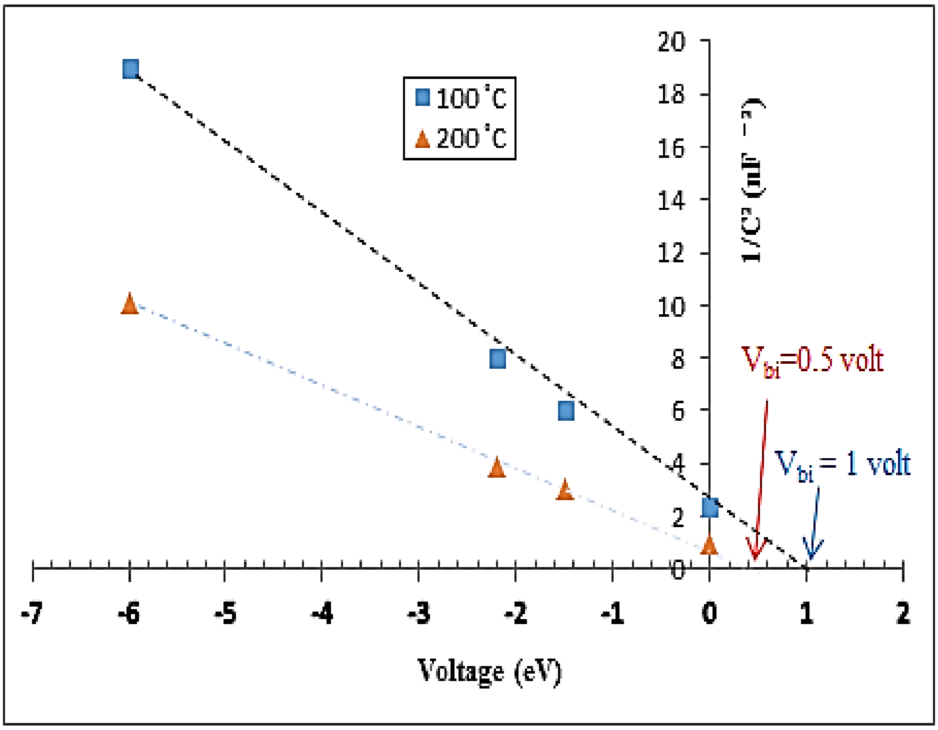

Fig. 8: $1/C^2$ versus reverse voltage off Al/ CdS/ p-Si/Al Hetrojunctions.

Conclusion

CdS thin film was deposited onto a glass substrate by using thermal evaporation technique. The salient conclusions arising from this study are summarized below:

1. XRD studies of Cadmium sulphide thin films reveal nanocrystalline nature of the films with mixed (cubic and hexagonal) crystal structures.

2. The Cadmium sulphide thin films deposited on glass substrate present excellent adherence, uniform deposition , homogeneous morphology and nanocrystalline properties, confir-med by AFM and XRD analysis.

3. The Optical absorption Cadmium sulphide of study revealed direct bandgap nature and bandgap is found to be of the order of 2.2 to 2.4 eV.

4.photovoltic characterization of Al/CdS/Si/Al hetrojunction showed that the films are semiconductors and can be used in solar cell devices.

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