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Study of Effect of Solar Light Irradiation on Structural, Optical and Electrical Properties of CdSe Thin Films

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Abstract

Thin films of CdSe (50:50 composition) were deposited on glass substrates by thermal evaporation technique. These films were then irradiated by visible light (Solar light) through magnifying glass for different duration of time (5 to 15 minutes). The energy of solar light radiation was measured to be ~ 0.3 MeV (calculated by E =hc/λ). The x- ray diffraction pattern at room temperature confirms the grain size of the solar irradiated CdSe films increases indicating the improvement in crystallinity. The optical characterization of as-deposited and solar light irradiated thin films were recorded by UV- visible spectrophotometer (200-1100nm) before and after irradiation. The transmission spectra have been studied to measure the optical constants like extinction coefficient (k), absorption coefficient (α), optical band gap (E_g) and urbach's energy (E_u). It was found that the optical band gap decreases from 2.68 eV to 1.99 eV. The value of extinction coefficient and Urbach's energy also decreases after solar light irradiation. The electrical studies show the value DC conductivity increases and the value of activation energy decreases after solar light irradiation.

Keywords: CdSe thin flims; Solar irradiation; Structural properties; Optical properties; Electrical properties

1. Introduction

CdSe belongs to wide band gap semiconductor of II-VI system [1] and is one of the most promising semiconductor material for optoelectronic and photovoltaic devices.

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CdSe has been studied for applications in solar cells, light emitting diodes, photodetectors, lasers and photo electrochemical cells [2, 3]. The properties of CdSe has been modified by different researchers using various techniques such as annealing [4], laser irradiation [5] and also by other deposition techniques such as chemical bath deposition [6], electron beam deposition [7], vacuum deposition [8] etc. The properties of CdSe have been widely investigated during recent years. Ausama et al [5] have reported that the optical band gap of CdSe decreases and the grain size increases after laser irradiation. Similar results were obtained by annealing [4, 9].

In the present study, we report the effect of visible light (solar light) of flux 150,000 and corresponding energy ~0.3MeV irradiation on the properties of CdSe thin films deposited by thermal evaporation technique on glass substrates. It is well known fact that when electromagnetic radiation interacts with the material, it can excite electrons of the target atom. When these electrons de-excite, the energy is transferred to the lattice through electron - phonon interaction. In this way the amplitude of lattice vibrations increases which leads to the increase in lattice temperature above melting point and hence improvement in crystallinity and the structure of the material. The main function of irradiation of materials is to deposit a large amount of energy into a material over a short time scale. During radiation-material interaction, photons will couple into the electronic or vibrational states in the material depend on the photon energy [10]. On the other hand, one can say that it depends on the wavelength of the incident photon. The energy of photons itself depends upon the temperature of the irradiation source according to Wein's displacement law. In case of solar light irradiation, high energy photons are present due to high temperature, so the chance of coupling is large incase of solar light irradiation as compared to annealing. That is why in this study the change of properties of CdSe solar light irradiated films was found to be large as compared to previous work.

2. Experimental

The bulk sample of CdSe (50:50 as per atomic weight percentage) was prepared by well-known thermal quenching technique. The mixture of CdSe was put into the quartz ampoule kept at pressure of 10^{-5}torr and then sealed.

The ampoule is then placed in the furnace for 15h at 900°C temperature. The ampoule was continuously rotated in furnace that results homogeneous mixing of material.

After 15h, the ampoule was taken out of the furnace and quenched in ice cooled water for obtaining amorphous state. Thin films of CdSe have been prepared by thermal evaporation technique on glass substrates at room temperature under a pressure of ~10^{-5}torr through molybdenum boat. The glass substrates was first cleaned by ultrasonic bath and then by acetone. For achieving metastable equilibrium, the films were kept inside the deposition chamber for 24h. The thickness was measured to be ~300nm by using ellipsometry technique. The films of CdSe were irradiated by visible solar light for different duration of time focusing on sample surface through magnifying glass in order to maximum flux falls on to the sample surface. The flux was measured to be 150,000 photons by using digital luxmeter (MS6610).The energy of solar light radiation was measured to be ~ 0.3 MeV calculated by $E = hc/\lambda$ is the planck's constant, 'c' is the velocity of light and 'λ' is the wavelength. In general the wavelength was taken as 0.5μm.The temperature was also found to be 100°C by using thermometer. The optical characterization of these films (as-deposited and irradiated) by using UV-spectrophotometer (Model: Comspec M550) in the wavelength range 200-1100nm. For structural study, XRD measurements were carried out by using X-ray diffractometer (Burker: D8 ADVANCE Cu$K\alpha$as X-ray source of wavelength 1.54056A0), 2θ spectrum from 150 to 600 was recorded for all CdSe thin films. Also the scanning speed was 0.50/min. The microstructure of CdSe as-deposited and solar light irradiated thin films was studied by using scanning electron microscope (SEM) (JEOL).The DC conductivity of CdSe thin films was carried out at 309 - 370.83 K temperature range in a vacuum of 10^{-3}torr at a constant voltage of 1.5 V in the specially designed metallic sample holder. The indium electrodes were used for electrical contacts.

3. Results and Discussions

3.1 X-Ray diffraction Studies
3.2

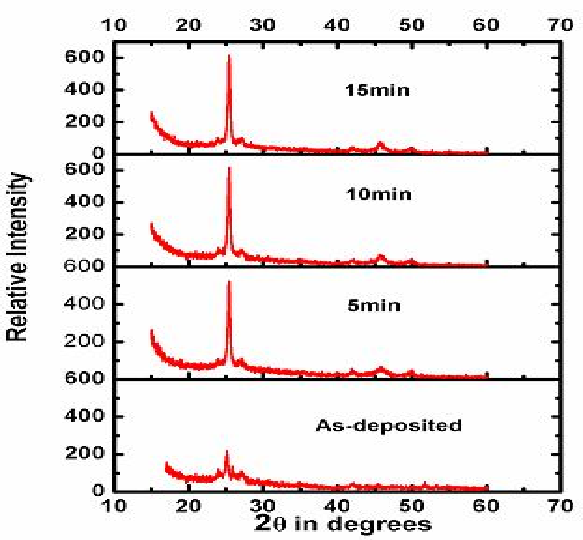


Fig.1: X-Ray diffraction Pattern of as-Deposited 5min, 10min and 15min Solar Light Irradiated CdSe thin Films

Fig.1. shows the x-ray diffraction pattern of CdSe as deposited and solar light irradiation thin films respectively. The peaks were indexed according to JCPDS files. All CdSe thin films show only one intense reflection peak at $2\theta = 25.16^0$, 25.40^0, 25.53^0 and 25.3^0 corresponding to (002) plane of as deposited, 5min, 10min and 15min irradiated CdSe films respectively. It is clear from the XRD pattern of as deposited and solar light irradiated CdSe thin films show there is increase in peak height and increase in grain size due to solar light irradiation indicates the improvement in crystallinity of the material. This may be due to the annealing effect produced due to the solar light irradiation.

The crystallite size of CdSe thin films was calculated by using Scherrer's formula [11].

$$D = 0.94\lambda/\beta\cos\theta \quad \cdots\cdots\cdots\cdots (1)$$

Where 'D' is the crystallite size, 'λ' is the wavelength of X-ray used, 'β' is the full width at half maximum (FWHM) and 'θ' is the Bragg's angle of reflection.

From Table.1, it was found that the crystallite size for CdSe hexagonal (002) plane is increased from 25.44nm to 47.17nm due to solar light irradiation results that the phase transition occurs in the material from amorphous to crystalline state.

The lattice spacing'd' has been calculated by the use of Bragg's formula

$$d = n\lambda/2\sin\theta \ldots\ldots\ldots\ldots\ldots (2)$$

Where 'λ' is the wavelength of the X-ray source used. The experimental value of d is approximately equal to the standard value as shown in Table.2. Similar trend was also observed after laser irradiation [5].

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

$$1/d^2 = (h^2+k^2+l^2)/c^2 \quad \ldots\ldots\ldots\ldots (3)$$

Where h, k and l represents the lattice planes. It has been found that the experimental value of lattice parameter 'c' nearly matches with the standard value.

The strain 'ε' values was evaluated by using the following relation:

$$\varepsilon = \beta\cos\theta/4 \ldots\ldots\ldots\ldots\ldots (4)$$

The dislocation density 'δ' (length of dislocation lines per unit volume) has been calculated by using the relation [12, 13].

$$\delta = 1/D^2 \ldots\ldots\ldots\ldots\ldots (5)$$

Where 'D' is the crystallite size. The positive value of residual strain for solar light irradiated CdSe films indicates a tensile strain. This may be due to the difference of thermal expansion co-efficient of the substrate and deposited material or crystallization process during solar light irradiation.

Also the decrease of density dislocation decreases due to solar light irradiation indicates the crystallinity of the films increases.

Table.1: Effect of Solar Light Irradiation on Grain Size, Strain and Dislocation Density of CdSe thin Flms

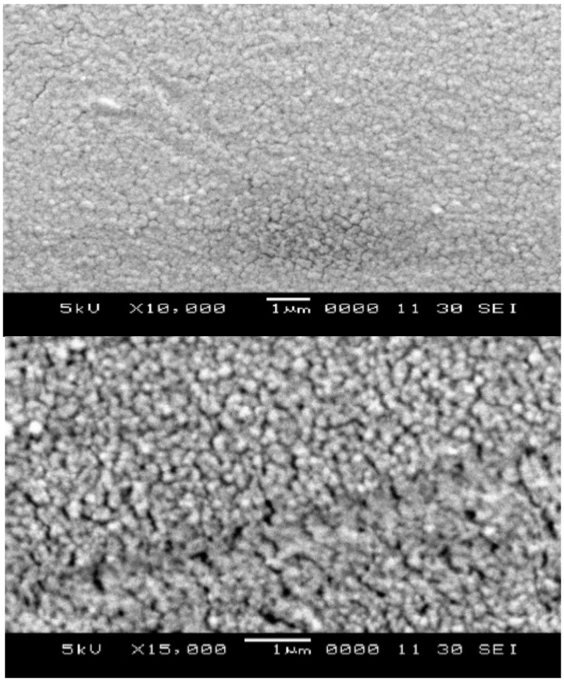
Irradiation Time	Grain size, D(nm)	Strain(ε) 10^{-4}lin^{-2}m^{-4}	Dislocation density δ $\times 10^{15}$(m^{-2})
As-deposited	25.44	14.22	1.54
5min	28.17	12.85	1.26
10min	32.10	11.27	0.97
15min	47.17	7.67	0.44

Table.2. Effect of Solar Light Irradiation on Structural Parameters of CdSe thin Flms

Irradiation Time	2θ	hkl	Lattice spacing d (A^0) Experimental	Lattice spacing d (A^0) Standard	Lattice spacing c (A^0) Experimental	Lattice spacing c (A^0) Standard
As-deposited	25.16^0	002	3.53	3.50	7.06	7.01
5min	25.40^0	002	3.50	3.50	7.0	7.01
10min	25.53^0	002	3.48	3.50	6.96	7.01
15min	25.39^0	002	3.49	3.50	6.98	7.01

3.3 . SEM Studies

Surface morphology of as-deposited and solar light irradiated thin films of CdSe were investigated by SEM as shown in fig.2 (a, b). The white and dark spots shown in all SEM images represents the bright and dark field images of particles. In white spots the concentration of Cd is more because light is scattered more from heavier elements than lighter one. SEM images of solar light irradiated film of CdSe show increase in gain size.



(a) (b)

Fig.2 (a, b): SEM Images of CdSe thin Films (a) as-Deposited (b) 15 min. Solar Light Irradiated

3.4 UV-Spectrophotometer Analysis

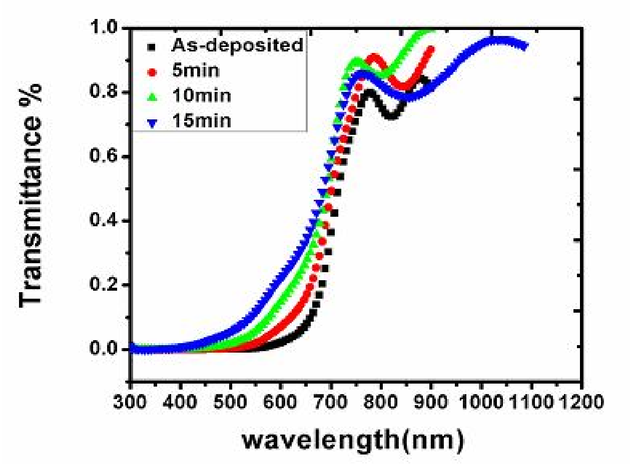


Fig.3: Shows the Variation of Transmittance with Wavelength of CdSe as-Deposited and Solar Light Irradiated thin Films

Fig.3. shows the optical transmission spectra of CdSe films before and after solar light irradiation. It has been found that the transmittance is increased and the curve shifts towards shorter wavelength (blue shift) after solar light irradiation. This may be due to the decrease of surface roughness and increase in crystallinity of the material after solar irradiation. For $\lambda \geq 738$ nm, the transmission spectra in each case of CdSe thin films shows oscillatory behavior because of the interference of reflected wave-fronts from the two surfaces of the thin film.

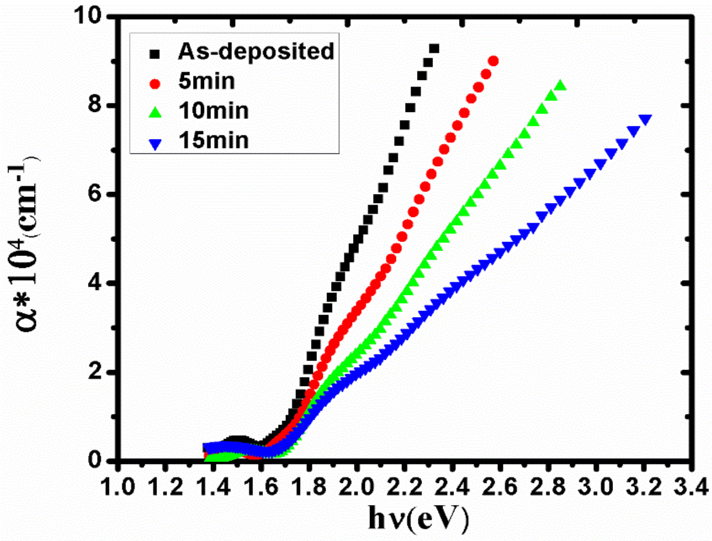


Fig.4: Shows the Variation of ($\alpha \times 10^4$) with Photon Energy of CdSe as-Deposited and Solar light Irradiated thin Films

The absorption co-efficient 'α' of the CdSe thin films has been calculated by using the relation [14, 15].

$\alpha = A/d$ …………. (6)

Where 'A' is the absorbance and'd' is the thickness of the film. The variation of absorption co-efficient (α) with photon energy is shown in fig. It is found that the value of absorption co-efficient decreases after solar light irradiation indicates that the crystallinity of the sample is increased after solar light irradiation.

The absorption coefficient near the band edge depends exponentially on the photon energy and hence obeys the Urbach's empirical formula [16].

$\alpha_\nu = \alpha_\nu e^{h\nu/Eu}$………….. (7)

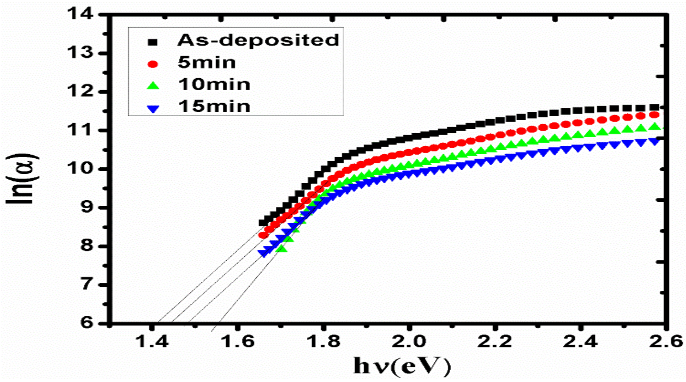


Fig.5. Shows the Variation of ln (α) with Photon Energy of CdSe As-Deposited and Solar Light Irradiated thin Films

Fig.5. shows the variation of ln(α) with photon energy. It has been found that near the band edge, the absorption co-efficient depends exponentially on the photon energy i.e., obeys the Urbach's empirical formula (7), Where'α_0' is a constant, 'h' is the plank's constant and 'E_u' is the energy width of the band tails of the localized states. Urbach's energy represents the degree of disorder in amorphous semiconductors. From Table.3, it has been found that the valve of Urbach's energy decreases after irradiation i.e., the disorder or defects of the sample are reduced due to solar light irradiation.

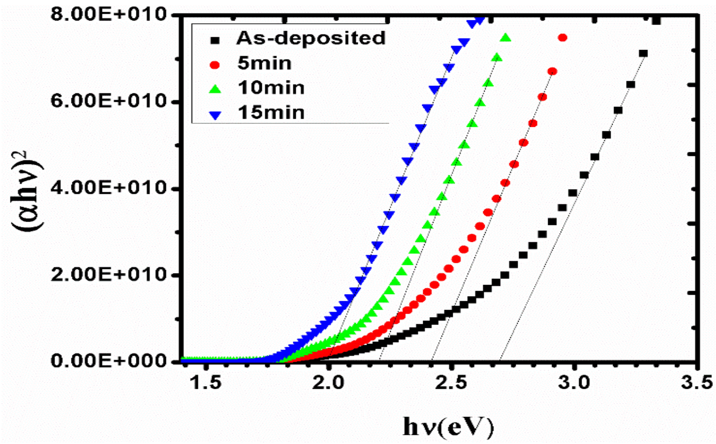


Fig.6: Shows the Variation of $(A h\nu)^2$ With Photon Energy of Cdse As-Deposited and Solar Light Irradiated Thin Films

From absorption spectra, the optical band gap has been calculated by using the relation of Tauc [17]

$$\alpha h\nu = A\,(h\nu - E_g)^m \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

Where 'A' is a constant and 'E_g' is the band gap of the semiconductor material. The value of 'm' decides the type of transition, where m = 1/2, 2, 3, 3/2 for direct allowed, indirect allowed, indirect forbidden, and direct forbidden transitions respectively. The present system obeys the rule of direct transition (i.e., m = 1/2). Solar light irradiation gives sufficient energy to CdSe system in the form of heat reduces the number of defect states in the material that results the decrease in optical band gap and there may be transition from amorphous to crystalline state.

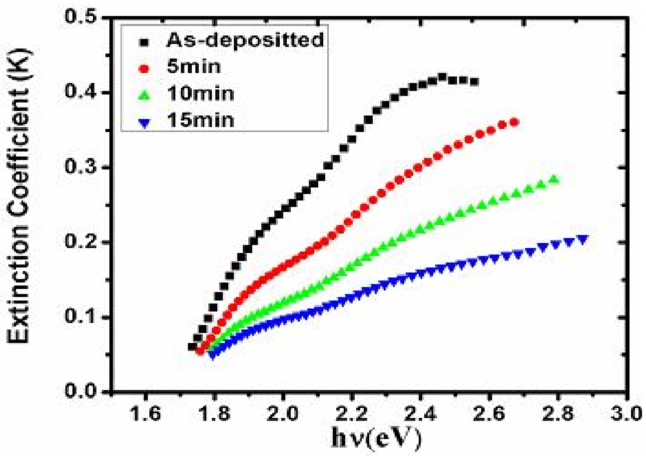


Fig.7: Shows the Variation of Extinction Coefficient with Photon Energy of Cdse As-Deposited and Solar Light Irradiated Thin Films

The extinction co-efficient and 'K' has been calculated by using the relation [18].

$$K = \alpha\lambda/4\pi \ldots\ldots\ldots\ldots\ldots \quad (9)$$

The value of extinction co-efficient decreases after solar light irradiation of CdSe thin films as shown in table. 3. Similar results were obtained (5) for CdSe irradiated with laser.

Table.3. Direct band gap (E_g), Absorption Coefficient (α), Extinction Coefficient (K), Urbach energy (E_u) and Transmittance (T) for the CdSe as-Deposited and Solar Light Irradiated thin Films at 620 nm

Sample	Irradiation Time	E_g(eV)	$\alpha * 10^4 (cm^{-1})$	K	E_u(eV)	T %
CdSe	As-deposited	2.68	4.856	0.239	0.103	3
	5min	2.41	3.353	0.165	0.101	9
	10min	2.20	2.392	0.118	0.099	19
	15min	1.99	1.946	0.096	0.065	26

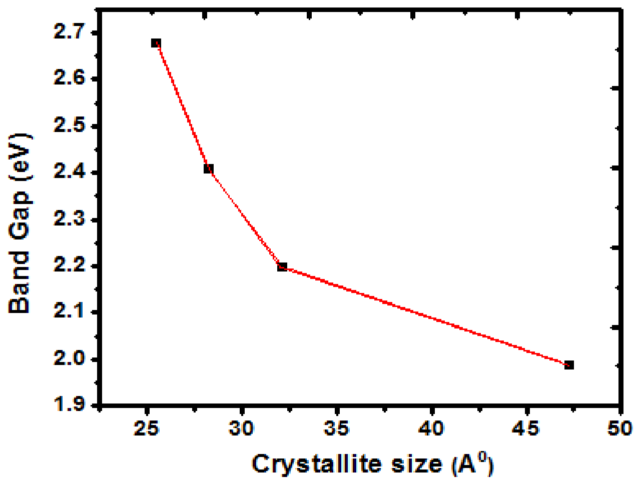


Fig.8: Shows the Variation of Band Gap with Crystallite Size of Cdse As-Deposited and Solar Light Irradiated Thin Films

It is clear from fig.8 the value of band gap decreases with the increase in crystallite size that also indicates the crystallinity of the material is increased.

3.5 Electrical Analysis

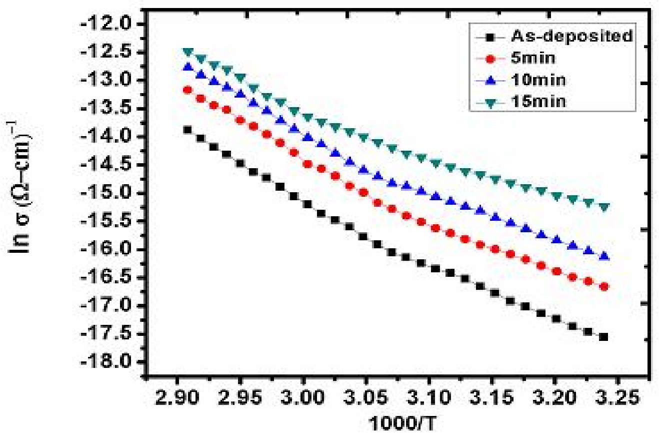


Fig.9. plot of ln (σ) Versus 1000/T of CdSe as-Deposited and Solar Light Irradiation Thin Films

Fig.9. shows the electrical DC conductivity of CdSe as-deposited and solar light irradiation thin films at 325.67 K. deposited on glass substrates with indium electrodes heating from 309K to 370K at a constant voltage of 1.5 V. The DC conductivity of semiconductor glasses can be expressed by Arrhenius relation

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{\Delta E}{KT}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(10)}$$

Where 'σ_0' is the pre-exponential factor related to the material, 'ΔE' is the activation energy, 'K' is the Boltzmann's constant ant 'T' is the temperature. The value of activation energy is estimated from the slope of ln (σ) versus 1000/T plot and eq. (10). The slope was estimated by using the linear fit. From table. (3), it is found that the values of activation energy, DC conductivity and pre-exponential factor decreases after solar light irradiation.

According to Davis Mott [19] the value of pre-exponential factor is useful for determination of electrical conduction mechanism. The value of pre-exponential factor should be about $10^4 (\Omega\ \mathrm{cm})^{-1}$[20] for all conduction in localized states. This is 2-3 orders smaller than for conduction in the extended states. In the present case, the value of 'σ_0' is the order of 10^7 as shown in Table.4. indicates that the conduction is through the extended states [21].

Table.4: Electrical Parameters of CdSe as-Deposited And Solar Light Irradiated thin Films at 325.67 K

Sample	Irradiation Time	$\Delta E(eV)$	$\sigma_{dc}(\Omega\, cm)^{-1}$	$\sigma_0(\Omega\, cm)^{-1}$
CdSe	As-deposited	0.88	1.07×10^{-7}	4.67×10^{7}
	5min	0.85	2.32×10^{-7}	3.19×10^{7}
	10min	0.81	3.62×10^{-7}	1.07×10^{7}

Conclusion

The main aim of irradiation is to dissipate large amount of energy into the material system over a short duration of time changes the properties of the material. Thus it becomes clear from this study that visible light (through magnifying glass) also changes the material properties like laser and swift heavy ion irradiation. X-ray diffraction pattern of CdSe thin films clearly shows the increase in grain size and strain after solar light irradiation indicates the improvement in crystallinity. Also the optical band gap decreases from 2.68 eV to 1.99 eV and electrical measurements the DC conductivity increases after solar light irradiation.

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