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Optimization of different temperature annealed nanostructured CdSe thin film for photodetector applications

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Abstract:

In this report, we have discussed the performance of highly sensitive CdSe based photodetector. The CdSe thin films were prepared by thermal evaporation method on the cleaned glass substrate at room temperature. The influence of post annealing on the optical, morphological, structural and photo-electrical properties at different temperatures were investigated. The formation of polycrystalline CdSe films was confirmed from X-ray diffraction (XRD) and Raman studies. The change in surface morphology along with the average grain size of films were observed by field emission scanning electron microscopy (FESEM). The stoichiometric ratio of Cd and Se elements in the deposited films was verified from Energy dispersive X-ray spectroscopy (EDS). The change in various optical parameters like absorption coefficient (α), extinction coefficient (k), optical band gap (E_g), refractive index (n) etc. of the studied films were calculated from the UV-Visible measurement. Importantly, the band gap values were decreased and increased with different annealing temperatures. The CdSe film annealed at 300 °C showed good photo-response and the corresponding optical properties which make them suitable for photodetector applications.

Keywords: photodetector, CdSe, band gap, refractive index

1. Introduction

In the recent years, several numbers of studies were done on the novel properties of chalcogenide-based semiconductors (band gap between 1-3 eV) as they found applications in many optoelectronic devices [1-3]. In particular, Cadmium Selenide (CdSe) is a part of II-VI elemental group and leading semiconducting alloy due to its direct band gap (~ 1.74 eV at room temperature), good absorption ability, cost effective, p-type conductivity, and excellent photosensitivity [4]. At present, researchers are focused on the development of CdSe based photodetector due to its high performance of photo sensing capability under visible to near IR radiation [5]. The photo-response of the CdSe film mainly depends on the photo generation and/or electron-hole pair recombination by the adsorption of higher incident power energy than the energy gap of the material and also the separation of electro-hole pairs by the external electric fields. Therefore, a CdSe photo-sensing behaviour can possibly enhanced by changing its band gap by tuning different parameters such as, different nanostructures, doping element, growth level, post annealing, etc. Especially annealing could play an important role for enhancing the photoelectric performance because, temperature can change the nanostructure shapes (grain sizes) and reduce the grain boundaries [6].

The physical and chemical properties of CdSe were mainly depending on the deposition conditions and techniques employed in the preparation of the films. In the past few decades, a number of deposition methods were used to fabricate CdSe film, like magnetron sputtering, thermal evaporation, spray pyrolysis, SILAR, chemical bath deposition (CBD) and electro deposition [7-9]. Among them, thermal evaporation is one of the most convenient and high vacuum assisted technique for obtaining uniform film. Also, the thermally evaporated semiconducting films have good mechanical stability due to its high-level of adhesion to the substrate. The rate of deposition was easily controlled by changing its power,

time duration of deposition, concentration of the powder and different substrate; also, it is used for large area thin film for wide range of industrial applications.

Some of the works related to CdSe photodetectors were investigated recently. Jiang et al. [10] prepared the CdSe nanoribbons in horizontal quartz tube by using the simple thermal evaporation technique, and they found the increase of photocurrent but decrease in the response time due to the reduction of recombination centers. Singh et al. [11] reported the solution processed CdSe nanowire (NW) and found the responsivity and detectivity are 0.1 AW^{-1} and 3.1×10^9 (jones) respectively. Also, the responsivity was increased by the increase of bias voltage from 1 to 35 V. Kung et al. [12] studied the CdSe nanowire for tunable photo detection sensitivity by using the lithographically patterned nanowire prepared by electro deposition method and the observed responsivity value was 1.7 AW^{-1} . Shelke et al. [13] reported the spray deposited CdSe films for visible spectral photodetector with the narrow band gap of 1.75 eV. The prepared photodetector showed high responsivity of 4.9 AW^{-1} for its direct optical band gap with very fast response time of 12 ms. Based on the previous reports, we strongly believe that CdSe based semiconducting films will perform well in photo sensor device fabrication under visible light radiation.

Herein, we have demonstrated the CdSe thin films prepared by thermal evaporation method at room temperature. Further, the as-deposited films were annealed at 100°C , 200°C , 300°C and 400°C . The as-deposited and annealed films were characterized by different experimental techniques to investigate the optical, structural, surface morphological, and photo response properties. Mainly, we have studied the photo sensing performance with the help of 532 nm laser. The influence of post annealing on photo detectivity, external quantum efficiency and responsivity of the films were calculated and reported in the present work. In addition, we have briefly studied and reported the linear and non-linear optical properties of the CdSe films for the first time.

2. Experimental with characterizations

The nanostructured CdSe films were deposited onto cleaned glass substrates at room temperature (RT) by using CdSe powder as an evaporation source material in thermal evaporation technique. The film deposition was done on 10 cm × 10 cm glass substrate and for large scale commercial application, the deposition can be done by varying the vacuum chamber. In brief, the deposition chamber was evacuated at 1×10^{-5} Torr. The deposited films were post annealed at 100 °C, 200 °C, 300 °C, and 400 °C respectively under nitrogen gas atmosphere. The topographical (top view), thickness (cross-sectional view) and elemental composition of the films were examined by FESEM (Carl Zeiss Ultra 55) and EDS (Oxford Instruments 50 mm²). The structural behaviour of the films were studied with X-ray diffractometer (XRD) (Rigaku MiniFlex 600) and Raman spectroscopy. The optical data were recorded at room temperature by using a UV–Vis spectrometer (SpectraPro2300i) in the spectral range of 200–1100 nm. The photo-electrical responses of the fabricated films were measured by Xenon arc lamp as a light source (Nova P/N 7Z01500, Ophir) and Keithley 2450 as a source meter.

3. Results and Discussion

3.1 Structural analysis by XRD

Fig. 1 shows the XRD patterns of the as-deposited and different annealed (from 100°C to 400 °C) CdSe thin films. The most intense peak observed at $2\theta = 25.42^\circ$ corresponds to (002) plane and the low intensity peak at $2\theta = 45.90^\circ$ represents (103) plane. The XRD pattern clearly indicates the polycrystalline nature with hexagonal structure (JCPDS No. 08-0459) of the deposited CdSe films [14]. The peak intensity initially increased up to 300 °C annealed film and then it was reduced for higher annealing temperature films. In general, annealing can enhance the grain growth level in to the native lattice due to the reason that periodical arrangement of atoms gets high energy at a particular lattice plane.

Consequently, there is an increasing trend of peak intensity along with increasing annealing temperature. The experimental d-values were calculated from Bragg's relation.

Fig. 1. XRD pattern of CdSe thin films for as-deposited and different annealing temperature

The average crystallite size of the prepared films (~ 12 to 100 nm) were calculated using Scherrer' formula and the obtained values are listed in table S1 (supplementary table). The obtained crystallite size was increased from 24 nm to 28 nm for (002) plane and 12 nm to 14 nm for (103) plane respectively. Thus, the increase in crystallinity of the films with the increase in annealing temperature leads decrease the FWHM value. Moreover, there is no identified impurity peaks related to CdO or others observed from the figure confirming the phase purity of CdSe with respect to increasing annealing temperature.

3.2 Raman analysis

Raman spectroscopy gives information regarding vibrational, electronic states, structural and phonon properties of the materials. The Raman spectra of CdSe films were recorded in the range of 100 – 500 cm^{-1} at room temperature. The standard Raman spectrum of the bulk CdSe sample shows peaks at 210 cm^{-1} and its overtone at 418 cm^{-1} which are referred to the longitudinal optical phonon mode (LO mode) [15]. In the present study, Fig 2.

shows the Raman spectrum of both annealed and as-prepared CdSe thin films. The two strong visible peaks at 203 cm^{-1} and 407 cm^{-1} are due to the confinement of optical phonons in the films. The 1st order LO phonon modes are present at 203 cm^{-1} and there is a shift of 6 cm^{-1} in the wavenumber as compared to the earlier reported values. Similarly, the 2nd order LO phonon modes are present at 407 cm^{-1} and there is a shift of 3 cm^{-1} as compared with the earlier reports. Such small Raman shift observed for both LO and 2LO modes might be due to the strain created in CdSe layers during deposition time [16]. This small change in wave number and LO mode peak broadening may be due to the change in crystallite size of the prepared films. It was observed that the intensity of this peak increased than the as-prepared one with annealing which shows the increase of Cd – Se bonds due to the annealing effect. In addition, all the films have one shoulder peak at around 164 cm^{-1} that corresponds to the contribution of surface optical (SO) vibrations attributed due to phonon confinement [17]. Dzhagan et al. noticed the same surface optical mode at 167 cm^{-1} for CdSe nanocrystals [18].

Fig. 2 Raman spectra of thermal evaporated CdSe thin films with different annealing temperature

3.3 Morphological and compositional analysis

Figure 3 (a-e) shows the FESEM micrographs of as-prepared and post annealed CdSe films. The surface of the film describes the deposited film uniformity (free from pin holes and cracks) and regular barley shape grain characteristics. Also, it clearly shows that the average grain size increased with annealing temperatures and the layers became dense with reduced film thickness (~900 nm to 720 nm) as given in Figure 4 (a, b). Due to the increase in the heat treatment on the materials, the film thickness might have decreased due to the reduction of grain boundaries; resulting the increase of photoelectric performance. Figure 4c presents the elemental compositions of different annealed CdSe thin films. It reveals that as a function of annealing temperatures, there was no significant change observed in their material stoichiometry. A shoulder peak originated at 3.2 keV which is indicating the characteristics L element peak of Cd.

Fig.3. FESEM images of (a) as-deposited and annealed at (b) 100 °C, (c) 200 °C, (d) 300 °C and (e) 400 °C.

Fig.4. EDS images of (a) as-deposited and (b) 300 °C annealed CdSe thin films, (c) elemental composition of each film

3.4 . Linear and non-linear optical properties

3.4.1 Transmittance, absorbance, band gap

To evaluate the linear optical parameters like as absorption, optical energy gap (E_g) and linear refractive index (n), the optical transmittance (T) spectra were collected and plotted in Fig. 5(a). The presence of fringes is because of the interference between the substrate and film surface which shows the homogeneity and smooth nature of the prepared films [19]. The transmitting power of the annealed film decreased and is lowest for the 300 °C annealed film as compared to the as-prepared films. The variation in transmission is due to the different degree of electronic polarizability in the annealed films. This behaviour also indicates the reduction in the transmittance of the film through introducing the structural defects. The optical absorbance spectra of different films are shown in Fig. 5(b) that indicates the rise in absorption capacity of the annealed films. The highest absorption is shown by the 300 °C annealed film which is a potential film as good photodetector.

Fig. 5 (a) Transmission and (b) absorbance spectra of as-prepared and annealed thin films

The fundamental absorption edge for the investigated films has been analysed to know the kind of optical transition and the optical energy gap value (E_g). The related information regarding band gap was calculated from the high absorption region ($\alpha \geq 10^4 \text{ cm}^{-1}$) by Tauc relation [20].

$$(\alpha h\nu) = B (h\nu - E_g)^m \quad (1)$$

where B is the Tauc parameter and depends on the transition probability, h and 'v' are Planck's constant the frequency of the incident photon respectively. The power 'm' possesses different values like 1/2, 2, 3/2 and 3 to determine the kind of electronic transitions. The values are for direct allowed (1/2), indirect allowed (2), direct forbidden (3/2) and indirect forbidden (3) transitions respectively [21]. The obtained data were fitted best for $m=1/2$ which shows the transition in the studied films is of direct allowed type. Fig. 6 shows the plot between $(\alpha h\nu)^2$ vs ' $h\nu$ ' in which the X-intercept gives the value of optical band gap. The bandgap of as-prepared film was 1.996 eV which increased upon annealing as shown in Table 1. This increase in E_g is well explained by Davis and Mott [22] based on the concept of density of state. The thermal energy given to the films annealed out the defects and thus the degree of disorder reduced. So, the decrease in the density of defects reduces the width of

the localized states for which the band gap increased for the annealed films. The 300 °C annealed film possesses the band gap of 2 eV which is good for visible photo detection performance.

Fig. 6. Optical band gap of the prepared CdSe thin films with different annealing temperatures

3.4.2. Linear Refractive index (n)

The first approximated refractive index (n_1) was evaluated by Swanepoel's envelope method [23] in the weak and moderate absorption region by the equation;

$$n_1^2 = [N + (N^2 - S^2)^{1/2}] \quad (2)$$

$$\text{where; } N = 2S \left(\frac{T_M - T_m}{T_M T_m} \right) + \left(\frac{S^2 + 1}{2} \right)$$

where, T_M and T_m and are the maxima and minima of transmittance at certain λ and 'S' represents the glass substrate refractive index (1.51). The actual linear refractive index (n) of the films at different ' λ ' values was evaluated and presented in Fig. 7. The value of ' n ' decreased with wavelength as shown in figure 7 which shows the normal dispersion behaviour of the films. It has been observed that the refractive index varies for different annealing temperatures and is more for the 300 °C annealed film. The increase in refractive index can be interpreted for the increase in polarizability (α_p) values [24]. Since, the increase in

polarizability increases the light polarization which leads to the increase in photocurrent in the materials like Bi_2Te_3 [25].

Fig. 7. Change in refractive index (n) vs wavelength for different annealing temperatures

3.4.3. Single oscillator energy (E_0) and Dispersion energy (E_d)

The dispersion parameters of the thin films give useful information's about its optical behaviour. These parameters are essential for designing spectral analysis devices in optical communications. The concept of single-effective-oscillator model proposed by Wemple–Di Domenico (WDD) [26] was used to measure the dispersion of $n(h\nu)$. The dispersion of 'n', below the absorption band gap ($h\nu < E_g$), relates the dispersion energy (E_d) and single oscillator energy (E_0) by using the relation [27].

$$n^2(h\nu) - 1 = \frac{E_d E_0}{E_0^2 - h\nu^2} \quad (3)$$

The dispersion study gives two important quantities such as; effective single oscillator energy (E_0) and dispersion energy (E_d). The E_0 gives information regarding the overall band structure of the films that is completely different from E_g and also average excitation energy for electronic transitions. Similarly, dispersion energy 'E_d' presents the oscillator strength which is related to the inter band optical transition. E_d measures the average intensity of the inter-band optical transitions, which depends on chemical bonding and charge distribution

within each unit cell. Fig. 8(a) shows the plot between $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ and the straight-line fitting gives the intercept as $\frac{E_0}{E_d}$ and slope as $(E_0 E_d)^{-1}$. The E_0 and E_d values were calculated from the slope and intercept which are given in Table 1. The value of E_0 and E_d are found to be changed with different annealing conditions and more for the 300 °C annealed film. This film is having high oscillator strength which is more stable for the photo detection. The oscillator strength, $f = E_0 E_d$ is presented in Table 1 that shows the highest strength of the film at 300 °C annealing. The static refractive index (i.e. n at $h\nu = 0$) was calculated from the formula

$$\varepsilon_\infty = n_0^2 = \left(1 + \frac{E_d}{E_0}\right) \quad (4)$$

The n_0 value increased like the linear refractive index (n) as shown in Table 1 which is responsible for the change in nonlinear optical parameters [28].

Fig.8 (a) plot of $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ for calculation of E_0 and E_d and (b) plot of n^2 vs λ^2 to calculate N/m^* for the as-deposited and different annealed films

(iii) High frequency dielectric constant (ε_L) and carrier concentration (N/m^*)

In order to evaluate the high frequency dielectric constant (ε_∞) and carrier concentration (N/m^*) in the films, the following formula was used. [29].

$$\varepsilon_1 = n^2 = \varepsilon_L - \left(\frac{e^2 N}{4\pi^2 c^2 \varepsilon_0 m^*}\right) \lambda^2 \quad (5)$$

where ε_1 , e , N , ε_0 , m^* and c denotes the real part of the dielectric constant, charge of electron, free charge carrier concentration, permittivity of free space, effective mass of charge carrier and velocity of light respectively. The linear fitting of the plot between n^2 vs λ^2 as shown in Fig. 8(b) gives ε_L as intercept and N/m^* was calculated from the slope. The obtained values of ε_∞ , ε_L and N/m^* for the films are presented in Table 1. It shows that the value of ε_L varies with variation in the carrier concentration. Though ε_L and ε_∞ represents the same high frequency dielectric constant, but the dissimilarity is because of the change in carrier concentration which could be due to the increase in lone-pair electrons of Se atoms. The $\varepsilon_L > \varepsilon_\infty$ is due to the increase in free charge carrier concentration in the films [30]. The 300 °C annealed film is having the high value of carrier concentration which is good for the photodetector.

3.4.4. Optical conductivity (σ_{opt}) and electrical conductivity (σ_{elec})

The optical and electronic behaviour of the films were evaluated by calculating the optical conductivity (σ_{opt}) and electronic conductivity (σ_{elec}) with the formula involving absorption coefficient (α) and refractive index (n) [31, 32].

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad , \quad \sigma_{elec} = \frac{\lambda n c}{2\pi} \quad (6)$$

The optical conductivity (σ_{opt}) gives information about the electronic state of the materials. Fig. 9(a) depicts the decrease of σ_{opt} with annealing temperature and also increase in wavelength. The high value of σ_{opt} for the 300 °C annealed film is due to the high value of absorption coefficient and linear refractive index. However, the increase in σ_{opt} at 300 °C annealing assures high photo-response and increment of electrons excitation of the films under consideration. The Fig. 9(b) shows the variation of σ_{elec} at different annealing temperatures which shows completely different behaviors than that of optical conductivity.

The σ_{elec} increased with wavelength and shows variation with annealing temperature. Again, the 300 °C annealed film is having the highest electrical conduction.

Fig. 9 Variation of (a) optical conductivity (σ_{opt}) and (b) electrical conductivity (σ_{ele}) with different annealing temperature

3.4.5 Nonlinear optical assessments

The nonlinear optical behaviour of the films is due to the change of the nonlinear polarization signal of a material to the incident radiation which plays an important role in nonlinear optics in recent years. The polarization of the material system is expressed in terms of nonlinearity and well evaluated by utilizing semi-empirical relations involving the film's refractive indices. The 3rd order nonlinear optical susceptibility ($\chi^{(3)}$) is an important factor that decides the of use of a particular material in nonlinear photonic devices [33]. The nonlinear refractive index ' n_2 ' is the material's disproportionate response to the applied electric field. Tichy et al. [34] formulated a rule that takes the linear refractive index ' n ' values and WDD parameters to evaluate the value of $\chi^{(3)}$ and ' n_2 ' by using the following formulas [35]:

$$\chi^{(3)} \cong A (\chi^{(1)})^4 \quad (7) \quad \{\text{where } A=1.7 \times 10^{-10} (\chi \text{ measured in esu})\}$$

In the long wavelength limit ($h\nu \rightarrow 0$), the above equation becomes

$$\chi^{(1)} = (n_0^2 - 1)/4\pi \quad (8)$$

The 'n₂' is related to the third-order susceptibility $\chi^{(3)}$ by the relation

$$n_2 = \frac{12\pi\chi^{(3)}}{n_0} \quad (9)$$

The obtained parameters are given in Table 1 that shows the changes with annealing temperature which is due to the different degree of polarization with annealing. The 300 °C annealed film is having the highest values of nonlinear parameters that makes the material as diffraction free and potential candidate for photodetector.

Table 1: Optical parameters of the prepared CdSe films with different annealing

Optical parameters	As-prepared	100 °C	200 °C	300 °C	400 °C
Thickness (nm)	900	837.1	828.7	720	703.6
Band gap (E _g) eV	1.996	1.999	2.001	2.003	2.093
Dispersion or strength energy, E _d (eV)	21.10	34.57	22.46	38.65	29.85
Effective single oscillator energy, E _o (eV)	4.72	4.75	4.49	4.98	4.79
Oscillator strength f=E _d E _o	99.59	164.2	100.84	192.47	142.98
Static refractive index (n ₀)	2.33	2.87	2.44	2.96	2.68
High frequency dielectric constant $\epsilon_\infty = n_0^2$	5.428	8.23	5.953	8.761	7.182
Dielectric constant of the lattice (ϵ_L)	6.43	9.87	7.13	10.52	8.49
Carrier concentration (N/m ³) in cm ³ gm	7.82x10 ³⁸	10.94x10 ³⁸	8.58x10 ³⁸	13.86x10 ³⁸	10.08x10 ³⁸
First order nonlinear optical susceptibility (χ^1)	0.353	0.576	0.394	0.618	0.492
Third order nonlinear optical susceptibility (χ^3) in esu	2.63x10 ⁻¹²	18.71x10 ⁻¹²	4.09x10 ⁻¹²	24.79x10 ⁻¹²	9.96x10 ⁻¹²
Nonlinear refractive index (n ₂) in esu	4.25 x10 ⁻¹¹	24.5 x10 ⁻¹¹	6.31 x10 ⁻¹¹	31.5 x10 ⁻¹¹	14.01 x10 ⁻¹¹

3.5 Photodetector analyses

We have prepared the CdSe based photodetectors for the detection of the visible light radiation for photo-sensor applications. Fig. 10 illustrates the schematic diagram of CdSe film-based photodetector device. To investigate the photoelectric performance, the suitable

light intensity was vertically incident on the prepared detector and the photocurrent was being observed at room temperature. Contact electrode (silver paste) was used on both sides of CdSe film surface to measure the photocurrent with respect to different bias voltage.

Fig. 10 Schematic diagram of the CdSe photodetector under visible light illumination.

The photocurrent performance of the constructed CdSe detectors were measured using ~532 nm light illumination. Fig. 11 shows the typical current–voltage (I–V) characteristics for both in dark and illumination of the CdSe films. The I–V spectra shows that all the prepared films exhibit similar behavior though it differs the order of magnitude with respect to annealing temperature. After illumination, the observed photocurrent value significantly increased with respect to bias voltage and is higher than that of the corresponding dark current. This increase in photocurrent is due to excitation of electron–hole pairs in the CdSe detector as a result, there is an increase of the conductivity. The consistent increase of photocurrent with increasing annealing temperature is attributed to the generation of more electron-hole pairs caused by the decrease of grain boundaries. The highest photocurrent was observed at 300 °C annealed film due to its low band gap and high crystallinity than that of the other films [36].

In common, the high crystallinity with uniform grains, low band gap and high absorption in the visible spectral line could help to enhance the photo-response for any semiconducting materials. The following investigations are necessary to understand the photoelectric

performance of the prepared CdSe detector. Responsivity (R) is one of the most important factor for any photodetector. R values were determined from the ratio of induced photocurrent with respect to the power of incident light by the equation [37].

$$R = \frac{I_p}{A \times P_{in}} \quad (10)$$

where, A is the area of the prepared CdSe detector, I_p is the photocurrent and P_{in} is the power of incident light. Figure S1 (supplementary figure) shows the variation of R with respect to different annealed CdSe films and the obtained values were given in table 2. It was found that

Figure 11 *I-V* characteristics of the fabricated CdSe photodetector measured both in dark and illumination conditions at a bias voltage between -5 V and +5 V.

the values increased from 0.0033 AW^{-1} to 0.011 AW^{-1} for increasing the annealing temperature up to $300 \text{ }^{\circ}\text{C}$ while it reduced slightly to 0.0038 AW^{-1} for higher annealing temperature ($400 \text{ }^{\circ}\text{C}$). The observed high R value is due to a higher electron-hole pair

generation by its low band gap. Previously, Shkir et al. [38] observed the maximum R of 2.71 AW^{-1} for 5 at. % Pr doped CdS thin film. Shelke et al. [13] reported the maximum R of 4.9 AW^{-1} for CdSe thin films at the power intensity of 40 mWcm^{-2} and 0.803 A/W for MoSe_2 at the power intensity of 40 mWcm^{-2} [39]. In the present work, we observed a maximum responsivity i.e 0.011 AW^{-1} which is reasonable better even at minimum power intensity at 5 mWcm^{-2} . In addition, the responsivity of the annealed film is one order higher than the as-deposited film.

Detectivity (D^*) is one of the other main factors which is used to understand the sensitivity of the CdSe. The higher value of D^* indicates the sensible capability in particular light intensity/or corresponding wavelength. The D^* can be expressed by the equation [40] using the value of responsivity.

$$D^* = R \sqrt{\frac{A}{2eI_d}} \quad (11)$$

here, I_d and e represents the dark current and electron charge, respectively. The D^* values are given in table 2 and the annealed film exposed the maximum D^* value (1.27×10^{10} jones) as compared to the as-deposited film (3.88×10^9 jones). The estimated D^* value of the prepared CdSe photodetector is almost close (even at very low power intensity 5 mWcm^{-2}) to the previous reported value (7.9×10^{11} Jones) for 40 mWcm^{-2} [39].

The external quantum efficiency (EQE) can be determined by the equation [41]; it provides the amount of conversion of the incident photons to electric current [42].

$$EQE = \frac{Rhc}{e\lambda} \quad (12)$$

where, h is the Planck's constant, c is the velocity of light and λ is the wavelength of incident light. The calculated EQE values are listed in table 2 and the values increased gradually with increasing annealing temperature. The increasing trend of EQE is may be due to the increase in carrier mobility of the films. This might be due to the increase of responsivity revealed

from the prepared CdSe based visible detector. However, the value of EQE is reasonably low than the previous reports [39]; due to its low film thickness and responsivity. Linear Dynamic Range (LDR) is also one of the key factors to realize the photodetector performance; and it

can be calculated by the relation $LDR = 20 \log \left(\frac{I_{\min}}{I_{\max}} \right)$ [43]. Here, $I_{\min}$ and $I_{\max}$ denotes the minimum in dark current and maximum in light current, respectively. The observed LDR of the prepared CdS: Al detector is 27 dB, which is reasonably close to the reported CdSe detector (37 dB) [39]. The obtained minimum LDR value can represents the low ratio of photocurrent and dark current. We believe that the LDR value can be increased by increasing the ratio of current in both dark and light in future.

Mechanism of photodetector: In air condition, the mechanism of photodetector under dark and light can perform by the adsorption and desorption of oxygen and H₂O on the film surface. Under dark condition, CdSe surface adsorbs the oxygen and H₂O molecules from the atmospheric air which trap the electron from the conduction band; thereby creating a depletion layer with low conductivity near the CdSe film surface and further the earlier depletion layer is widened. Upon illumination condition, electron–hole pairs are generated as the photon energies above than the CdSe bandgap energy. This is because of the desorption of oxygen due to trapping of photo-generated holes as well as the direct photo-excitation of the captured electron from the conduction band (CB) [44]. The photon-generated holes transfer to the surface by the desorption of oxygen [$O_2^- + h^+ - O_2 (g)$] from the CdSe surfaces [45]. This process is continuing until the desorption of O₂ reaches a stable state, as a result there is an increase of electron and holes until saturation during illumination. The desorption process can follow the above band/ and below band energy illuminations. Based on the observed CdSe band gap (~2.0 eV) which is opted for the above band energy illumination; accordingly, the electron and holes are directly generated in conduction band. The functions

of both electron-hole pair generation and direct photo-excitations were gradually increased with respect to increase of different power intensity; resulting increase the photocurrent.

Figure 12. Plots of current Vs. time of CdSe photodetector using different power intensity from 1 mW/cm^2 to 5 mW/cm^2

The transient photocurrent investigation is necessary to understand the photodetector performance of the prepared CdSe films. Time dependent photocurrent was performed with respect to different light intensities from 1 to 5 mW/cm^2 as given in Fig 12. When the light

interacts with the prepared film surface (ON light), the current level is quickly increased due to increase of the photo-generated charge carriers; while it decreased rapidly and reached to the base current when the light is turned OFF. Figure 12 revealed that the current level increases gradually with the increase of light intensity from 1 mW/cm² to 5 mW/cm². The photocurrent rise time and decay time can also be analyzed from the time dependent photocurrent measurement. The total time required to rise the photocurrent up to 90% from the base current called as rise time (τ_{ris}) whereas the total time taken to reach 10% of photocurrent from the maximum current is called as the decay time (τ_{dec}). The obtained both rise and decay times for as-deposited and different annealed CdSe films are listed in table 2. In our case, both the rise time and decay time of CdSe (300 °C) film is found to be 1 s and 2 s, respectively, which is quite faster than the previous report [46] for CdSe nanorods.

Table.2 Observed photo sensor parameters of the prepared CdSe thin film detectors.

CdSe thin films	Responsivity (A W⁻¹)	Detectivity (Jones)	External quantum efficiency (EQE) (%)	Rise time	Decay time
As-dep	0.0033	3.88×10 ⁹	0.77	1.2 s	2.1 s
100 °C	0.0040	7.29×10 ⁹	0.94	1.2 s	2.1 s
200 °C	0.0053	7.45×10 ⁹	1.25	1.1 s	2 s
300 °C	0.011	1.27×10 ¹⁰	2.67	1 s	2 s
400 °C	0.0038	5.56×10 ⁹	0.90	1 s	2.2 s

4. Conclusions

CdSe thin films were successfully deposited on glass substrates by using thermal evaporation method. The XRD diffractograms indicated that the polycrystalline films are

oriented along (002) and (103) plane. The SEM micrograph revealed the uniform distribution of the deposited films (free from cracks or pin-holes). EDS analysis showed that the CdSe thin films contain Cd, and Se with appropriate quantities. The energy band gap was found to be increasing from 1.996 eV to 2.093 eV with annealing. Further, the films were analyzed for photodetector performance and the various parameters such as photo responsivity (R), photo detectivity (D), external quantum efficiency (EQE) were calculated. The 300° C annealed CdSe film exhibited the highest photo-detectivity of 1.27×10^{10} Jones. Importantly, it shows remarkably faster response time and decay time under the visible illumination. From the complete analysis, we believe that the prepared CdSe thin films can be used as an effective material for visible photodetector applications.

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Supplementary figure

Fig. S1 Variations of responsivity (R), linear dynamic range (LDR) and detectivity (D^*) with respect to different annealed CdSe films

Supplementary table

Table -S1 Structural parameters of CdSe thin films with different annealing temperatures

Annealing Temperature (° C)	2 θ (Deg)	d (Å)	D (nm)	hkl
RT	25.49	0.31285	25.74	002
	45.91	0.60096	14.19	103
100 °C	25.48	0.29379	27.41	002
	45.92	0.64186	13.29	103
200 °C	25.51	0.3325	24.22	002
	45.94	0.64004	13.33	103
300 °C	25.48	0.28994	27.82	002
	45.93	0.682	12.51	103
400 °C	25.474	0.2782	28.95	002
	45.91	0.63584	13.41	103

RT-room temperature; D-crystallite size; 2 θ -angle; d-inter-planar distance; hkl-miller indices

Declaration

We certify that the manuscript, or any part of it, has not been published and will not be submitted elsewhere for publication while being considered by “**Inorganic and Organometallic Polymers and Materials**”, There is no conflict of interest in the work.

Thanking You.

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