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# Structural, Optical and Electrical Properties of Neodymium doped CdSe Thin Film

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**Abstract:** CdSe is a II-VI group material which has various applications in different areas of physics, such as display devices, solar cells, photodetectors, electro photography and lasers. The pure and different volumes of neodymium (Nd) doped CdSe thin films are prepared onto glass slides by chemical bath deposition method. The structural property shows the cubic structure of pure and Nd doped prepared thin film materials and the average crystal sizes 22.61 and 15.82nm for pure and Nd doped CdSe materials respectively. The optical bandgap energy were obtained in the range 1.98 and 2.02eV for pure and different volumes of Nd doped CdSe films. The electrical property shows the semiconducting behavior of the films. The samples also give increased dark current in the presence of neodymium. The absorption spectra exhibit the absorption of solar spectra in the visible range.

**Keywords:** Thin film, XRD, SEM, optical and electrical properties.

## 1 Introduction

II-VI semiconductor materials are very important because of their size and shape dependent properties. The nanomaterials have high surface to volume ratio and this property enhances the different properties of the materials. This surface property has a strong impact on their structural and optical properties. It also plays an important role in several applications like electronic and optoelectronic devices [1]. Among all the materials of II-VI group, the cadmium selenide (CdSe) has received more attention. It has great fundamental, experimental and applied interest [2]. The CdSe nanocrystals will be useful in the fabrication of PV cells [3], lasers [4], TFTs [5], light-emitting diodes [6] and other nanoscale devices [7].

The cadmium selenide thin films have been prepared using different methods, such as chemical bath deposition (CBD) [8], electro deposition [9] molecular beam epitaxy [10], spray pyrolysis [11], successive ionic layer adsorption and reaction [12]. The chemical bath deposition method is a low cost and a simple way to deposit large area nanocrystalline as well as polycrystalline metal chalcogenide thin films. The properties of materials prepared by CBD method depends on various preparation parameters, such as concentration of metal ions, deposition time, deposition

temperature, the pH of resultant solutions etc. [13].

In the present work, pure and neodymium doped CdSe thin films were prepared by using CBD method at 70°C for 6 hours. The different characterization studies like, XRD, SEM, optical and electrical properties are discussed. This is the first attempt of Nd doping on CdSe film prepared by chemical bath deposition technique and its effect are discussed in this paper.

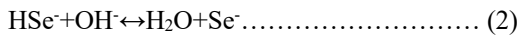
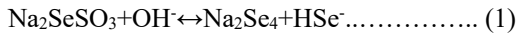
## 2 Experimental Sections

### 2.1 Materials

The glass slide (75mm×25mm×2mm) has been used as a substrate and it is cleaned using nitric acid and deionized water. Cleanliness of the substrates used is very important in the film deposition. The cadmium acetate aqueous solution was used as a cadmium source and freshly prepared sodium selenosulphate (Na<sub>2</sub>SeSO<sub>3</sub>) was used as a selenium ion source. The cleaned glass slide was dipped in the beaker making an angle 20° with the wall of the beaker. The bath temperature was maintained at 70° C for 6 hrs of deposition time. The film deposited glass slide was then removed from the beaker and is gently washed with doubled distilled water to remove any loosely adhered CdSe particles on the surface. The glass slide film dried in

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air. The as-deposited film was uniform and well adherent to the substrate. A red-orange color thin film formed. Similar procedure were followed for doped CdSe thin films. The thin film formation mechanism is described as:



### 2.2 Deposition Method of Microsoft Word

Chemical Bath deposition method is used.

## 3 Results and Discussion

### 3.1 XRD Studies

The pure and Nd doped CdSe films were structurally characterized using Pan Analytical X' Pert PRO MRD was used for X- Ray diffraction studies. Obtained peaks were co-related with JCPDS files No. 19-191 and 65-2891 and lattice constants by calculation and their comparison with the reported values. The different assigned peaks are mentioned in the figure and were found to match prominently with these three cubic planes, (111), (220) and (311) of cubic crystal structures. This orientation of crystal planes and structural details of the deposited films were estimated using Bragg's equation: from the diffraction peaks,

$$2d \sin \theta = n\lambda \dots\dots\dots (3)$$

where n is the order of the corresponding reflection, λ is the wavelength of X-rays, d is the atomic spacing and θ is characteristic angle.

Lattice constants are then calculated for observed peaks. The lattice parameter 'a' for the cubic structure is calculated using the relation:

$$a = d_{hkl} (h^2 + k^2 + l^2)^{1/2} \dots\dots\dots (4)$$

Average particle sizes (D) in the films deposited were calculated from the highest intensity peak of the obtained XRD pattern using Debye-Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \dots\dots\dots (5)$$

where D is the particle size of CdSe nanoparticles, λ is the X-ray wavelength (1.5406 Å), θ is Bragg diffraction angle, β is the full width at half-maximum (FWHM) of the peak, and k- is a constant having a value of 0.94.

The dislocation density δ was calculated by Williamson and Smallman's formula,

$$\delta = \frac{1}{D^2} \text{lines}/\text{m}^2 \dots\dots\dots (6)$$

And microstrains calculated by the formula

$$\varepsilon = \beta \cos \frac{\theta}{4} \dots\dots\dots (7)$$

Fig. 1(a) presents the XRD diffractograph (2θ vs I curve) of undoped CdSe film deposited on a glass substrate. The peaks correspond to angles 26.56°, 42.29° and 46.41° of CdSe material respectively. The highest intensity reflections is obtained along the (111) plane and two weak reflections are along the (220) and (311) planes. These results confirm that the films prepared were crystalline and composed of cubic phase of CdSe with preferred orientation along the (111) plane [14]. The average crystallite size, dislocation density and micro strain parameters are presented in Table1.

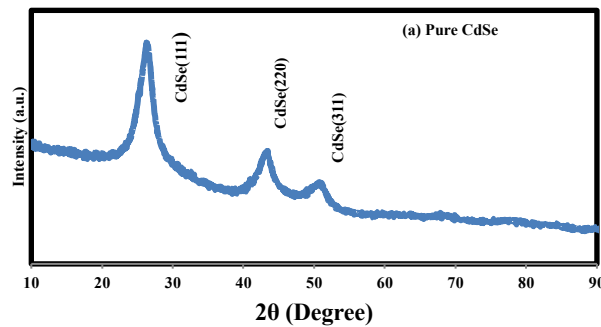


Fig.1 (a): XRD pattern of undoped CdSe.

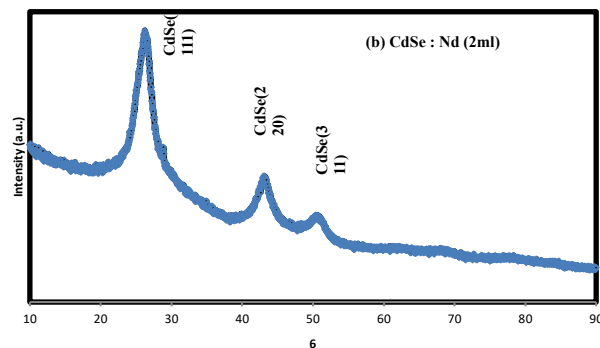


Fig.1 (b): XRD pattern of CdSe :Nd, 2ml.

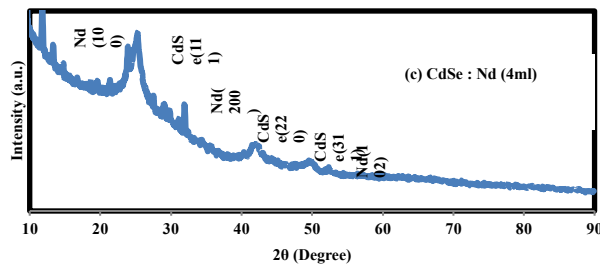
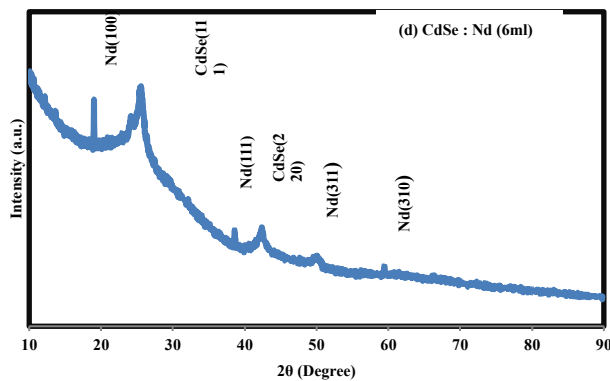
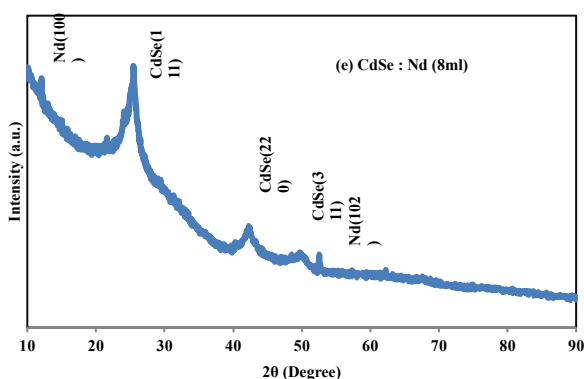


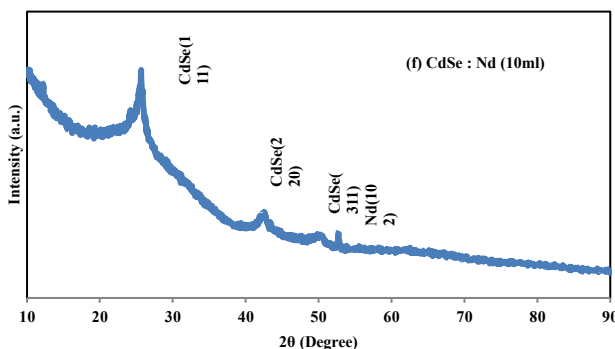
Fig.1 (c): XRD pattern of CdSe :Nd, 4ml.



**Fig.1 (d):** XRD pattern of CdSe :Nd, 6ml.



**Fig.1 (e):** XRD pattern of CdSe :Nd, 8ml.



**Fig.1 (f):** XRD pattern of CdSe :Nd, 10ml.

Additional peaks appear at around  $12^\circ$ ,  $32^\circ$  and  $52^\circ$  in the XRD pattern of Nd doped CdSe films when prepared with  $\text{Nd}(\text{NO}_3)_3$ . New peaks corresponding to  $\text{Nd}^{3+}$  are designated in the X-ray diffractographs. Doping of Nd in the host CdSe causes an increase in FWHM and slight reduction in peak intensity peaks. The XRD spectra of Nd doped CdSe nanocrystalline films at different volumes are presented in Fig.6.1 (b-f). For these films too, the dominant peaks observed were well associated to (111), (220) and (311) of

cubic CdSe crystal. This indicates the increase in nanocrystallinity of thin film with an addition of  $\text{Nd}(\text{NO}_3)_3$  in the bath solution. With doping of 2ml to 10ml (0.01M) of  $\text{Nd}(\text{NO}_3)_3$ ; broadening of (311) peak is obtained and peak's intensity slightly decreases. This change in the feature of diffractographs and the measure of FWHM leads to a subsequent change in lattice parameters, crystallinity and crystal sizes. The position of peak also shifted a bit in comparison to that of undoped CdSe as shown in Fig.6.1 (b). As the volume of dopant is increased to 4ml and further, few additional peaks appear in the XRD pattern which represents the presence of Nd planes. This also confirms the doping of Nd in the prepared sample. Amorphousity seems to increase with doping in CdSe films as expected for crystalline films. Increase in doping concentration further enhances this effect as shown in Fig 6.1(c-f) till 6ml volume of  $\text{Nd}(\text{NO}_3)_3$  but as the doping concentration increases in the film to 8ml and 10ml of  $\text{Nd}(\text{NO}_3)_3$ ; the effect seems to diminish and again FWHM decreases for the most dominant phase.

The XRD spectra of different volumes (2, 4, 6, 8, 10 ml, 0.01 mol) of Nd doped CdSe nanocrystalline films are presented in Fig.1 (b-f), respectively. New peaks appear in XRD pattern due to incorporation of Nd in CdSe host lattice, whereas variation in intensity of diffraction peaks were noticed. The dislocation density  $18.64 \times 10^{16}$  lines/cm calculated for undoped CdSe films for (311) peak, increases significantly to  $41.30 \times 10^{16}$  lines/cm for CdSe:Nd films for 2 ml doping of Nd. Similar change is observed for increased doping volumes of Nd as presented in table 1. The micro strain decreases for CdSe:Nd films as compared to undoped CdSe. Possibly the atomic bonding gets affected in the presence of Nd. Microstrain slightly increases for further doping volume of Nd.

The crystallite size were calculated and average over all the diffraction peaks for undoped CdSe; decreases slightly to few nanometers for CdSe:Nd films.

### 3.2 SEM Studies

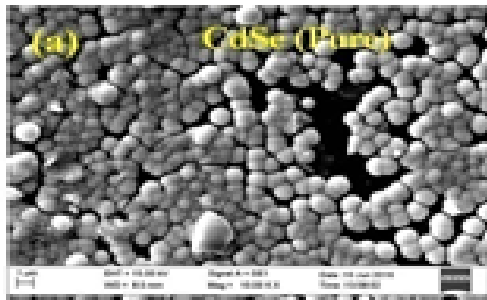
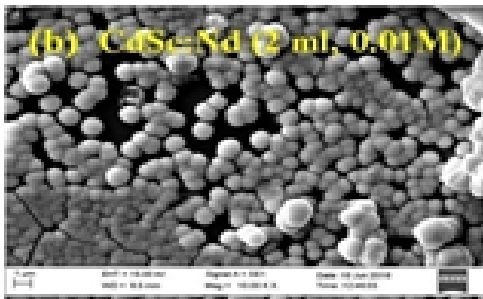
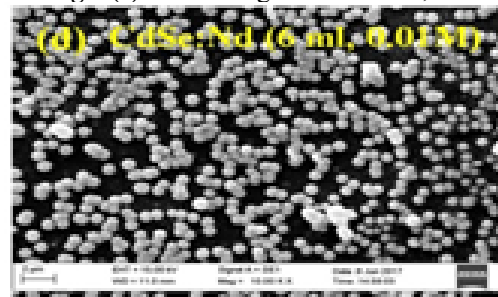
Analysis of surface morphology and approximate particle sizes were estimated from the scanning electron micrographs of pure and Nd doped CdSe. Micrograph of undoped CdSe thin films (Fig. 2(a)) shows homogenous, uniform, dense and well adherent to substrate surface consisting of spherical ball type structures. It might be considered as particles of 10-20 crystallites having diameter around 10-12nm. These small spherical grains are interconnected with each other forming large surface area. The size of the particles are found to almost similar even after doping with  $\text{Nd}(\text{NO}_3)_3$ . The substrate to is almost covered with the prepared films.

### 3.3 UV-Visible Spectroscopy Study

The absorption onset is observed at around 636nm, which is some 70-80nm blueshifted when compared to the reported values.

**Table 1:** Structural parameters of Undoped and Nd doped CdSe thin films.

CdSe:Nd concentration (0.01 Mole)	$2\theta$ ( $^\circ$ )	(hkl)	Dislocation density ( $\delta$ ) $\times 10^{16}$ lines/cm	Micro strain ( $\epsilon$ ) $\times 10^{-3}$	Crystalline size (nm)	Average Crystal size (nm)
CdSe (Pure)	26.56	111	20.9458	4.2250	21.85	22.61
	42.29	220	19.2030	5.5625	22.82	
	46.41	311	18.6433	1.2451	23.16	
CdSe:Nd (2ml)	26.01	111	19.8589	0.6713	22.44	20.20
	42.58	220	19.5614	0.9609	22.61	
	46.41	311	41.3029	0.7260	15.56	
CdSe:Nd (4ml)	25.33	111	16.9212	1.4575	24.31	15.82
	42.96	220	61.6114	2.6806	12.74	
	50.54	311	92.4556	8.3403	10.40	
CdSe:Nd (6ml)	25.34	111	30.4904	4.6658	18.11	22.09
	42.05	220	12.1574	4.2634	28.68	
	47.11	311	26.3525	3.2314	19.48	
CdSe:Nd (8ml)	25.45	111	14.1544	4.7026	26.58	28.28
	41.94	220	12.1151	2.5439	28.73	
	47.64	311	11.4599	4.5252	29.54	
CdSe:Nd (10ml)	25.61	111	13.2617	3.9798	27.46	25.38
	41.86	220	12.0815	3.3152	28.77	
	47.11	311	25.2265	3.6144	19.91	

**Fig.2 (a):** SEM image of undoped CdSe.**Fig.2 (b):** SEM image of CdSe :Nd, 2ml.**Fig.2 (c):** SEM image of CdSe :Nd, 4ml.**Fig.2 (d):** SEM image of CdSe :Nd, 6ml.

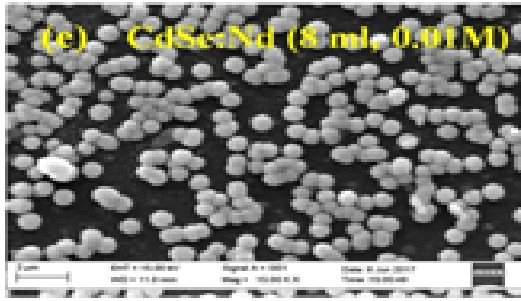


Fig.2 (e): SEM image of CdSe :Nd, 8ml.

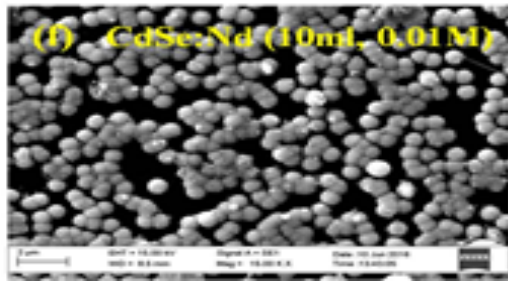


Fig.2 (f): SEM image of CdSe : Nd, 10ml.

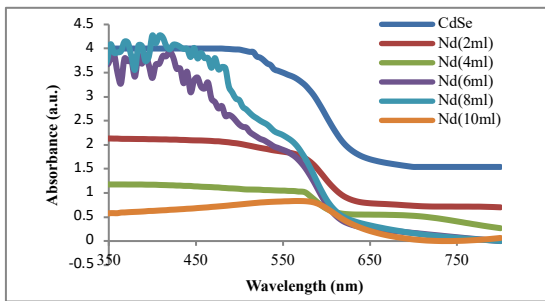


Fig.3: Comparative absorption plot of undoped and different volumes of Nd doped CdSenanocrystalline

Fig.3 presents the absorption spectra of pure and different volumes of Nd doped CdSe:Nd films. All undoped and doped CdSe films shows large amount of absorption in visible and near UV region. Absorbance in infrared, visible and near UV region decreases for CdSe:Nd, 2ml and 4ml concentration of Nd(NO<sub>3</sub>)<sub>3</sub>. It is again found to increase for 6ml, 8ml of Nd(NO<sub>3</sub>)<sub>3</sub>.

The absorption data were analyzed for estimation of band gap using relation

$$\alpha h\nu = C(h\nu - E_g)^n \dots\dots\dots(8)$$

where  $\alpha$  is absorption coefficient,  $h\nu$  is photon energy,  $E_g$  is band gap energy and  $C$  is constant.  $n$  is an integer having values  $\frac{1}{2}$ , 2,  $\frac{3}{2}$  and 3 for allowed direct, forbidden direct, indirect and allowed indirect, respectively. Tauc's plot between  $(h\nu)$  and  $(\alpha h\nu)^2$  is plotted to analyse the nature of transition and band gap using the formula given below.

Table 2: Film thickness for undoped and different volumes of Nd doped nanocrystalline thin films.

S.No.	Sample	Thickness (nm)
1	UndopedCdSe (prepared)	620
2	CdSe:Nd (2ml, 0.01 mol)	600
3	CdSe:Nd (4ml, 0.01 mol)	540
4	CdSe:Nd (6ml, 0.01 mol)	515
5	CdSe:Nd (8ml, 0.01 mol)	480
6	CdSe:Nd (10ml, 0.01 mol)	435

Film thickness reduces with increasing the doping volume. Tauc's plot between  $h\nu$  and  $(\alpha h\nu)^2$  were obtained from absorption data using equation (8) for the prepared thin films and presented in Fig. 4 (a-f).

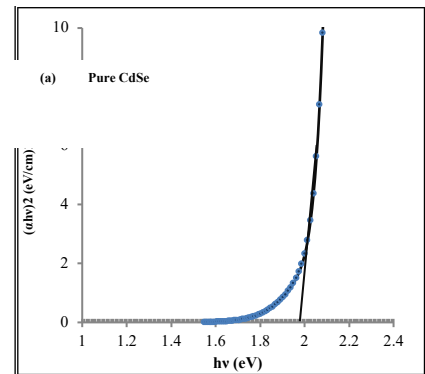


Fig.4(a): Tauc's plot for undopedCdSe.

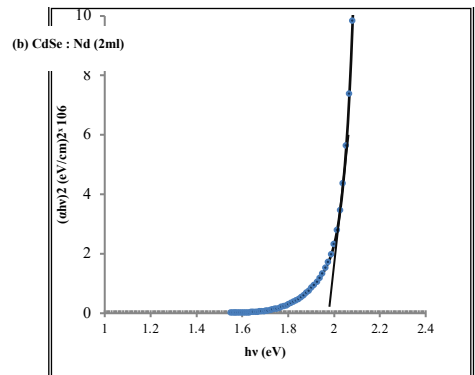


Fig.4(b): Tauc's plot for CdSe : Nd, 2ml.

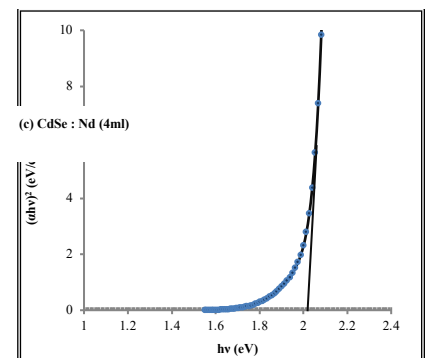
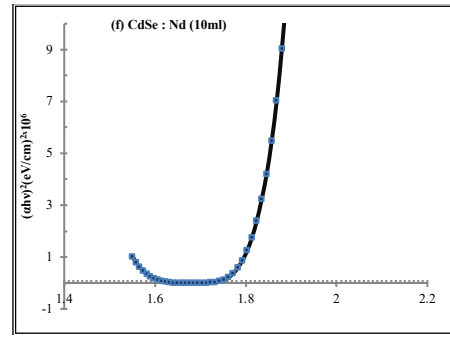


Fig.4(c): Tauc's plot for CdSe :Nd, 4ml.



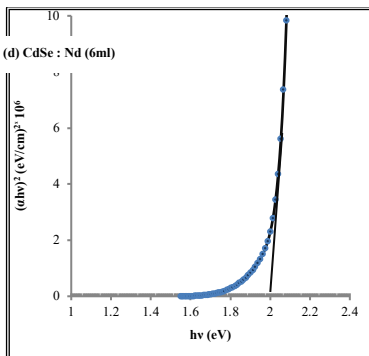
**Table 3:** Energy bandgap of undoped and Nd doped CdSe nanocrystalline films with different Nd concentration.

S.No	Sample	Band gap (eV)	Change in Bandgap ( $E_n - E_b = \Delta E_g$ )	Particle size /radius (nm)
1	UndopedCdSe (reported)	1.74	-	-
2	UndopedCdSe (prepared)	1.98	0.24	10.3
3	CdSe:Nd (2ml)	1.99	0.25	10.09
4	CdSe:Nd (4ml)	2.02	0.28	9.54
5	CdSe:Nd (6ml)	2.00	0.26	9.34
6	CdSe:Nd (8ml)	2.00	0.26	9.34
7	CdSe:Nd (10ml)	1.84	0.1	15.96

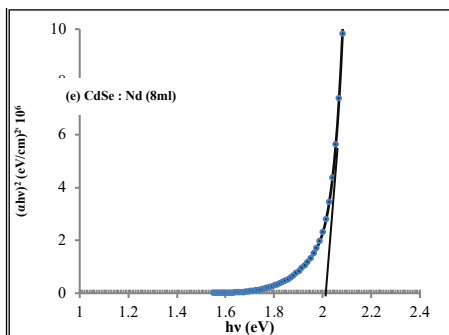


**Fig.4(f):** Tauc's plot for CdSe : Nd, 10ml.

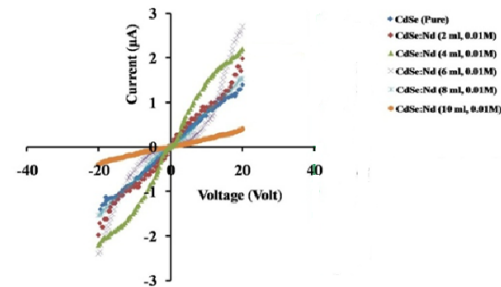
Figure 4 (a-f) presents the Tauc's plot for pure and different volumes of Nd doped CdSe thin films. Table 3 enlists energy bandgaps estimated from Tauc's plot. From these values, blue shift is observed when compared to the reported values for all undoped and doped CdSe films. Similar results are found for undoped CdSe film. The blueshift initially increases for increasing volume of Nd doping. It gets saturated at 6ml volume of Nd(NO<sub>3</sub>)<sub>3</sub>, however band gap decreases to 1.85eV which is smaller than 1.95eV for undoped films when doping concentration increases beyond 8ml. Increased band gap values for the undoped and doped films are indicative of the decreased crystallite sizes of the prepared films. Estimated and calculated values of particle size are presented in Table 3.



**Fig.4(d):** Tauc's plot for CdSe : Nd, 6ml.



**Fig.4(e)** Tauc's plot for CdSe : Nd, 8ml.

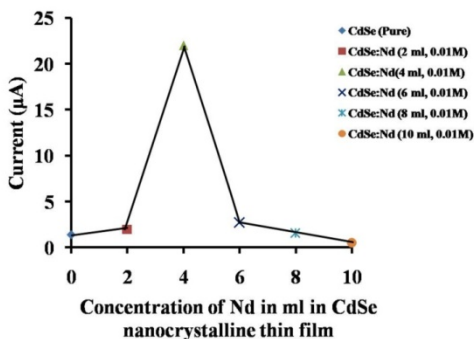


**Fig.5:** Current–voltage (I–V) characteristics curve obtained for undoped and different volumes of Nd doped CdSe thin films without illumination.

The I-V plots for all films appear as straight lines as shown in Fig.5. The linearity of the plots suggests formation of ohmic contact at metal-semiconductor (Ag/CdSe and Ag/CdSe:Nd) junction. It indicates that the work function of metal Ag is higher than semiconductor CdSe. This points out that the Fermi level of Ag aligns with the upper band edge of valence band of CdSe.

As the doping volume increases from 2ml to 4ml volume of Nd(NO<sub>3</sub>)<sub>3</sub>, the dark current from the junction increases and is found maximum for 4ml doping volume. Further, by increasing the doping volume of Nd(NO<sub>3</sub>)<sub>3</sub> the dark current

through the junction decreases. Maximum current 22.5μA is found for 4 ml Nd doping.



**Fig.6:** Variation of dark current with doping volume of Nd in CdSe :Nd films.

The electrical resistivity ( $\rho$ ) of the deposited thin film was calculated using the relation.

$$\rho = 2\pi s \frac{V}{I} \dots\dots\dots(10)$$

$$\rho = 2\pi s/sl \dots\dots\dots (11)$$

Here, s is the distance between inner pair of electrodes is 2mm.

And V/I can be calculated from I-V curve and is equal to inverse of the slope of I-V curve.

The resistivity calculated from eq.10 for undoped CdSe thin film is  $0.2 \times 10^5 \Omega\text{-m}$  and for CdSe:Nd (4ml) is  $0.18 \times 10^5 \Omega\text{-m}$ .

### 4 Conclusions

PureCdSe and Nd doped CdSe thin films were prepared by using chemical bath deposition method. The structural studies imparts information about the cubic structure of the prepared materials. The particle size is found to vary with Nd doping. The optical absorption study shows the absorption in visible and UV region. In the presence of rare earth  $\text{Nd}(\text{NO}_3)_3$ , dark current is found to increase (electrical studies).

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