Nd: YAG LASER –INDUCED EFFECTS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF NANOSTRUCTURED CdS THIN FILM

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Cadmium sulfide (CdS) thin films were deposited on a glass substrate using the thermal evaporation method at room temperature. The changes in the optical properties (optical band gap and absorption coefficient) after irradiation by Nd: YAG laser at wavelength 532 nm have been measured in the spectral range 190-650 nm. It is found that optical band gap is decreased after irradiating the thin films. The samples were characterized using XRD and the grain size of the CdS thin film the calculated from the XRD data was found as 25.91 nm as-deposited. The grain size is also found to increase with laser exposure.

1. Introduction

Metal chalcogenides (sulfides, telluride and selenide) are of great importance for researchers because they are potential candidates for optoelectronic applications such as photodetectors, solar cell, thin film transistors etc. [1]. Cadmium sulfide (CdS) is an important metal chalcogenides. Its CdS thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. Wide band gap (Eg =2.4 eV) has been used as the window material together with several semiconductor such as CdTe, Cu_2S and InP with 14-16% efficiency [1].

Laser crystallization of thin films on glass is widely used to improve the electronic transport. In the production of flat panel displays, laser crystallization increases the carrier mobility in thin film transistors. Suitable laser intensity profiles in combination with multiple scanning sequences have been used to reduce the number of grain boundaries [2].

The crystallization process of amorphous CdS films on glass substrates is also   important from the technological point of view for its potential use in the production of hybrid, amorphous/polycrystalline CdS solar cells. Laser crystallization appears to be more promising compared to the thermal crystallization as it does not damage the glass substrate and that almost all of the laser energy is directly absorbed into the CdS film [3].

Many techniques have been reported for the deposition of CdS thin film. These include evaporation, sputtering, chemical bath deposition, spray pyrolysis, metal organic chemical vapour deposition; molecular beam epitaxy technique. In the present work, thermal evaporation technique has been chosen for the deposition of CdS thin films.   We have studied the optical and structural properties of CdS thin films using the optical absorption and X-ray diffraction techniques. Detailed

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studies are made on the structural and optical properties of cadmium sulfide thin films before and after irradiation with pulsed Nd: YAG laser.

2. Experimental

Thin films of CdS were deposited on a glass substrate by using the vacuum evaporation technique at room temperature and vacuum of ~10^{-5} torr, using a molybdenum boat. The films were kept inside the deposition chamber for 24 h to achieve the metastable equilibrium. The thickness of the films was measured by Ellipsometry which was found as ~ 100 nm. The thin films were irradiated by pulsed Nd: YAG laser (wavelength 532 nm, energy 2mJ, pulse duration 5 nsec) for different durations of time. For measuring the optical absorption and transmittance of thin films, a double beam UV/VIS/NIR Spectrophotometer (Camspee-M550) was used. The XRD measurements were carried out using an X-Ray Diffractometer PW 1830 PANalylical which has tube anode; copper using the wavelength 1.54056Å. The X-ray diffraction and optical absorption measurements were carried at before and after irradiation of the sample by the laser.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1 shows the XRD of CdS thin film. The peak corresponding to the (111) plane at $2\theta=26.535°$ and the type of structure of cubic zincblende (ZB) which are found to be in agreement with the standard value JCPDS [4]. The grain size of CdS thin film was calculated by Scherrer's formula [5] from the full width at half maximum (FWHM) and was found as 25.91 nm.
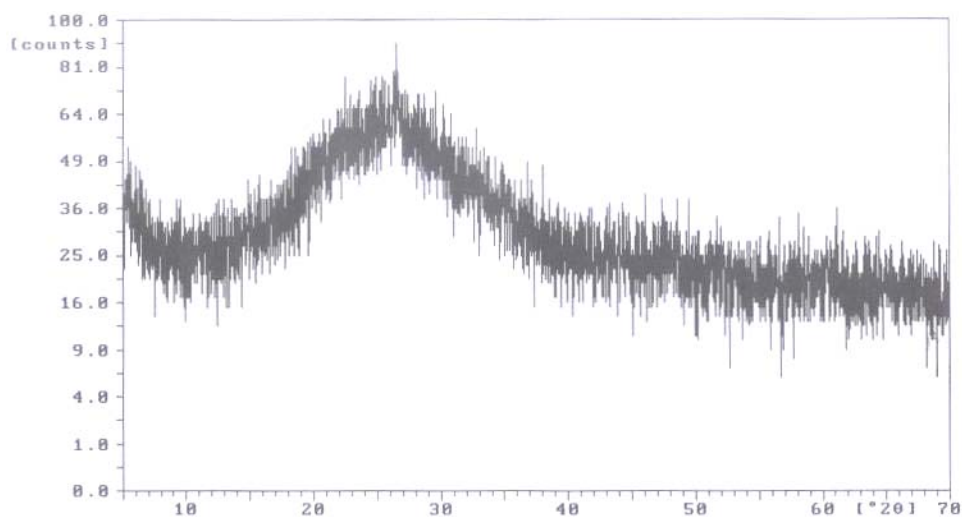

Fig. 1. XRD of CdS thin film as-deposited

Fig. 2 shows the XRD of CdS thin film after 1 min irradiation by Nd: YAG laser. The XRD analysis showed that the CdS thin film was amorphous. The peak corresponding to the (111) plane at $2\theta=26.505°$. The type of structure is found to be cubic zincblende (ZB) [4]. The grain size increases from 25.91 nm to 34.54 nm, which is in agreement with the finding of Shailaja [6].
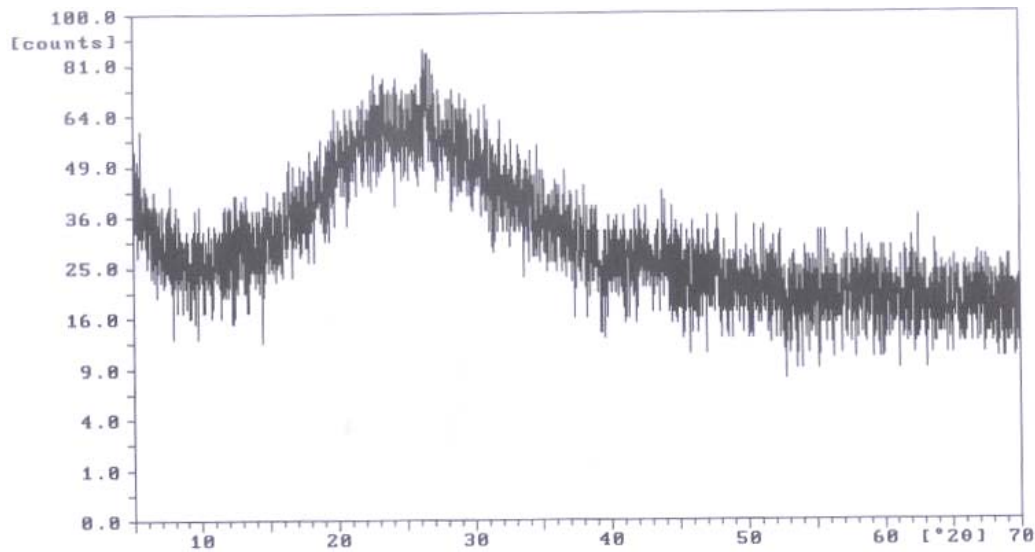
Fig. 2. Shows the XRD of CdS thin film after 1 min irradiation by Nd: YAG laser.

Figure 3 shows the XRD of CdS thin film after 2 min laser irradiation. The XRD analysis showed that the CdS thin film was change to polycrystalline and the intensity of the reflection peak increases due to lager volumes of crystalline material present. The peak corresponding to the (002) plane at $2\theta=26.475°$ [4] is obviously shifted to lower 2θ values after irradiation. The value of the shift is of the order of $0.06°$ that is beyond the limit of the experimental determination of the peak position [7]. The type of structure is hexagonal wurtzite (W) [4]. The grain size of CdS thin film increases from 25.91 nm to 69.09 nm after laser irradiation.
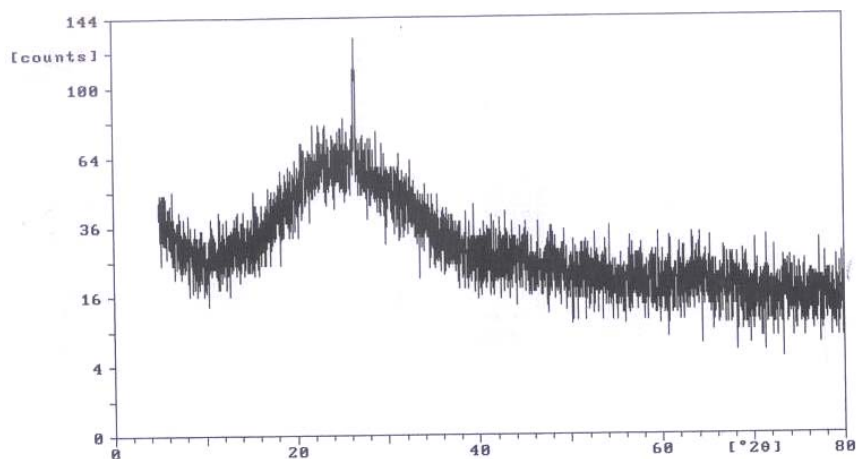

Fig. 3. Shows the XRD of CdS thin film after 2 min irradiation by Nd: YAG laser.
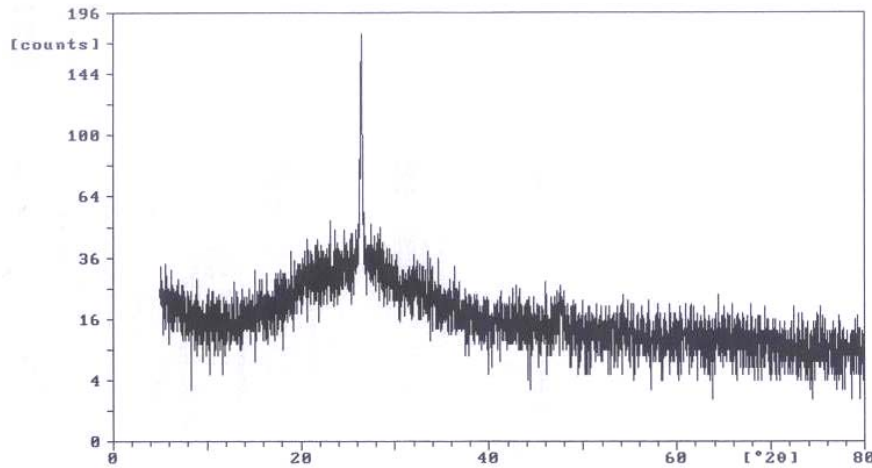
Fig. 4. Shows the XRD of CdS thin film after 5 min irradiation by Nd: YAG laser.

Figure 4 shows the XRD of thin film CdS after 5 min laser irradiation. The XRD analysis showed that the CdS thin film was changed to more polycrystalline and the intensity of the reflection peak increase due to lager volumes of crystalline material present. The peak corresponding to the (002) plane at $2\theta=26.450º$ [4]. The type of structure of hexagonal wurtzite (W) [4]. The grain size increases from 25.91 nm to 103.69 nm after laser irradiation.

The strain values ε can be evaluated using the following relation [5],

$$\varepsilon = \beta\cos\theta/4 \tag{1}$$

The lattice spacing d is calculated from the Bragg's formula,

$$d = \lambda/2\sin\theta \tag{2}$$

The lattice parameter c is determined for hexagonal structure by the following expression,

$$1/d^2 = (h^2 + k^2 + l^2)/c^2 \tag{3}$$

where h, k and l represent the lattice planes.

The grain size, the strain (ε), 2θ, the lattice spacing (d) and the lattice parameter (c) are given in Tables 1&2 it is clear from those Table that all parameters change before and after irradiation by the laser.

Table 1. Laser effect on grain size and thermal strain of CdS films deposited.

Sample	Grain size ,D(nm)	Strain(ε)* 10^{-4}
1- Thin film CdS	25.91	13.96
2- Thin film CdS after laser irradiation at time 1 min	34.54	
3- Thin film CdS after laser irradiation at time 2 min	69.09	5.237
4- Thin film CdS after laser irradiation at time 5 min	103.69	3.489

Table 2. Structural parameters of CdS films deposited.

Sample	2θ	hkl	Lattice spacing d(Å) Experimental	Lattice spacing c(Å) Experimental
1-Thin film of CdS	26.535º	111	3.362	5.823
2- Thin film of CdS irradiated by laser at time 1min	26.505º	111		
3- Thin film of CdS irradiated by laser at time 2min	26.475 º	002	3.5017	7.0034
4- Thin film of CdS irradiated by laser at time 5min	26.450º	002	3.365	6.7314

The diffraction peaks in the XRD pattern of laser irradiation samples are very sharp with the high intensity indicating the significant increase in crystallite size with the hexagonal modification. This behavior indicates the phase transformation from the as-deposited metastable amorphous cubic phase of the CdS film to the stable polycrystalline hexagonal after laser irradiation. Thus after laser irradiation the film at a higher temperature, recrystallization takes place and the hexagonal polycrystalline phase prevails over the amorphous one. The occurrence of phase transformation is probably due to the increase in crystallite size and the change in atomic configuration of the CdS thin film [8,9].

It is important to remark that CdS cubic change from ZB to W polycrystalline phase after 2 min irradiation. The lattice parameter of CdS thin film is increased with laser irradiation, which is caused primarily due to the rearrangement of ions of Cd and S inside the CdS lattice and the diffusion of atoms or ions into its volume. The metastable crystalline structure ZB of CdS tries to change with laser induced to the stable phase W of CdS, fact that makes the ions move inside the lattice, and from here, the volume of unit cell has also a tendency to make itself equal to the unit cell of the phase W, and hence experiences an increasing [10].

The studies show that the CdS layers have a hexagonal structure after heat treatment [8].

3.2. Optical properties

The optical absorption spectra of CdS films deposited onto a glass substrate were studied at room temperature in the spectral range 190–650 nm. Figure 5 shows the variation of absorption coefficient (α) with wavelength (λ). The absorption coefficient is found to increase after laser irradiation of the thin film. This is possibly due to the increase in grain size and the decrease in the number of defects [11]. It is clearly seen from the optical spectra that the absorption edge is red shifted for irradiated films. This shift indicates a decrease of the optical band gap 'E_g' which was calculated using the following relation [1, 12]:

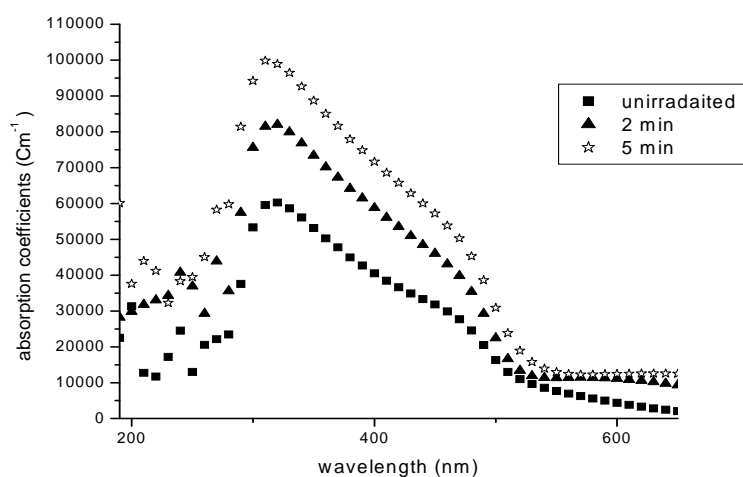$$\alpha = A (h\nu - E_g)^n / h\nu \qquad (5)$$

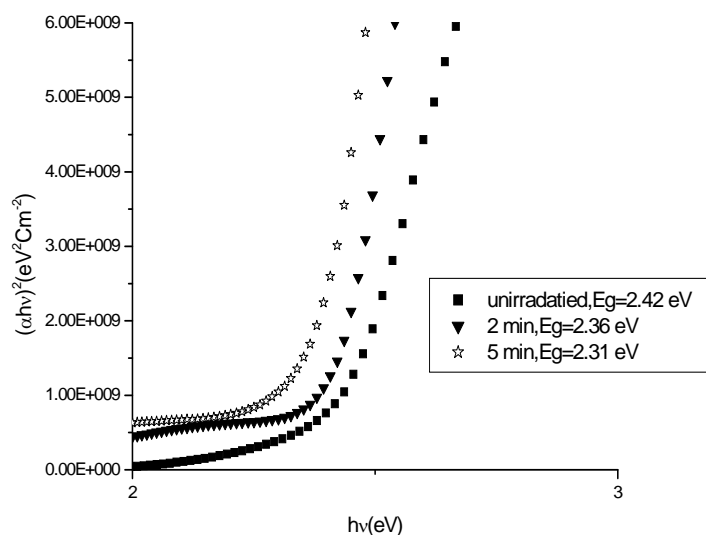*Fig. 5. Shows the variation of absorption coefficient (α) with wavelength (λ).*

Fig. 6. The estimated band gaps from the plots of (αhv)² versus hv are for 'as-deposited'
and irradiated CdS films by pulsed Nd: YAG laser at time 2 min &5 min .

where A is a constant and n is a constant, equal to 1/2 for direct band gap semiconductors. The estimated band gaps from the plots of $(\alpha hv)^2$ versus hv are shown in Fig. 6 for 'as-deposited' and irradiated CdS films. The linear nature of the plot indicates the existence of direct transition. The band gap 'Eg' was determined by extrapolating the straight portion to the energy axis at α = 0. It was found to be 2.42 eV [1,12] for as-deposited CdS films and shows 'red shifts' by 2.37 eV and 2.31 eV after irradiation by Nd:YAG laser for different exposure times of 2 and 5 min, respectively. The band gap decreases as shown in Table 3.

Table 3: Optical parameters of CdS system at 400 nm before and after irradiation by Nd: YAG Laser of energy 2 mJ.

Sample	$\alpha * 10^4$ cm^{-1}	k	Eg (eV)
1-Thin film of CdS	4	0.1274	2.42
2-- Thin film of CdS Irradiated by laser at time 2min	5.8	0.1847	2.36
3-Thin film of CdS Irradiated by laser at time 5 min	7.1	0.2261	2.31

The decrease in band gap shows that the irradiated film causes a strong 'red shift' in the optical spectra due to sintering of the nanocrystalline into larger crystallites. Lozaca-Morales et al. [13] have reported that while the lattice parameter and grain size are increased, the optical band gap is decreased. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. Similar 'blue/red shift' in band gap energy 'E$_g$' values for the films with smaller thickness and/or crystallite sizes have been reported for thermally deposited CdS thin films [9,11,14].The presence of a high concentration of localized states would produce absorption at energy less than the band gap and thereby is responsible for such low values. The weak absorption region at lower energy side is attributed to the presence of intraband transitions at localized states in the gap. It is clearly observed Fig.6 that the optical gap is lowered to 2.42 eV after laser irradiation the well known effect of photodarening [15]. As seen also from Fig.5 as a result of irradiation, the absorption edge shift to longer wavelengths which confirm the photodarkening. The red shift manifests the fact that Urbach tail light can generate mobile carriers, holes in present CdS thin film

The absorption coefficients of these films are high ($\approx 10^4$ cm^{-1}) and are given in Table 3. Extinction coefficient k has been calculated using the well known relation [14].

$$\alpha = 4\pi\kappa/\lambda \tag{6}$$

where λ is the wavelength of incident beam .The extinction coefficient k is found to decrease as the time of radiation increases in CdS system as shown in Fig. 6.
The values of the extinction coefficient before and after irradiation are given in Tables.

4. Conclusions

The optical absorption spectra of thin film CdS are obtained in the wavelength range 190-650 nm before as well as after irradiation with Nd: YAG laser. The band gap is decreased and absorption coefficient (α) is increased after laser irradiation. The XRD data show the grain size being increased after laser irradiation and the structure was change from cubic zincblende (ZB) to hexagonal wurtzite (W).

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