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REACTION TEMPERATURE EFFECT ON THE STRUCTURAL, SURFACE TEXTURE AND OPTICAL PROPERTIES OF CdS NANOSTRUCTURE THIN FILMS DEPOSITED BY HYDROTHERMAL METHOD

Abstract: *Cadmium Sulfide (CdS) nanostructure thin films were deposited on conductive glass (FTO) substrates by hydrothermal method at different reaction temperatures (140, 160 and 200 °C) for 4 hours. The structure, surface texture and optical characteristics were studied by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV-Vis spectrophotometer. The XRD results of CdS nanostructure thin films deposited on FTO substrate showed that the films have a polycrystalline structure nature and hexagonal wurtzite phase. The preferential orientation was along (002) and (112) planes. A strong peak with a high intensity related to the FTO substrate appeared in all samples. The crystallite size of the nanostructure films was increased with the increase of reaction temperature which about (21-29) nm. Structure parameters such as lattice constants, dislocation density, the number of crystallites, and microstrain have been determined. The surface texture of nanostructure CdS thin film includes dense uniform and homogenous surface without pinholes or cracks with fine grain size. The nanostructure CdS thin films with small nanosized grains (37-203) nm were successfully obtained on FTO substrates. The optical properties of the prepared CdS nanostructure thin films were investigated in the wavelength region (400-800) nm. The transmittance spectra exhibit a high transmittance value of about 88% in the visible and near infrared regions. The results demonstrated a red shift in the fundamental absorption edge towards the lower energies long wavelengths. The optical energy gap for the permissible direct transmission decreases from (2.435 to 2.389) eV with increasing the reaction temperature from (140 to 200) °C, respectively.*

Key words: *CdS nanostructure; Hydrothermal method; structure parameters: Surface morphology; Optical band gap.*

Language: *English*

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Introduction

Chalcogenide II–VI semiconductor nanostructure thin films attractive essential interest for their used in wide range of applications. Cadmium sulfide (CdS) one of the promising chalcogenide n-type materials for avariety of photovoltaic, electronic, optoelectronic devices applications due to its wide band gap (2,42 eV), high absorption coefficient ($>10^4 cm^{-1}$), high electron affinity and high photosensitivity [1-5]. CdS thin films play a very important roles in potential applications such as in photoelectrochemical hydrogen production [1,6], window layer for solar cells [7], photodetectors in visible light [8], optical waveguides, and wastewater

Treatments [9]. CdS nanostructure thin film was synthesized by various methods and techniques such as chemical bath deposition method (CBD)[5], spray pyrolysis technique [1,10], thermal evaporation [10], chemical precipitation method [11], successive ionic layer adsorption and reaction method (SILAR) [12], doctor-blade technique [13], solvothermal method [14, 15] and hydrothermal method [16, 17]. Most of these methods and techniques require a high preparation temperature or annealing process, by using these methods the micro-cracks defects could be formed because of the thermal expansion coefficient mismatching between the film and the substrate [18, 19]. Among these methods, simple and one step, low coast, high quality, high purity, very high crystallinity, and low-temperature method, the hydrothermal method was selected to preparative chalcogenide dS thin films [18-20].

In present paper CdS nanostructure chalcogenide thin films were hydrothermally deposited on FTO substrate at various reaction temperature. The influence of reaction temperature on the structure parameters, surface morphology and optical band gap was investigated.

1. Experimental details

Cadmium sulfide CdS nanostructure thin films were deposited on fluorine tin oxide FTO substrates by hydrothermal method. Cadmium acetate (BDH company) $((CH_3.COO)_2Cd.2H_2O)$ and thiourea $(NH_2.CS.NH_2)$ in 1:3 weight ratio were used as a precursors. 0.3 g of Cadmium acetate and 0.9 g of thiourea were dissolve in 40 ml of deionized water, using magnetic stirrer for 30 minutes, the ultrasonic bath resulting solution was transparent clear. The FTO substrates with different areas were cleaned in an ultrasonic bath containing isopropanol, acetone, and distiled water for 10 minutes separately for each one and then and then, dried by air drier. The prepared solution (40 ml) of (Cadmium acetate and thiourea 1:3) was transferred into a 50 ml Teflon lined stainless steel autoclave contain two pieces with different areas of cleaned FTO substrate. Then the hydrothermal fabrication is carried out in the oven heated at various reaction temperature (140, 160 and 200) ºC for 4 h. Then the obtained samples was rinsed with deionized water to remove any residual organic species form the preparation process. The crystal structures of the prepared CdS nanostructure films were studied by X-ray diffraction technique (XRD) using Shimadzu XRD-7000 diffractometer with Cu Kα radiation 1.54056 Å. The surface morphology of the prepared samples were performed by a field emission scanning electron microscopy (FEI FESEM Nano SEM Nova 450. The optical absorbance and transmittance in the UV–Vis regions (300-800) nm was measured using Mega-2100 (Sinco.) spectrophotometer.

Results and discussion

The crystal structure of CdS nanostructure thin films deposited on FTO substrates by hydrothermal method at various reaction temperatures (140, 160 and 200) °C for 4 h was investigated by x-ray diffraction. The diffraction patterns of prepared samples revealed sharp and strong peaks indicate that the prepared CdS films well crystallized and have polycrystalline nature and hexagonal wurtzite phase as illustrated in figure 1. The diffraction peaks were appears at diffraction angles (2Ɵ) of 25.3, 26.95°, 28.60°, and 51.93°, that were indexed to the (100) (002), (101), and (112), planes which well matches with the standard card (JCPDS No. 77-2306). Whereas the diffraction peak corresponding to the diffraction plane (200) was found at (2Ɵ = 38.24º) which refer to the tetragonal structure of FTO substrate, according to the standard card (JCPDS No. 41-1445). From the x-ray diffraction patterns of the prepared thin films, no additional peaks were observed which indicates the high purity of the samples. The preferential orientation of the CdS crystal is along (112) plane indicate that the growth was perpendicular to c-axis, which is in good agreement with the literature [3,6]. It can be notice from the figure that with increase of reaction temperature the diffraction intensity was slightly increased for the diffraction planes (002) and (112) which confirms the films crystallinity, as well as for FTO diffraction peaks. This can be attributed to the reduced the crystal defects with the increase of the reaction temperature and the CdS atoms relax reach their lattice point in the wurzite phase. Then it can be conclude that the reaction temperature modified the crystal structure of CdS lattice and improve their crystallinity [5, 18]. The interplanar spacing $\mathbf{d_{hkl}}$ was calculated used Bragg's law and the lattice constants **a** and **c** were calculated using the equation [21]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{(h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

The results was tabulated in Table (1) and clearly revealed that the interplanare distance $\mathbf{d_{hkl}}$ and the lattice constants a and c are well matched with the standard values of (JCPDS No. 77-2306) as well as with the literature [3, 24, 25].

The crystallite size D (nm) of the prepared CdS thin films was calculated using Scherrer's formula [22]:

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \qquad (2)$$

Where λ is the wavelength of the used x-ray (1.5406 Å) and β is the full width at half maximum intensity of the peaks in radian. The crystallite size was increased from 21.34 nm to 29.62 nm with the increase of reaction temperature from 140 to 160 ºC, whereas crystallite boundaries and dislocation defects were reduced.

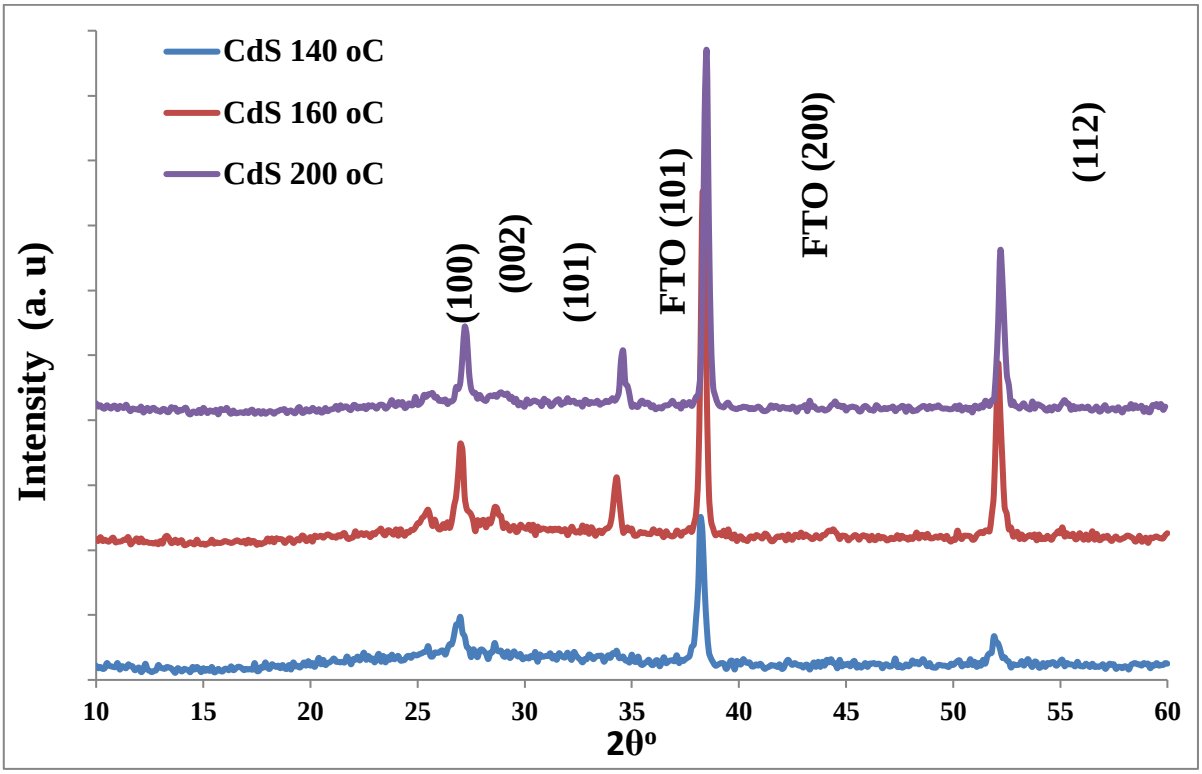

Figure 1: XRD Pattern of CdS nanostructure thin films deposited at reaction temperatures (140 and 160 and 200) °C.

Table 1: Structural Parameters of CdS nanostructure thin Films obtained from XRD data at various reaction temperature for preferential orientation (002).

CdS (nanostructure thin film) At reaction temperature °C	2 θ	d_{112}	Crystallite Size D (nm)	Dislocation density (δ) $*10^{-3}$ (lines/m^2)	a	c	Micro-Strain (ε) $*10^{-3}$
140	51.93	1.75925	21.43	2.177	4.155	6.610	1.689
160	52.107	1.75382	29.06	1.183	4.142	6.590	1.245402
200	52.027	1.75631	29.62	1.139	4.149	6.597	1.221992

The dislocation density **δ** of CdS thin films can be defined as the number of dislocation lines per unit area of the crystal and calculated by using the relation [23]:

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

It is obvious from Table (1) that the dislocation density decreased with the increase of reaction temperature which can be related to the enhancement of the crystallinity and the growth of the crystallites in the preferred orientation [25, 26]. The lattice micro-strain (ε) is the deformation created in the material lattice during the growth of the film or arises from expansion or compression and can be calculated from the relation [27]:

$$\varepsilon = \frac{\beta cos\theta}{4} \qquad (5)$$

The micro-strain was found to be expansive in nature and decreased with the increase of reaction and preparation temperature as shown in Table (1).

Figures (2) illusterate the FESEM images of CdS nanostructure thin films prepared at (140, 160, 200) °C respectively. The surface includes small and large grain size and has a regular shape, dense uniform and homogenous surface without pinholes or cracks with fine grain size. So, it can be concluded that nanostructure CdS thin films with small nanosized grains about (37-105) nm were successfully obtained on FTO substrates . The density of CdS grains on the FTO substrate was very high, this confirms its high degree of crystallinity with FTO substrate which represents the wurtzite phase [28, 29].

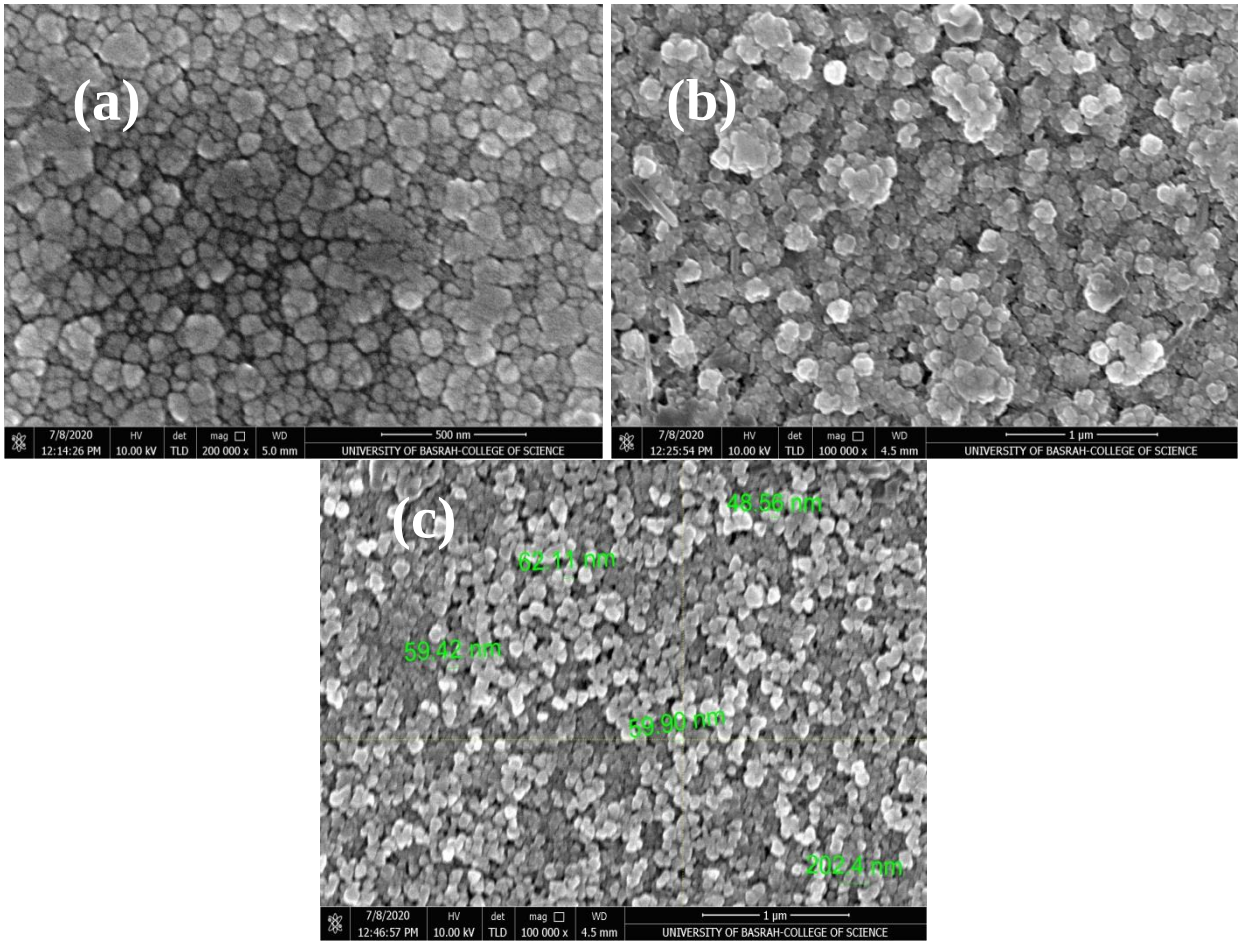

Figure 2: FESEM Images of CdS Nanostructure thin Film Prepared at a. 140 b. 160 and c. 200 °C.

The optical transmittance spectra of CdS nanostructure thin films deposited on FTO substrate, deposed at different reaction temperatures (140, 160 and 200) °C were shown in figure (3).

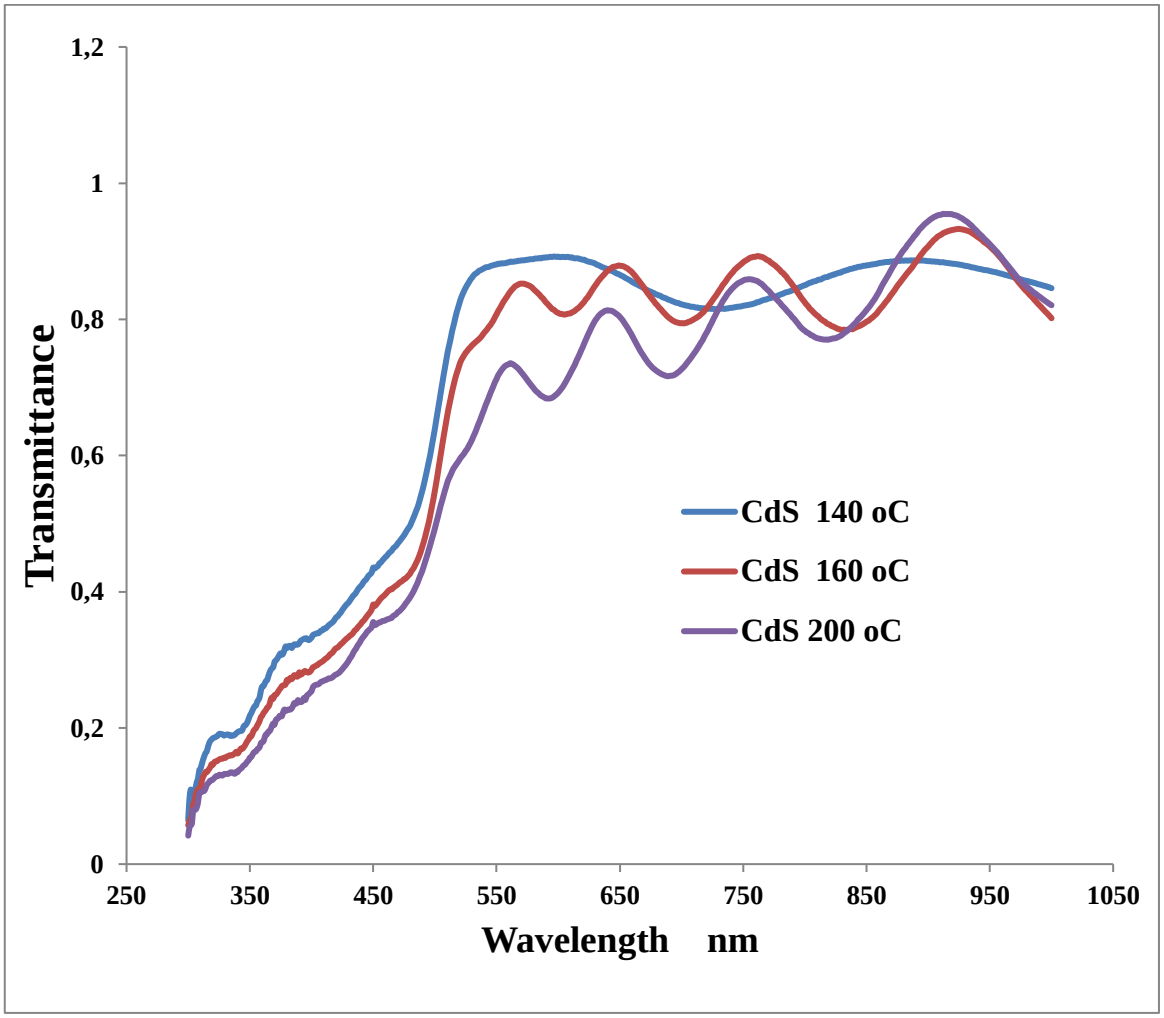

Figure 3: Transmittance spectra of CdS nanostructure thin films deposited at different reaction temperatures (140, 160 and200) °C.

The transmittance spectra exhibit high transmittance value and decrease from 88% in the visible and infrared regions. In the beginning at lowest reaction temperature (140 °C) the transmittance was high and slightly decrease with the increase of reaction temperature and the absorption edge shifted towards long wavelength and low energies (red shift). The decrease in the transmittance values of the film in the UV- region were resulted by absorption of light, which may be attributed to the good crystal structure which eliminates light scattering [3]. The studies about fundamental absorption edge revealed that the deposited films are absorptive at the UV- region, and is more appropriate for optical coating[30]. The absorption coefficient $\boldsymbol{\alpha}$ was calculated using the equation $\boldsymbol{\alpha = (2.303 \times A)/t}$ where A and t is the absorbance and the thickness of the films. Figure (4) shows the absorption coefficient as a function of photon energy. The absorption coefficient depends on the incident photons energy and on the characteristic semiconductor represented by band gap and the type of electronic transitions which happens between energy bands, The most value of the absorption coefficient of all samples is larger than (104 cm^{-1}) which indicates that the electronic transitions are direct. The values of the absorption coefficient increase with the increasing hydrothermal reaction temperature beyond the absorption edge shifting towards low energies.

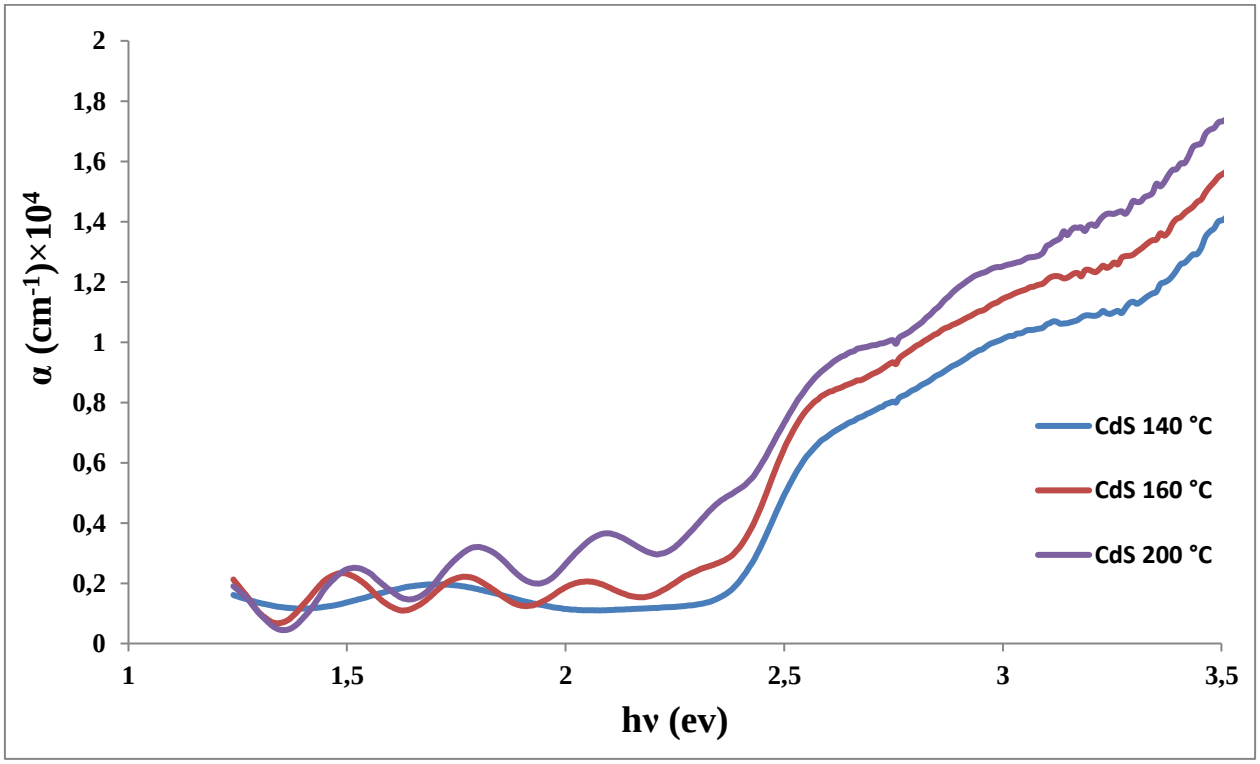

Figure 4: The variation of absorption coefficient with the incident photon energy of CdS nanostructure thin films.

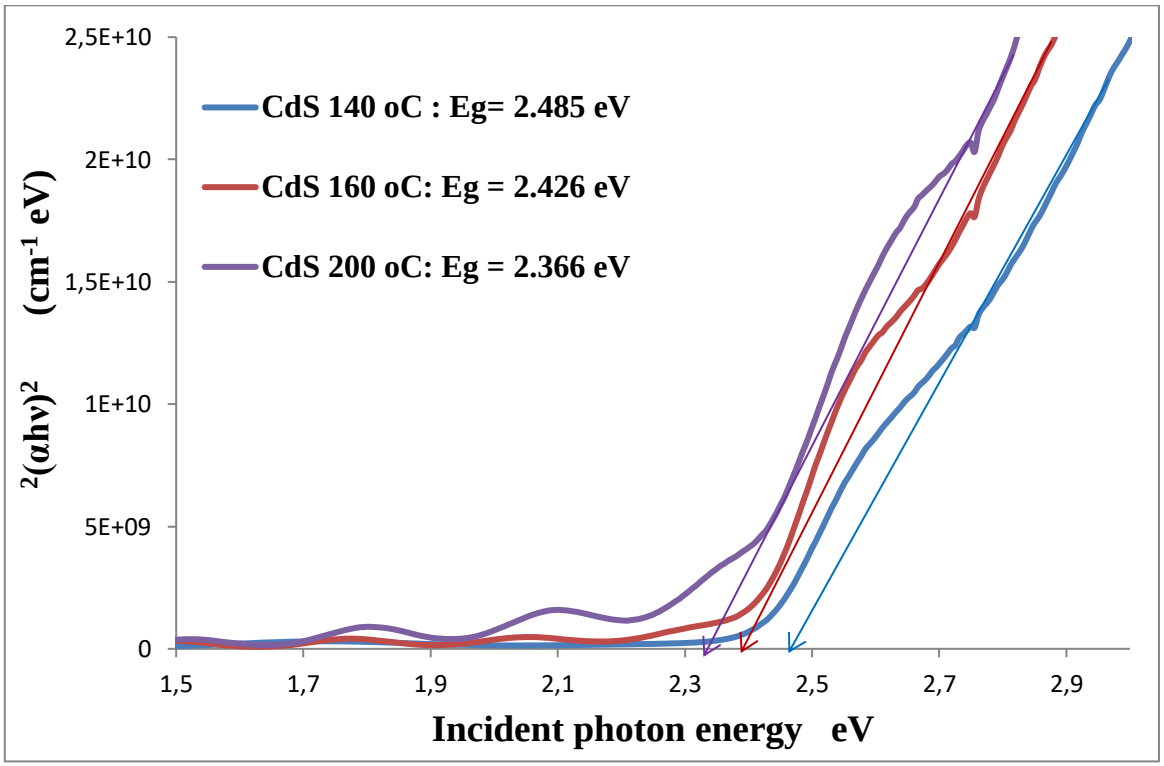

Figure 5: Optical energy gap of CdS nanostructure thin films hydrothermally deposited at 140,160 and 200 °C.

The energy gap E_g of the prepared CdS nanostructure thin films was determined using Tauc relation [28,31]:

$$(\alpha h\nu) = B(h\nu - E_g)^r \qquad (6)$$

The optical energy band gap for allowed direct transition of the prepared films (Figure 5) is estimated from the plot of $(\alpha h\nu)^2$ versus hν using Tauc relation eq. (2.12), which is determined by extrapolating the straight-line portion of the Plot to the point α = 0. The optical energy band gap of CdS nanostructure thin films at (140,160 and 200) °C was found to be decreased from 2.485 eV to and 2.366 eV with the increase of the reaction temperature. The reduced of energy gap can be attributed to the enhancement of the crystallinity and the improved of the crystallite size. The results was in good agreement with the literature [32, 33].

Conclusion

CdS nanostructures thin films showed high crystallinity, and the crystallite size tend to increase with increase the hydrothermal reaction temperature, and the deposition method was very suitable fro deposited high crystallinity CdS nanostructure films. Form morphology analysis it has been observed that there is uniform nucleation of all the grains, over the entire surface without any voids or pores. All the film surfaces appear to be smooth and densely packed with grains uniformly distributed. CdS nanostructure thin film exhibits high transparency of nearly about 88% in the visible region. which is distinctive for solar cell window applications. So it can be used as a windows for wavelength> (520) nm, and as afilters for wavelength< (520) nm. The optical measurement shows that the CdS nanostructure thin films have allowed direct energy gap (Eg) that decreased from 2.485 eV to and 2.366 eV with increase reaction hydrothermal temperature.

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