Effect of Deposition and Annealing Temperatures on Physical Properties of CdSe Nanoparticles Thin Film for Solar Cell Applications.

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Abstract

High quality nanoparticles Cadmium Selenide, CdSe, thin films were prepared by Chemical Bath Deposition (CBD) technique. The films were deposited on glass substrate at different bath temperatures, using cadmium chloride as 〖Cd〗^(+2) ion source and sodium selenosulphite as 〖 Se〗^(-2) ion source. The pH of the bath was kept constant around 11 ± 0.1. The air annealed film at different temperatures for 1h was included in this work. The effect of chemical bath temperatures and annealing in air on structure and optical properties were studied. The structural properties were studied by X-ray diffraction for all thin films and revealed a Polycrystalline nature with cubic structure having preferential orientation along (111) plane direction. The calculated crystallite size was found to be between 4.902 nm and 7.937 nm, and this indicates that all the prepared CdSe thin films are nanoparticles. It has been found that crystallite size increases with increasing deposition temperature and annealing temperature. Optical properties were studied by UV-vis spectrophotometer for all films, which shows blue shift in the peak. The values of the energy gap (allowed direct transitions) calculated from the absorption spectra, were between 2.2 and 3 eV, in contrast to the bulk, energy gap which is 1.74 eV. The temperature dependence of electrical resistivity of CdSe nanoparticles (at powder form) measured in the temperature range of 300- 455 K. The electrical measurement results show that the electrical resistivity of the samples decreases with temperature down to 4.5× 〖10〗^5 Ω cm at 455 K.

Keywords: *Chemical Bath Deposition, Effect of Deposition temperature, Annealing effect.*

1: Introduction

Semiconductors are very important and interesting because of their technological applications in optoelectronics and microelectronic devices like photodiodes, sensors light emitting diodes, solar cells, photoelectrochemical cells, photovoltaic cells and photodetectors for optical communications etc. [Shinde et al., 2014]. Among them, Cadmium Selenide (CdSe) is II-VI group compound semiconducting material of the periodic table. The transition metals find greater solubility in II–VI compound semiconductors when compared with III-VI semiconductors. Among II–VI semiconductors, cadmium selenide (CdSe) is a well-known semiconductor, crystallizing in either the wurtzite or the zinc blende structure. This compound is a highly photosensitive material in the visible region due to their suitable band gap (1.74 eV). Different processes such as chemical vapour deposition [HEGAZY et al., 2019], physical vapour deposition, thermal evaporation technique, spray-pyrolysis, chemical bath deposition, dip coating and electrodeposition, have been used for depositing cadmium selenide thin films [Purohit et al., 2015]. However, the electrodeposition process is one of the simplest and low-cost techniques because it is easy to manage and it requires a very simple arrangement. Deposition rate is easily controlled by changing deposition potential, concentration and pH value of the electrolyte. The optoelectronic, microelectronic and other applications of cadmium selenide thin films depend on their structural and electronic properties affecting device performance. Thermal treatment is one of the important factors to enhance the efficiency and stability of photosensitive devices. Thus, studies of the effect of annealing on structural, optical and electrical properties of thin films are very important in understanding and enhancing device sensitivity [Purohit et al., 2015]. These properties are strongly influenced by the deposition parameters such as deposition time, deposition potential, concentration of electrolytic solution, pH of the electrolyte and thermal annealing. The CBD method for the deposition of thin films from an aqueous solution is a promising technique because of its simplicity, affordability, convenience for large-scale deposition and having easily controllable parameters such as concentration, pH, deposition temperature and deposition time, etc. The preparation conditions such as solution concentration, pH value, and deposition time and bath temperature are optimized in order to get good quality of CdSe thin films. The aim of the present work is preparing a good quality of CdSe thin films at different deposition temperatures (from 60 to 120 oc) and investigating the effect of deposition and annealing temperatures on the structural, morphological and optical properties of CdSe thin films [Kar˙ıpera et al., 2015].

2: Expermental

The CdSe was deposited on substrate via CBD. Selenium powder (99.95%) was mixed with solution of sodium sulphate with ratio 1:5 (e.g., 1 gm Se with 5 gm 〖Na〗_2 SO_3). Concentration of solution (Na_2 SeSO_3) was kept constant around 0.23Mol. The mixture was heated under reflux at 90 oC for 3 h to form a clear Na2SeSO3 solution. The cadmium precursor was prepared by dissolving 0.2 M of CdCl2 in DI water. Then, ammonia solution was added into the cadmium solution slowly to adjust the pH of the solution at 11 ±1. This was to prevent a reverse reaction of Cd (NH3)4+2 to form stable cadmium hydroxide (Cd (OH) 2). Both precursor solutions were mixed until becoming homogenous. The substrate was soaked vertically inclined into the CdSe bath solution for the deposition process for 1 h. The deposition temperature varied from 60 to 120 oC. A digital programmable hotplate (Torrey Pines Scientific) was used in this experiment. The temperature of the chemical bath was set and, upon the deposition process, the solution's temperature was checked using a thermometer for confirmation. Throughout the deposition process, the temperature of the chemical bath was checked from time to time. Then, the samples were then rinsed with DI water and dried in an oven overnight. All chemical materials were purchased from Scharlau Co. All the chemicals were of analytical grade and used as purchased. The dissociation relation and the equation for the chemical reaction are:

$$2CdCl_2 + 4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+} + CdCl_4$$

$$[Cd(NH_3)_4]^{2+} \leftrightarrow Cd^{2+} + 4NH_3$$

$$Se + Na_2SO_3 \xrightarrow{reflex} Na_2SeSO_3$$

$$Na_2SeSO_3 + OH^- \leftrightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \leftrightarrow H_2O + Se^{2-}$$

$$Cd^{2+} + Se^{2-} \leftrightarrow CdSe \downarrow$$

Equations used in this work:

$$D = M\lambda/\beta\cos\theta \quad \ldots\ldots..1$$

$$a = d\sqrt{h^2 + k^2 + l^2} \ldots\ldots\ldots.2$$

$$n\lambda = 2d\sin\theta \ldots\ldots\ldots\ldots\ldots..3$$

$$\delta = {}^{n}/_{D^2} \ldots\ldots\ldots\ldots4$$

$$\varepsilon = (\beta\cot\theta)/4 \ldots\ldots\ldots..5$$

$$\alpha(h\nu) = B\left(h\nu - E_g\right)^{1/2} \ldots\ldots\ldots.6$$

$$\alpha = 2.303\, A/l \ldots\ldots.7$$

$$E_{shift} - E_{bulk} = \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{C_1 e^2}{\varepsilon R} - C_2 E_{RY}^* \ldots\ldots8$$

$$\sigma \propto exp\left(- {}^{E_a}/_{K_B T}\right) \ldots\ldots.9$$

$$\rho = (\pi t/\ln 2)\, R \ldots\ldots\ldots10$$

3: Result and Discussion

3.1: structural Properties

The X-ray diffraction spectra have taken for CdSe films deposited on quartz substrate at different deposition temperatures. The structural elucidation of CdSe thin films for the bath temperatures 323K, 333K, and 343K of samples presented in Fig. (1). All the deposited thin films found to be polycrystalline in nature. The XRD pattern shows the reflections of the cubic structure type. The observed *d*-spacing and the respective prominent peaks correspond to reflection from the (1 1 1), (2 2 0) and (3 1 1) planes, which coincide well with the JCPDS data [file NO. 19-0191, file NO. 65-28961] and previously published papers [Ebrahim, 2016]. These observations show out of plane (perpendicular to the substrate) orientation of the thin film with (1 1 1) preferred orientation. The position of the prominent peaks in the diffraction patterns correspond to their respective positions in the JCPDS data. The estimated lattice parameter (a) of CdSe thin films are in good agreement with the JCPDS data, Table (1). The Values of FWHM "β" has been evaluated from the highest intensity plane represent (1 1 1), where found FWHM decrease as bath temperature increase, Table (1). The Grain size is determined from the XRD peaks by using Scherrer's formula Eq. (1). The calculated grain size lied between 5.925 nm and 6.767 nm Table 1, the grain size "D" increase with deposition temperature (bath temperature) increase which may indicate that the reaction temperature have important influence on the crystallinity of CdSe nanocrystals and this coincide well with earlier reports [Tadesse et al., 2018, Facher and Afef, 2016, Agrawal et al., 2014]. It has seen that the values of the lattice constant (a) for thin film sample are close to the value in the standard data JCPDS. The strain may also alter the physical properties of the thin film. Strain and dislocation density of thin films are calculated. The prepared CdSe thin film annealed in air for 1h at 573 and 723K. Figure (2) shows the XRD patterns of as-deposited and annealed CdSe thin film. The XRD pattern exhibits three diffraction peaks corresponding to the (1 1 1), (2 2 0) and (3 1 1) planes of polycrystalline cubic with slight improvement in crystallinity, while the XRD pattern of the same sample air-annealed at 723K shows that the diffraction peaks become sharper with decrease in β, which coincide well previous studies, [Sabah and Raghd., 2018]. The observed d-spacing of the diffraction peaks were evaluated and compared with the standard d-values, confirming the formation of polycrystalline cubic phase of CdSe JCPDS Table (2) and earlier work [Narayana et al., 2017, Ugwu et al., 2013]. The lattice constant (a) of CdSe thin films had estimated, and it was in good agreement with the JCPDS data, Table (2). Values of FWHM "β" of the strong peak corresponding to the characteristic (1 1 1) plane were shown in Figure (2). The FWHM values has seen to decrease as the temperature of annealing were increased, and it shows improvement in crystalline of the CdSe thin film with increase in temperature of annealing [Narayana et al., 2017, Ugwu et al., 2013]. The size of the crystallites evaluated from the high intense peak of XRD pattern. The average evaluated grain size lied between 7.103 and 7.937 nm, where noticed the grain size "D" increase with annealing temperatures increase [Somnath et al., 2017]. The strain (ε) and dislocation density (δ) evaluated.

Table(1)-Structural parameters of CdSe thin films at different deposition temperature.

Deposition temperature (K)	2θ (deg.)	d (nm)	a (nm)	β (rad.)	D Grain size (nm)	ε $\times 10^{-3}$	δ $\times 10^{12}$
323	25.87	0.344	0.596	0.024	5.925	5.8	2.849
333	25.71	0.346	0.600	0.023	6.181	5.6	2.618
343	25.51	0.349	0.604	0.021	6.767	5.1	2.184

Table (2)-Structural parameters of CdSe thin films for as deposited and air annealed.

Annealing temperature (K)	2θ (deg.)	d (nm)	a (nm)	β (rad.)	D Grain size (nm)	ε $\times 10^{-3}$	δ $\times 10^{12}$
As deposited	25.351	0.349	0.605	0.0200	7.103	4.9	1.982
333	25.400	0.350	0.607	0.0189	7.517	4.6	1.769
343	25.379	0.351	0.607	0.0179	7.937	4.4	1.587

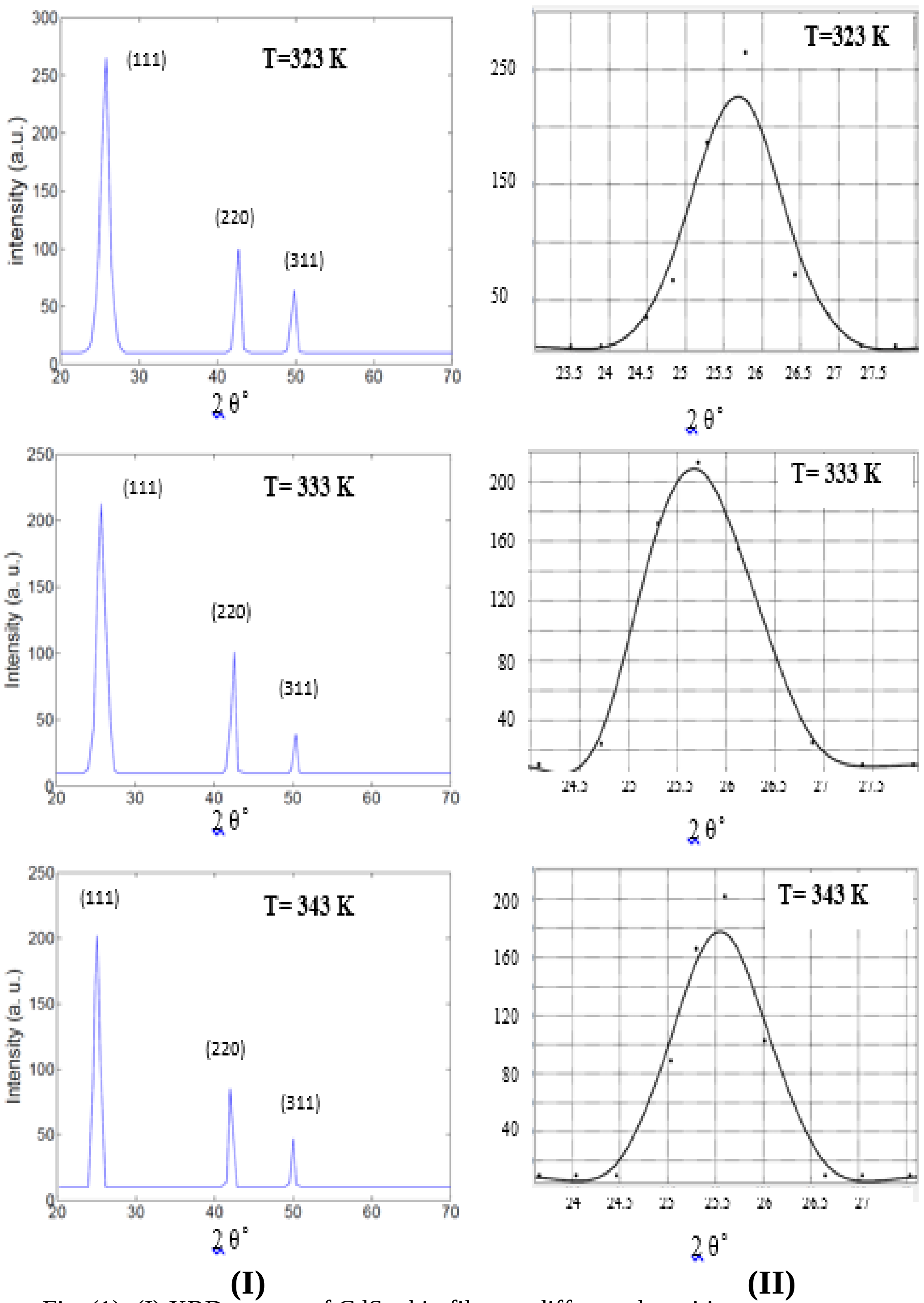

Fig. (1): (I) XRD pattern of CdSe thin films at different deposition temperature.

(II) FWHM of CdSe thin films at different deposition temperature.

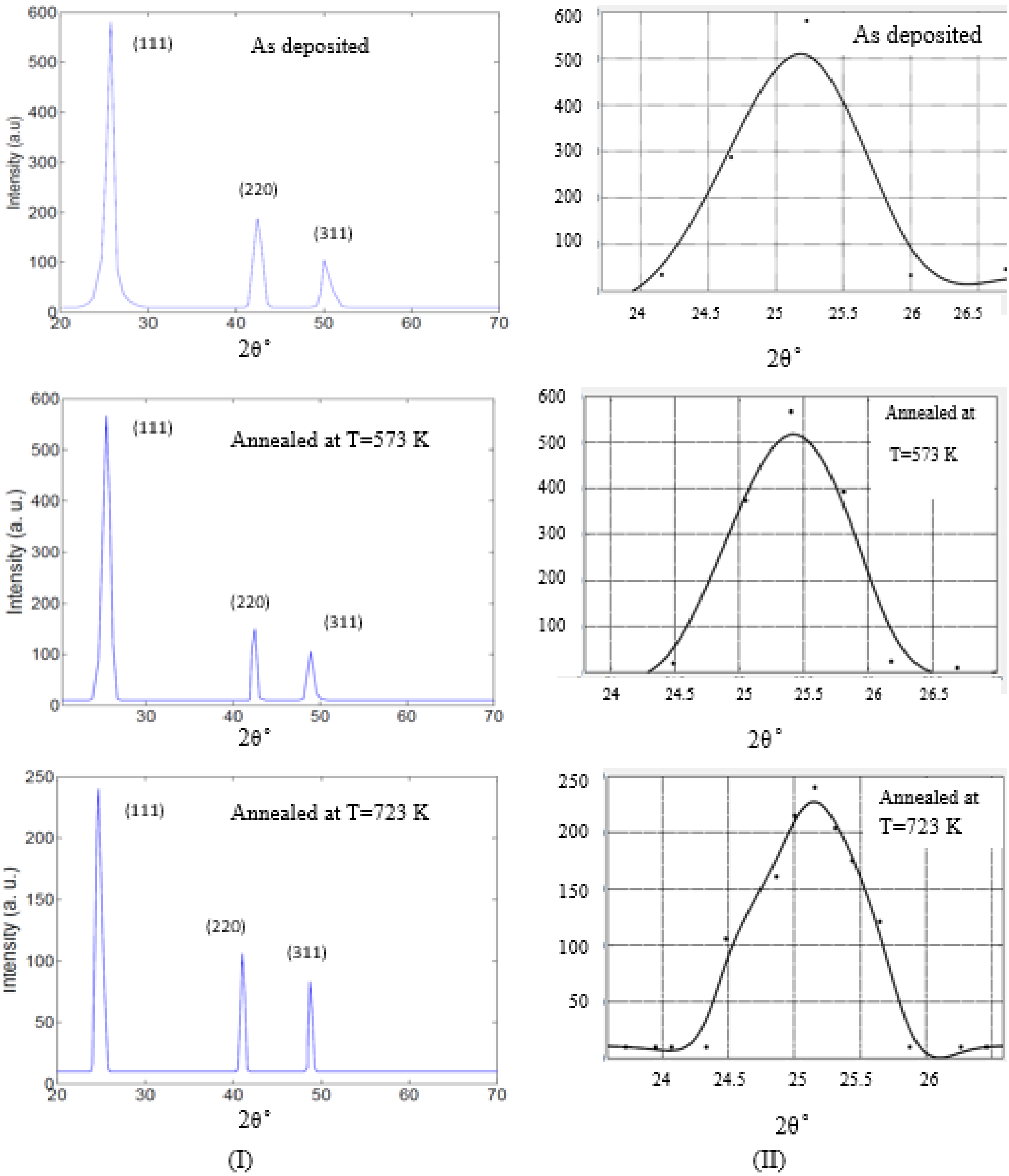

Fig. (2): (I) XRD pattern for as-deposited and annealed CdSe thin film. (II) FWHM for as-deposited and annealed CdSe thin film.

3.2: Optical Properties

In this work the absorption spectrum of CdSe nanoparticle thin film grown at three different deposition temperatures (323, 333 and 343 K), measured in the wavelength 300-1100 nm at room temperature. During whole reaction process; the growth particles were clearly evidence by shift absorption edge to longer wavelengths, as shown in fig.(3) and suddenly increase in the absorption with increase in deposition temperature as consequence of quantum confinement effect. With the reaction temperature increased, the growth rate of CdSe nanocrystals increase. The calculated absorption coefficient (α) was plotted vs. wavelength, as shown in figure (4); it can be seen that shift towards longer wavelengths as deposition temperature increase. The experimental values of the optical gap calculated from the plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$, figure (5), are (3.02 ± 0.01) eV, (2.64 ± 0.01) eV and (2.44 ± 0.01) eV. The value of energy band gap found to decrease with deposition temperature (323, 333 and 343 K) increase, fig. (6) [Ebrahim et al., 2016]. The increase in the energy gap with respect to bulk CdSe can be due to the influence of the grain size [Tadesse et al., 2018, Facher and Afef, 2016, Agrawal et al., 2014].The calculated particle sizes of prepared films found approach to exicton Bohr radius of bulk CdSe. It's observe that particle size increase with deposition temperature, figure (7). Table (3) shows the experimental values of energy gap, blue shift and particles size. The absorption spectra of as-deposited and annealed CdSe thin film were studied without taking into account the reflection and transmission losses. Thin film annealed in air for 1 h at three different temperatures (373, 473 and 573 K). Figure (8) shows the optical absorbance of as-deposited and annealed CdSe thin film. As shown in figure (8) the optical band edge shifts to higher wavelengths with increasing the annealing temperature [Sabah, et al., 2018]. It may be due to increase in crystallite size, decrease in defects and change in color from red-orange, dark brown to dark black. We can see from fig. (9). Fig. (10); show the plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$. The energy band gap was calculating in the range of 2.4-2.05 eV. The decrease in energy band gap after annealing can be attribute to improvement in the crystallinity with annealing temperature as supported by XRD studies [Narayana, et al., 2017]. As the annealing temperature was increase, the crystallite of the CdSe also increased resulting into decrease in the energy gap [Ugwu, et al., 2013]. The temperature dependent parameters that affect the energy gap are reorganization of the film, selenium evaporation and self-oxidation of the film. The reorganization of the film occur at all annealing temperatures [Somnath, et al., 2017]. We can see from figure (11) variation energy gap with annealing temperature. The calculated particle size of as deposited and air-annealed films found in range 4.765 - 6.953 nm; these values are in good agreement with XRD studies. It is observe increasing in particle size with increase temperature of annealing, figure (12). Table (4) shows the experimental values of energy gap, blue shift and particles size.

Table(3)-Experiment values of energy gap, blue shift and particles size for deposited films at different deposition temperatures.

Sample name	Deposition temperature K	Energy gap E_g (eV)	Blue shift E_{shift} (eV)	Particle size D (nm)
W2	323	3.02	1.28	3.422
H2	333	2.64	0.9	4.081
S2	343	2.44	0.7	4.627

Table(4)-Experiment values of energy gap, blue shift and particles size of as deposited and annealed CdSe film.

Temperatures of annealing K	Energy gap E_g(eV)	Blue shift E_{shift}(eV)	Particle size D(nm)
As deposited	2.4	0.66	4.765
373	2.27	0.53	5.318
473	2.10	0.36	6.452
573	2.05	0.31	6.953

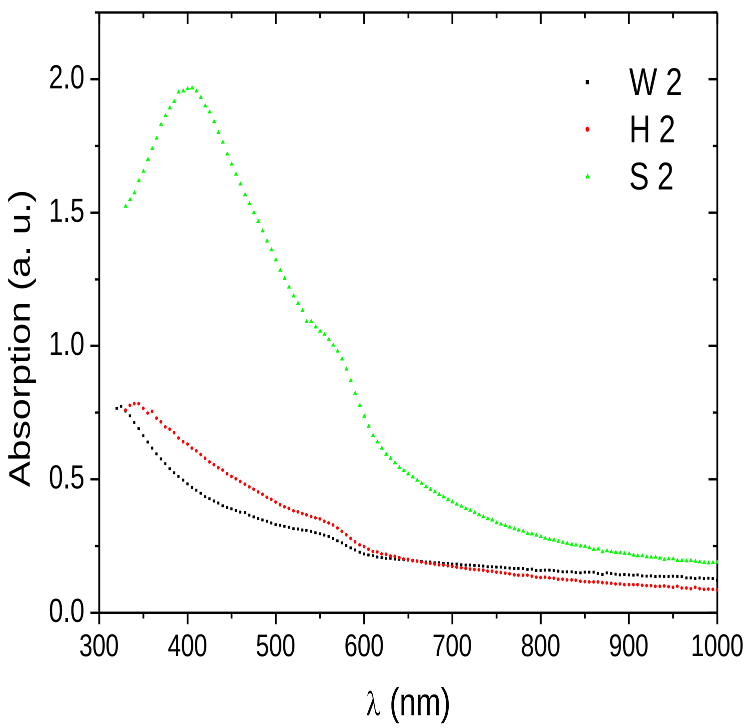

Fig. (3):UV-vis Absorption of as deposited CdSe thin film at different deposition temperatures.

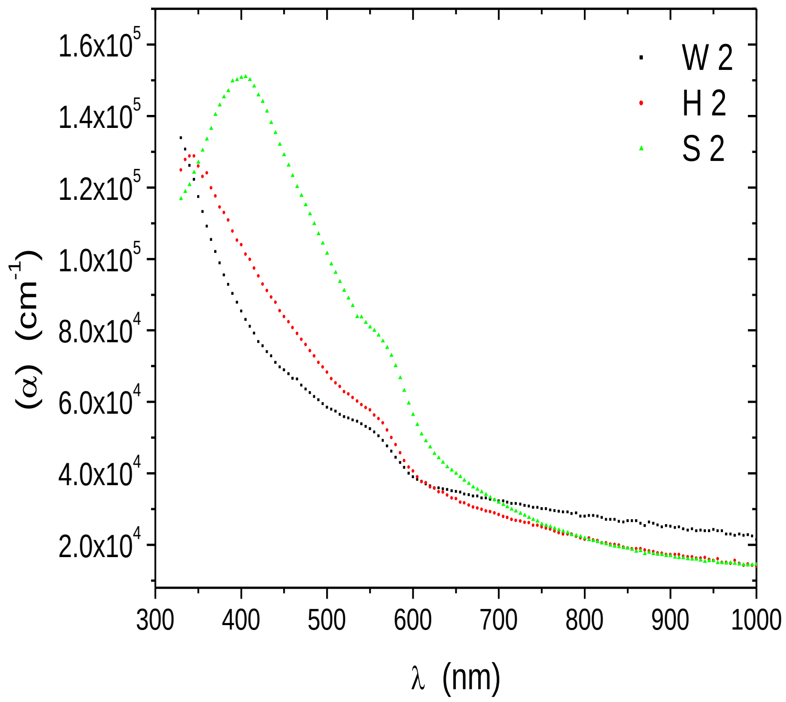

Fig. (4) Absorption coefficient "α" as a function of wavelength "λ" of as deposited CdSe thin film at different temperatures.

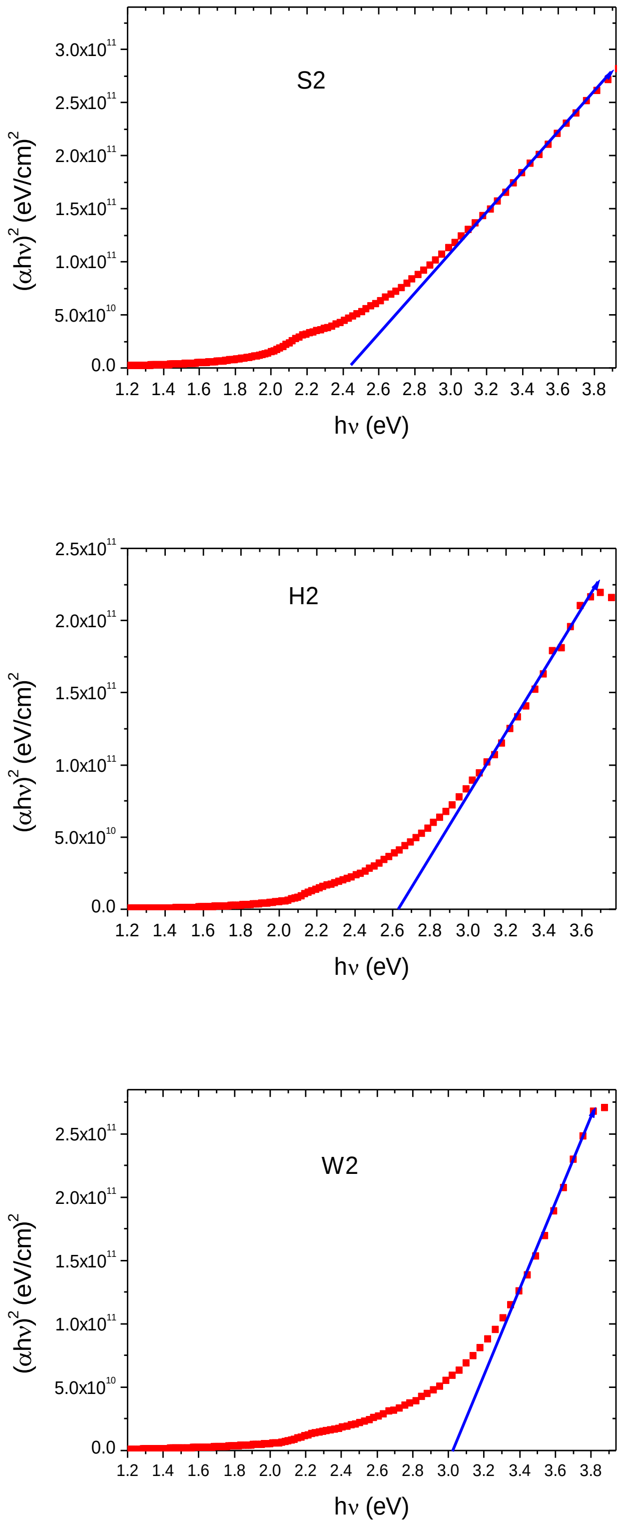

Fig. (5) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of CdSe thin films at different temperatures.

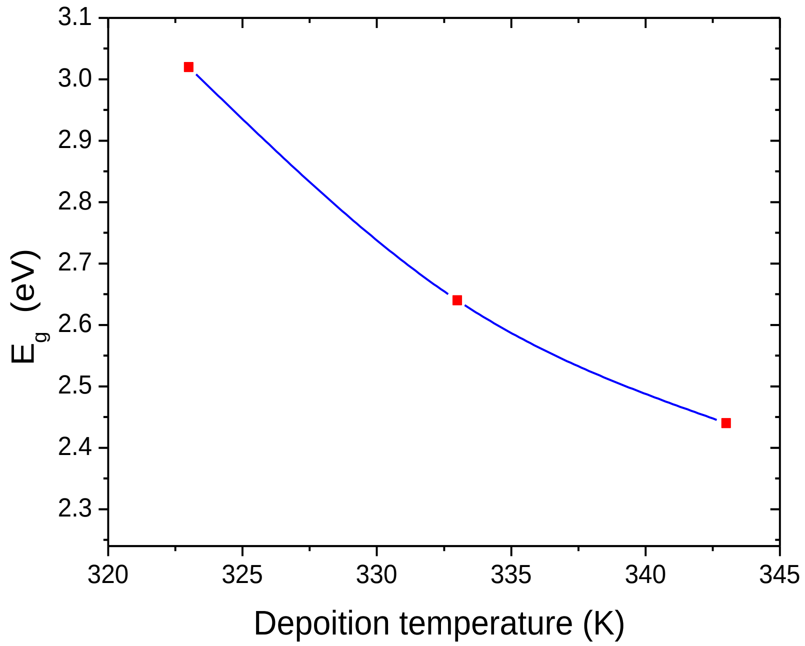

Fig. (6) Variation energy gap with deposition temperatures.

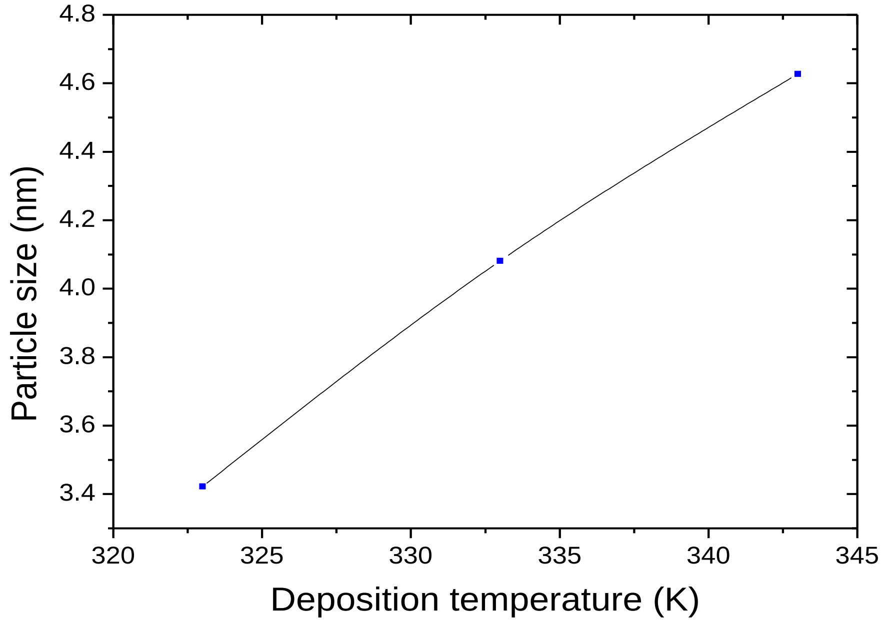

Fig. (7) Variation in particle size with deposition temperatures.

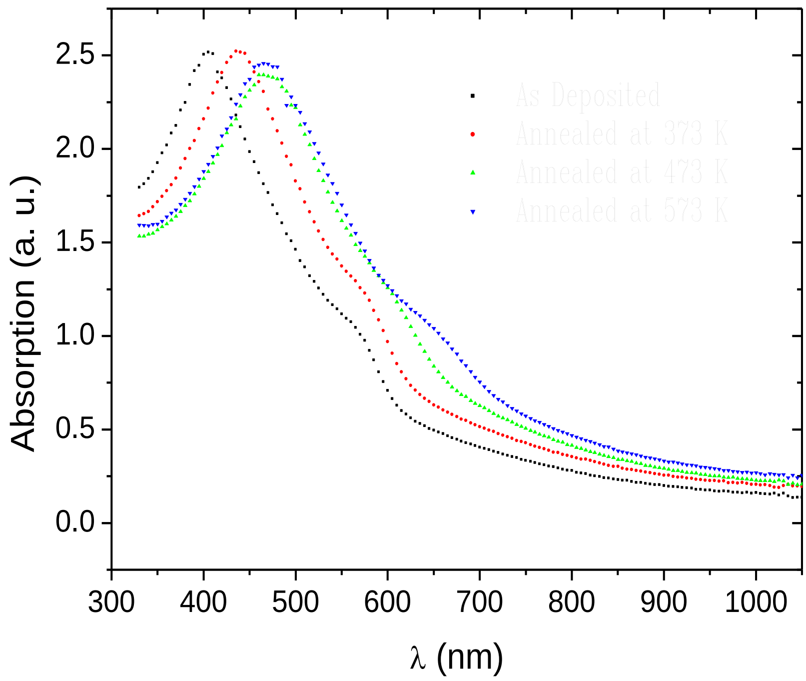

Fig. (8) UV-vis Absorption for as deposited and air annealed CdSe thin film .

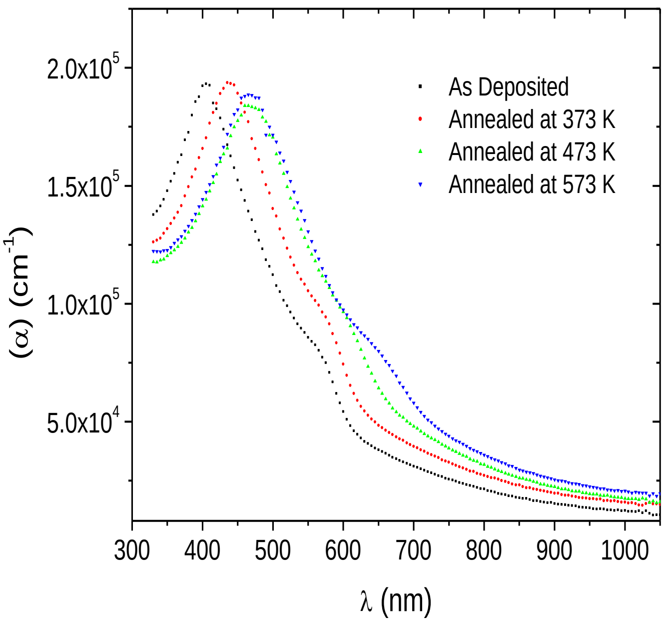

Fig (9) Absorption coefficient "α" as a function of wavelength "λ" for as deposited and air annealed CdSe thin film .

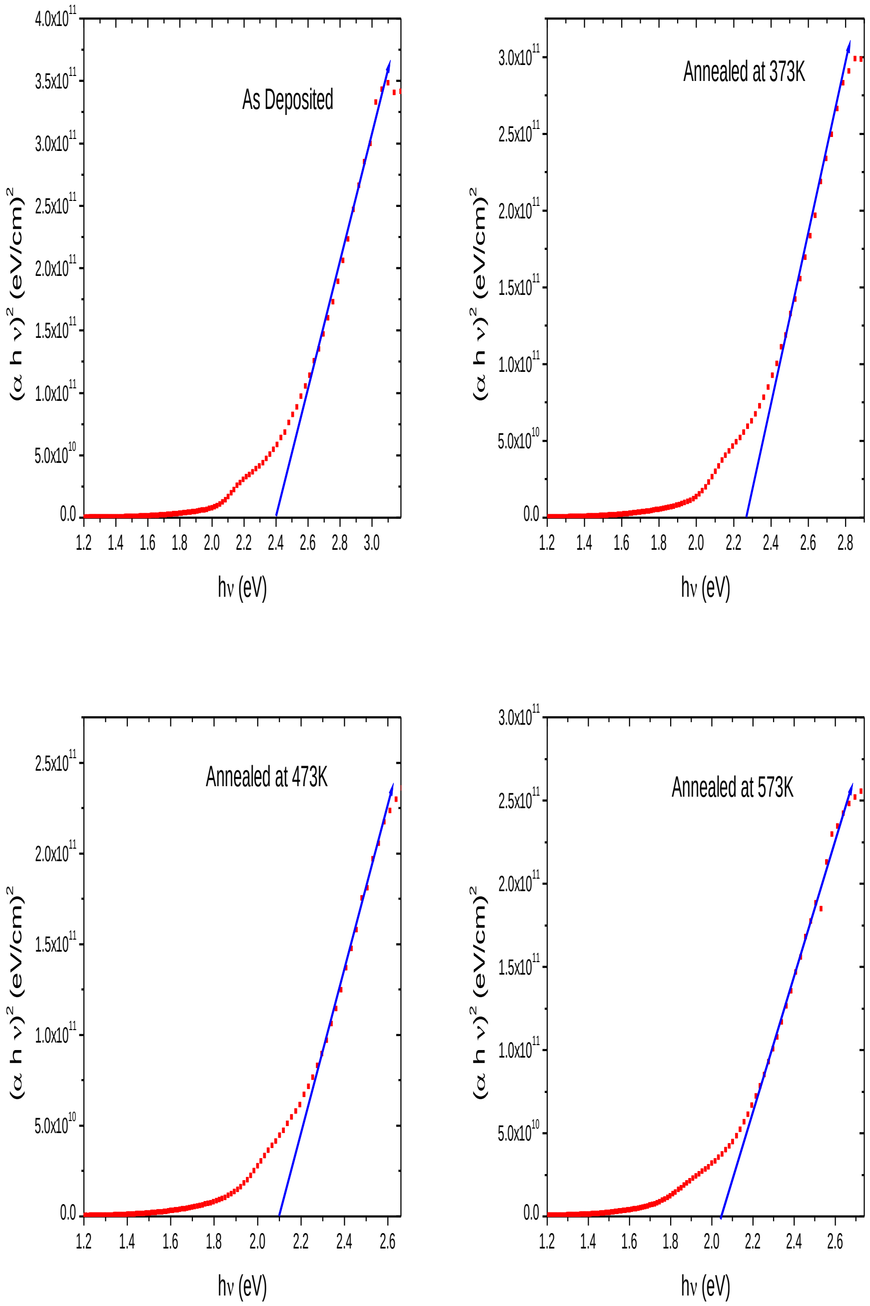

Fig. (10) Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for as deposited and air annealed CdSe thin film.

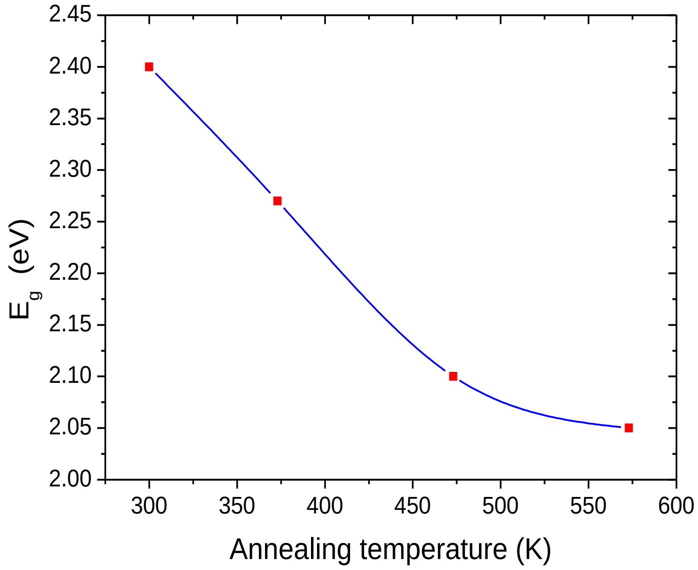

Fig. (11) Variation energy gap with annealing temperature.

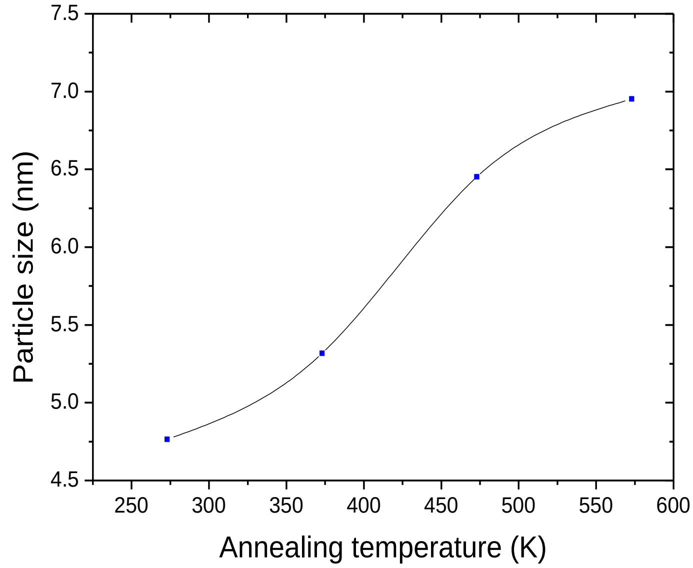

Fig. (12) Variation in particle size with annealing temperature.

3.3: Electrical properties

Activation Energy of CdSe Nanocrystals

The electrical resistivity (ρ) of CdSe nanocrystals powder at disk form with thickness 0.06 cm and area 0.622 cm^2 was measuring as a function of temperature in the temperatures range of 300-455 K as shown in figurer (13). The disk was painting by black carbon for conduction. From figure (13), it is observed that the resistivity of CdSe powder decrease with increase in temperature, confirming semiconducting behavior of CdSe nanocrystals. The electrical measurement results show that the electrical resistivity of the samples decreases with temperature down to 4.5×10^5 Ω cm at 455K [Mahato, et al., 2015]. For calculating Activation energy, we used electrical resistivity of CBD CdSe. The activation energy can be calculating by using the equation (9) and plotting log (ρ) vs. (1000/T). Figure (14) represent log (ρ) vs. (nanocrystals 1000/T) of sample. Three regions had observed in plot, such type of high and low temperature regions. The non-linear nature of the plot is also indicates three types conduction mechanism may due to defect in the CdSe nanocrystals. The activation energies found from the slope of two different regions of high temperature (region II and region III) and one of low temperature (region I) as shown in Figure (14). The E_a was found about 0.0172 eV in the region (I), 0.38 eV in the region (II) and 0.73 eV in the region (III) of the chemical bath deposition CdSe thin films .

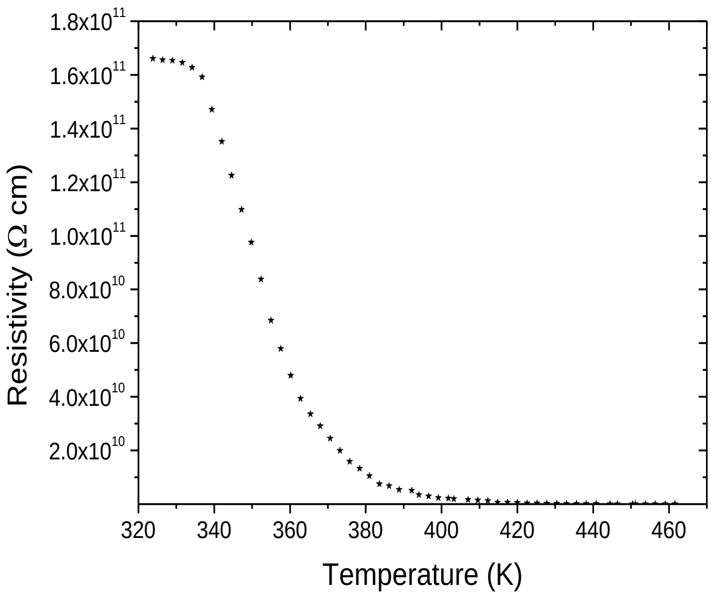

Fig. (13): Temperature dependence of the resistivity of CdSe powder.

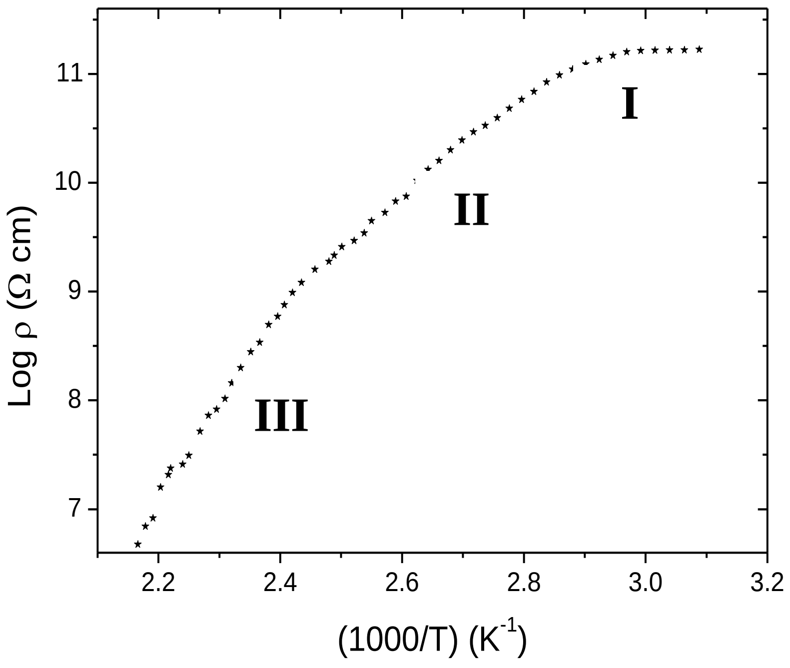

Fig.14: Plot of log ρ vs. (1000/T) of CdSe powder.

4: Conclusion

CdSe thin films have been successfully prepared on glass substrates using CBD (chemical bath deposition). In CBD technique, it was found that the values of molarities, pH, and speed stirrer, deposition temperature are greatly affecting the growth of the film and it is necessary to optimize them. Thus, in order to obtain good adherence and high quality films, it is important to make balance or trade-off in preparation conditions. Deposition temperature (Growth temperature) effect on structure properties was studied. All prominent diffraction peaks correspond to (111), (220) and (311) planes of cubic, this indicates not all films change its phase with temperatures. It was observed, increase in average grain size with increasing growth temperature. Air annealed film effects on structure properties showed prominent peaks diffraction correspond to (111), (220) and (311) cubic structure. This indicates not all-annealing process film change its phase with temperatures of annealing, but the peaks became sharper. Increase in grain size with annealing temperature. As the growth's temperatures increase suddenly the absorption spectra increase, and the absorption edge shifts towards highly wavelength. A blue shift in the optical gap has been observed for the absorption spectrum of the synthesized CdSe sample, as an indication of quantum confinement effect. It was found as the growth temperature increase the energy gap decrease. The absorption edge shifts towards lower energy region (i.e. higher wavelengths) as annealing temperature increases. It has been observed that as the annealing temperature increases the energy gap decreases. These changes had been attributed to the increase in the grain size of the CdSe nanoparticles. The temperature dependence of electrical resistivity of CdSe nanoparticales (at powder form) measured in the temperature range of 300- 455K. The electrical measurement results show that the electrical resistivity decreases with temperature down to 4.5×105 Ω cm at 455K. The plot of log (ρ) vs. (1000/T) showed three separate regions such type of low temperature region (I) and high temperature regions (II, III). The Ea found about 0.0172eV in the region (I) and 0.38eVin the region (II) and 0.73 eV in the region (III).

Acknowledgements

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