

# **STUDY ON STRUCTURAL, MORPHOLOGICAL, OPTICAL AND PHOTOVOLTAIC PERFORMANCE OF CdS<sub>1-x</sub>Se<sub>x</sub> (x=0.2 mol) THIN FILMS BY CHEMICAL BATH DEPOSITION TECHNIQUE**

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## **Abstract**

The CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol ) sol-solution was prepared by Chemical Bath Deposition(CBD) Technique. The temperature treatment in the water bath was at 100 °C for 1 h. CdSSe thin films were formed onto the pure glass substrates by chemical bath deposition method. Phase identification and crystallographic properties of CdSSe thin films were examined by X-ray diffraction (XRD) technique while the surface appearances (morphology) of fabricated films were also identified by Scanning Electron Microscope (SEM). Optical properties of CdSSe films were used by UV-Vis spectroscopy. The electrical properties of CdSSe thin film solar cells have been studied the photovoltaic (PV) performances with a focus on the influence of temperature treatment at 350 °C and 400 °C. The capacitance-voltage characteristics of CdSSe thin films deposited at room temperature and the effect of different thermal annealing were carried out. The maximum power output, series resistance, shunt resistance and built in voltage were calculated from the I-V and C-V measurements. This research has been focused on the investigation of structural, optical and photovoltaic performances of CdS<sub>1-x</sub>Se<sub>x</sub> (x=0.2 mol) thin films by chemical bath deposition technique.

**Keywords:** CBD, XRD, SEM, UV-Vis spectroscopy, PV

## **Introduction**

Nowadays, II–VI chalcogenide semiconducting compounds and alloys have received the attraction of many researchers due to the considerable progress in the epitaxial growth techniques as well as because of their

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potential usages in several optical devices operating in the visible and near infrared ranges. [Hassanien, A. S., Akl, A. A., 2015].

The synthesis of binary metal chalcogenide of II-VI semiconductors in thick film, thin film, and nanocrystalline form has been rapidly growing area in the material research due to their important non-linear optical, photo luminescent and other physical and chemical properties. It is found that the band gap of CdSe material is 1.7 eV whereas of cadmium Sulphide is 2.4 eV, both these are suitable for solar spectrum. This feature makes these materials useful for solar energy conversion in photovoltaic form. These materials can be synthesized in thin film form from several methods [Patil, L. A., & Rane, D. S., et al, 2015].

The II-VI group cadmium sulphoselenium is an important alloy with excellent properties like, good photo conductivity material, response time and band gap. CdS (Cadmium Sulfite) and CdSe (Cadmium Selenite) are two very important wide band gap semiconductors, because of their wide applications in optoelectronics, such as non-linear optics, visible-light emitting diodes and lasers. For optoelectronic applications, it is very important to tune the emission wavelength. For the efficient optoelectronic device application, the material should be between CdS in which very high sensitivity is possible but response time is high. CdSe as a great material for electrochemical solar cell has a narrower bandgap than CdS. Instead of incorporating cation, anion doping such as Se doping in CdS could bring promising improvement for both light absorption and photoactivity [Rui Xie, Jinzhan Su, Ya Liu, Liejin Guo, et al, 2013].

In CBD method, the film can be grown on any suitable substrate by dipping it in appropriate solution of metal salt. The deposition may occur either by homogenous or heterogeneous chemical reaction. The cation of respective metal, complexed with suitable complexing agent is allowed to react with chalcogen ion. The cations and anions were to generate slowly by increasing temperature of reacting bath. The ions produced combine on substrate via nucleation. The growth usually takes place by ion-by-ion condensation process. Typically, a liquid solution containing precursors to the eventual film was prepared and a substrate was exposed the solution. Over the course of second or minutes (depending on the reagents and their

concentrations), the precursors reacted to produce a solid material that grows, atom by atom, on all the surfaces exposed to the bath. Chemical bath deposition is regularly used in the photovoltaic industry to deposit thin films of cadmium sulfite. The growth of thin films strongly depended on growth conditions, such as duration of deposition, composition and temperature of the solution, and topographical and chemical nature of the substrate.

### Experimental Procedure

$\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) was deposited onto a glass substrate at  $80^\circ\text{C}$  by using chemical bath deposition method. Starting materials used for preparing of  $\text{CdS}_{1-x}\text{Se}_x$  thin films were Cadmium Chloride ( $\text{CdCl}_2$ ), Selenium (Se), Thiourea  $\text{SC}(\text{NH}_2)_2$ , Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) and Ammonia ( $\text{NH}_3$ ). Thiourea  $\text{SC}(\text{NH}_2)_2$  was used as anionic precursor solution. Sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) was used as a solvating agent for anionic precursor solution. Selenium (Se), Sodium Sulphite ( $\text{Na}_2\text{SO}_3$ ) and Ammonia ( $\text{NH}_3$ ) were mixed in a beaker by using magnetic stirrer and annealed with water bath at  $80^\circ\text{C}$  for about 7 h. A solution of sodium selenosulphate ( $\text{Na}_2\text{SeSO}_3$ ) was obtained. It was sealed and kept overnight, on cooling, small quantity of selenium settles down at the bottom of the solution. It was then filtered to obtain a clear solution.  $\text{H}_2\text{O}$  was used as a cationic precursor solution. Thiourea  $\text{SC}(\text{NH}_2)_2$ , Cadmium Chloride ( $\text{CdCl}_2$ ) and Ammonia were mixed into another beaker by using magnetic stirrer. This mixture solution was added into the previous sodium selenosulphate solution and stirred by magnetic stirrer for 1 h. For maintaining the pH of the precursor solution was 10 to 11, 25 % concentrated  $\text{NH}_3$  solution was used. All solutions were prepared in deionized water. This mixture final solution (Cadmium sulphoselenide solution) was put onto the water bath at  $100^\circ\text{C}$  for 1 h. The color of this solution was found to be orange color. Glass slides of dimension (1cmx1cm) were used as the substrates for deposition of  $\text{CdS}_{1-x}\text{Se}_x$  thin films. The glass substrates were dipped into the orange color Cadmium sulphoselenide solution and heated at  $120^\circ\text{C}$  for 1h. After that they were annealed at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  for 1h to change from oxide layer into CdSSe thin films respectively.

In this research work, preparation of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films were reported. The properties of the thin films and aspects of growth mechanism can be well understood by its characterization of the films. The  $\text{CdS}_{1-x}\text{Se}_x$  thin films were characterized for their structural, surface morphological, optical, electrical properties, and photosensitivity of the films. I-V characteristics in dark and under illumination with in visible range were studied for the measurement of photosensitivity of  $\text{CdS}_{1-x}\text{Se}_x$  thin films. The structural analyses of the films were made by an X-ray diffractometer. The surface morphology was studied by scanning electron microscopy (SEM). UV-Vis spectrophotometer (automatic computer data acquisition) was employed to record optical spectra over the wavelength range of 400-1100 nm.

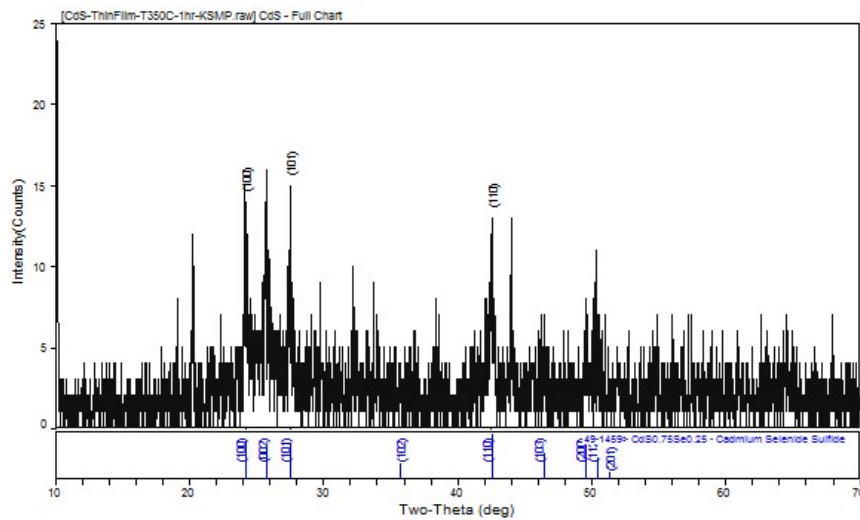
## **Results and Discussion**

### **Structural properties of $\text{CdS}_{1-x}\text{Se}_x$ thin films by XRD**

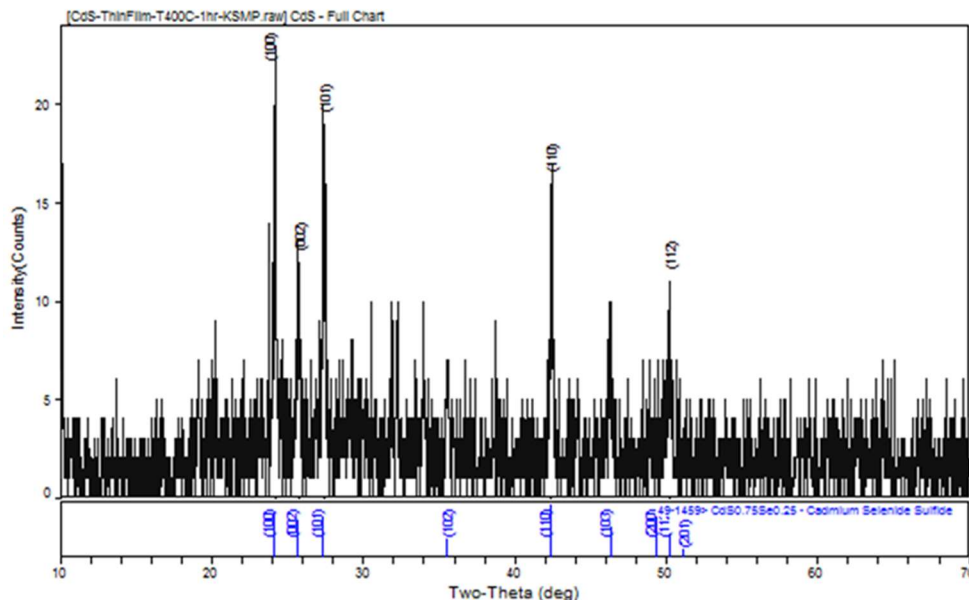
X-ray diffraction (XRD) technique is one of the most important analytical tools for the thin film structural analysis. The Rigaku RINT 2000-Multi Flex 2kW X-ray diffractometer was used in this work. "d" values were determined using the  $\text{Cu-K}_\alpha$  radiation with wavelength of 1.54056 Å. In diffractographs of powders not free from phase shift, several diffraction patterns of different crystalline fractions could be superimposed. The X-ray diffraction data obtained is printed in tubular form on paper and is compared with Joint Committee on Powder Diffraction Standard (JCPDS) or American Standard Testing for Materials (ASTM) data cards. The crystallite size (G) was determined by Debye-Scherrer formula.

From Figure 1, three of nine distinct peaks were formed on observed spectrum. Three of nine diffracted peaks were matched with those of angle CdSSe standard. From Figure 2, five distinct were formed on observed spectrum. Five of nine diffracted peaks were matched with those of CdSSe Standard. On the XRD pattern from Figure 1, the (100), (101) and (110) peaks and from Figure 2, (100), (002), (101), (110) and (112) were clearly observed. They were compared the data with the library (or) standard file. The most dominant peak was also occur at (101) for 350 °C and (100) for 400 °C. According to the observed XRD, the dopant material (modifier)  $\text{Se}^{2-}$  ion

doped into  $S^{2-}$  ion of the CdS lattice with hexagonal structure. The crystallographic phases of samples were in good agreement with the typical hexagonal structure. The polycrystalline structure  $CdS_{1-x}Se_x$  thin film was considered to be an alloy of hexagonal CdS and CdSe crystallite grains.  $CdS_{1-x}Se_x$  was successfully formed onto substrate at given temperatures for both samples. The observed XRD profile (upper side) and JCPDF library or reference XRD profile (lower side) were partially matched. FWHM and crystallite size of  $CdS_{1-x}Se_x$  ( $x = 0.2$  mol) thin films at  $350^\circ C$  and  $400^\circ C$  were listed in Table 1 and 2. Annealing temperature, lattice constants ( $a$  &  $c$ ) and lattice parameter ( $c/a$ ) ratio of  $CdS_{1-x}Se_x$  ( $x = 2$  mol) thin films were calculated and listed in Table 3.



**Figure 1.** XRD spectrum of  $CdS_{1-x}Se_x$  ( $x = 0.2$  mol) thin film at  $350^\circ C$



**Figure 2.** XRD spectrum of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin film at  $400^\circ\text{C}$

**Table 1.** Crystallite size of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin film for all identified peaks at  $350^\circ\text{C}$

No	Peaks	FWHM(degree)	Crystallite Size (nm)
1	(100)	0.26	31.48
2	(101)	0.26	31.69
3	(110)	0.16	55.04
<b>Average crystallite size</b>			<b>39.40</b>

**Table 2.** Crystallite size of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin film for all identified peaks at  $400^\circ\text{C}$

No	Peaks	FWHM(degree)	Crystallite Size (nm)
1	(100)	0.19	44.26
2	(002)	0.11	74.77
3	(101)	0.16	50.92
4	(110)	0.25	33.76
5	(112)	0.07	127.44
<b>Average crystallite size</b>			<b>66.23</b>

**Table 3.** Annealing temperature, lattice constants (a and c) and lattice parameter (c/a) ratio of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films

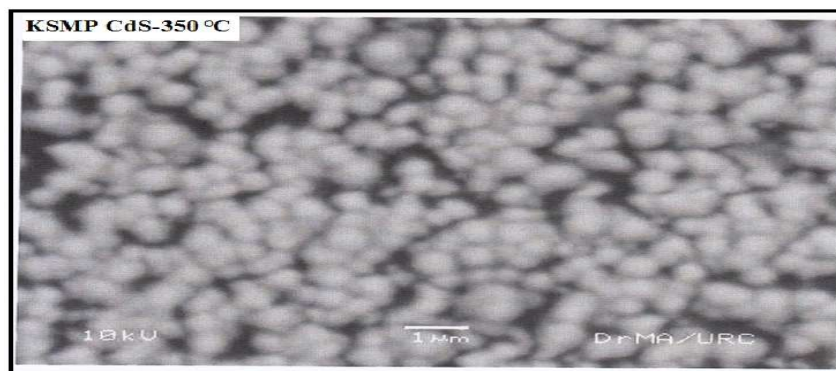
Annealing Temperature(°C)	Average Lattice Constant, a (Å)	Average Lattice Constant, c (Å)	Lattice Parameter (c/a) ratio
350	4.24	6.86	1.62
400	4.25	6.94	1.63

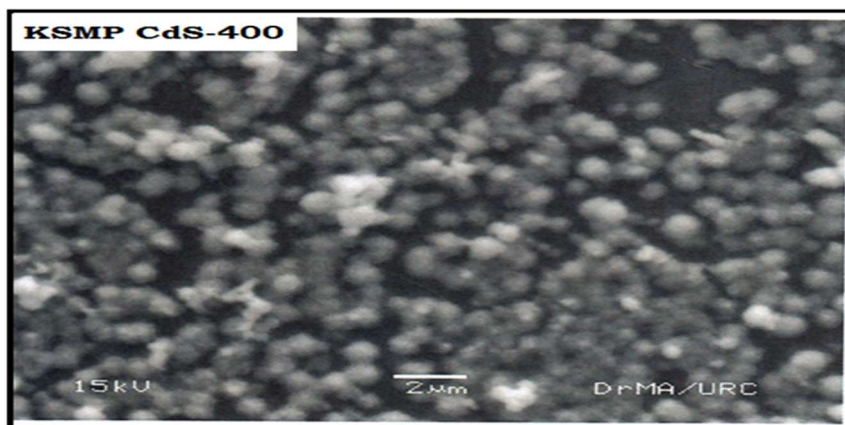
### Scanning Electron Microscopy (SEM)

SEM is one of the most versatile instruments available for the examination and analysis of the microstructure characteristics of a solid. The Scanning Electron Microscope generated a beam of electrons in a vacuum. The scanning electron microscope (JEOL, JSM- 5610 LV) with acceleration voltage 10 and 15 kV and magnification 5500x and 10000x which was used in this research work. Table 4 shows average grain size of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films at 350 °C and 400 °C. Figure 3 and 4 show the SEM image of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin film at 350 °C and 400°C.

**Table 4.** Average grain size of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films at 350 °C and 400 °C

Annealed Temperature (°C)	Grain size (nm)
350	405
400	684

**Figure 3.** SEM image of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin film at 350°C



**Figure 4.** SEM image of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin film at  $400^\circ\text{C}$

### UV-Visible optical absorption studies

Ultra-violet radiation is the part of the electromagnetic radiation spectrum below visible light. The band gap properties of a semiconductor can be controlled by using different semiconductor allays. The spectral absorption was taken by using UV-Vis spectrometer (UV-1800 SHIMADZU UV SPECTROPHOTOMETER). Table 4 shows the optical band gap energy of CdSSe thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$ . Fig. 5 and 6 show the plot of  $(\alpha h\nu)^2$  vs  $h\nu$  for CdSSe thin film at  $350^\circ\text{C}$  and  $400^\circ\text{C}$ .

**Table 4.** Optical band gap energy of CdSSe thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$

Temperature ( $^\circ\text{C}$ )	Optical band gap energy (eV)	Standard band gap energy (eV)
350	1.44	1.67-2.35 [ Rui Xie et al]
400	1.67	



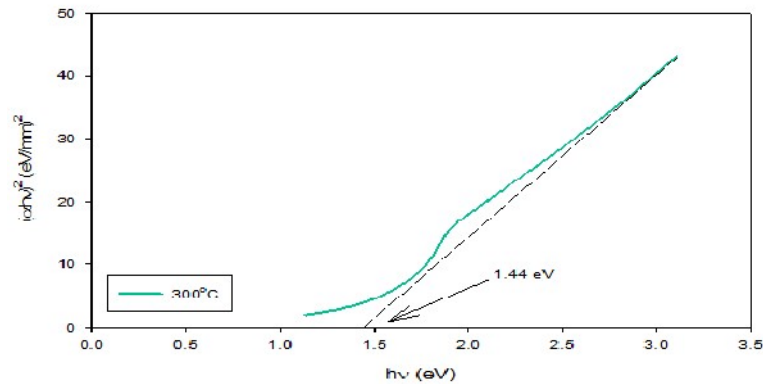


Figure 5. Plot of  $(\alpha hv)^2$  vs  $hv$  for CdSSe thin film at 350 °C

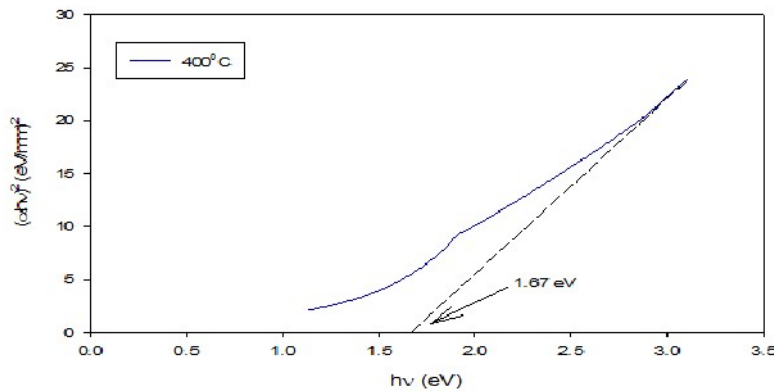
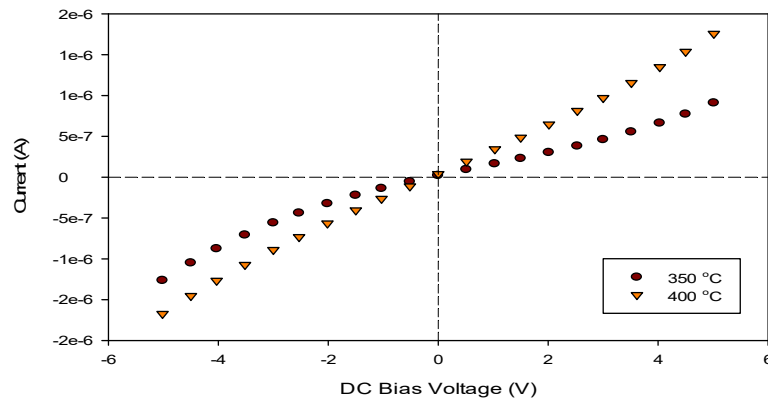


Figure 6. Plot of  $(\alpha hv)^2$  vs  $hv$  for CdSSe thin film at 400 °C

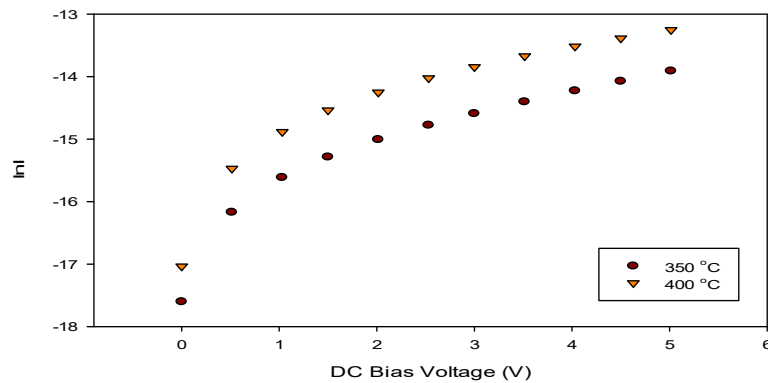
### I-V Measurement

The basic characterization tool for a solar cell was the current-voltage (IV) measurement under illumination and dark. The main parameters were the open-circuit voltage ( $V_{oc}$ ), the short-circuit current ( $I_{sc}$ ), the fill factor (F), maximum power point ( $P_{max}$ ), the energy conversion efficiency, ( $\eta_{con}$ ) and the conversion efficiency, ( $\eta_{con}$ ). Variation of photovoltaic voltage and photovoltaic current with illumination intensity were also investigated. Most solar cell parameters can be obtained from the simple I-V measurement. Figure 7 shows current Vs. voltage characteristic graph for  $CdS_{1-x}Se_x$  ( $x = 0.2$  mol) thin films at 350°C and 400°C under dark condition. Fig. 8 In I

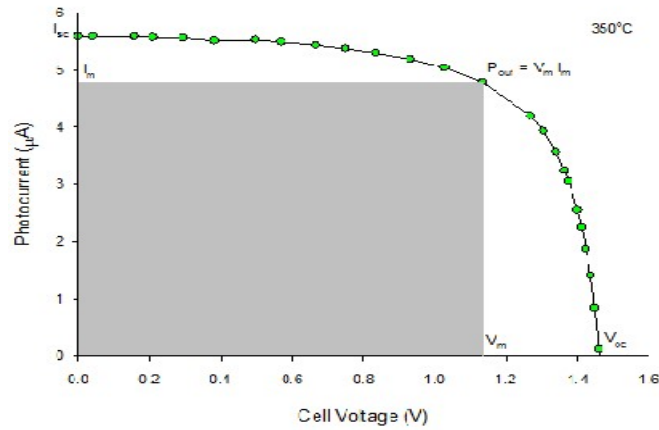
Vs. Voltage characteristic graph for  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under dark condition. Fig.9 and 10 show photocurrent Vs. cell voltage curves for CdSSe thin film at at  $350^\circ\text{C}$  and  $400^\circ\text{C}$ . Table 5 shows saturation current, ideality factor and zero bias barrier height for  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under dark condition. Table 6 shows photovoltaic parameters of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under illumination. Table 7 shows Efficiency and Fill Factor of  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under illumination.



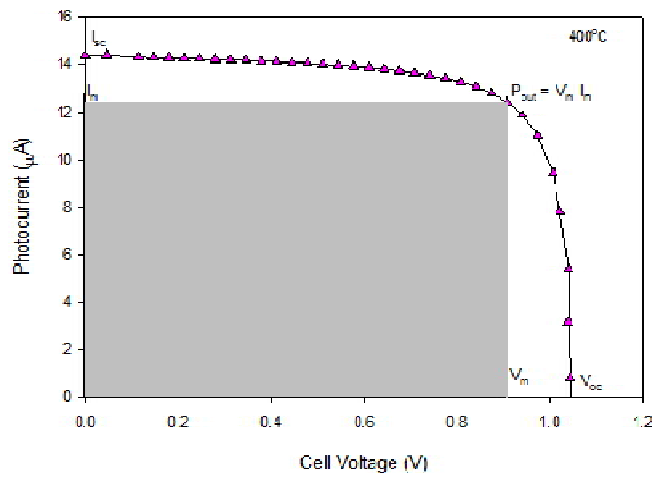
**Figure 7.** Current Vs. Voltage characteristic graph for  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under dark condition



**Figure 8 .**  $\ln I$  Vs. Voltage characteristic graph for  $\text{CdS}_{1-x}\text{Se}_x$  ( $x = 0.2$  mol) thin films at  $350^\circ\text{C}$  and  $400^\circ\text{C}$  under dark condition



**Figure 9.** Photocurrent Vs. Cell voltage curves for CdSSe thin film at 350°C



**Figure 10.** Photocurrent Vs. Cell voltage curves for CdSSe thin film at 400°C

**Table 5.** Saturation current, ideality factor and zero bias barrier height for CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films at 350 °C and 400 °C under dark condition

Temperature (°C)	I <sub>s</sub> (A)	φ <sub>bo</sub> (eV)	η
350	6.30x10 <sup>-8</sup>	0.39	1.64
400	1.27x10 <sup>-7</sup>	0.37	1.59

**Table 6.** Photovoltaic parameters of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films at 350 °C and 400 °C under illumination

Temperature (°C)	I <sub>m</sub> (μA)	V <sub>m</sub> (V)	I <sub>sc</sub> (μA)	V <sub>oc</sub> (V)	P <sub>max</sub> (μW)
350	4.83	1.13	5.61	1.45	5.48
400	12.42	0.90	14.40	1.07	11.27

**Table 7.** Efficiency and Fill Factor of CdS<sub>1-x</sub>Se<sub>x</sub> (x = 0.2 mol) thin films at 350 °C and 400 °C under illumination

Temperature (°C)	η <sub>con</sub> (%)	FF	Standard η <sub>con</sub> (%) and FF
350	1.18	0.67	η <sub>con</sub> = 0.59%, 0.67% and FF = 0.55, 0.56 (PUJARI V.B et al, 2013)
400	2.42	0.73	η <sub>con</sub> = 0.79%, 2.12% and FF = 0.46, 0.49 (Abhijit A .Yadav et al, 2011)

### Conclusion

Fabrication and characterization of CdS<sub>1-x</sub>Se<sub>x</sub> thin films have been successfully investigated. The XRD results showed a polycrystalline films with hexagonal structure and lattice distortions (c/a) of 1.61 and 1.63 at 350°C and 400°C. The crystallite sizes of CdS<sub>1-x</sub>Se<sub>x</sub> thin films were calculated to be 39.40 nm and 66.23 nm at the growth temperature 350°C and 400°C. SEM photographs showed homogeneous film and spherical shape. The average grain size of the films varied with annealing temperature. The grain sizes of CdS<sub>1-x</sub>Se<sub>x</sub> thin films were estimated to be 405 nm and 684 nm at 350°C and 400°C. The films had a direct band gap with an optical value of 1.44 eV and 1.48 eV at 350°C and 400°C from the absorption spectrum. According to the band gap energy obtained by the absorption method, all optical band gaps in this study were 1.44 eV and 1.48 eV, nearly ranged between the standard values of CdS<sub>1-x</sub>Se<sub>x</sub> thin films (1.67 - 2.35 eV). All films were found the good absorbance, low transmittance in the visible/ near infrared region from about 400 nm to 1100 nm. Conversion efficiency of

CdS<sub>1-x</sub>Se<sub>x</sub> thin films were 1.18 % and 2.42 % at 350°C and 400°C. Fill factor of CdS<sub>1-x</sub>Se<sub>x</sub> thin films were determined to be 0.67 and 0.73 at 350°C and 400°C. The maximum power outputs were 5.48 μW and 11.27 μW at 350°C and 400°C. Finally,  $V_{bi}$  obtained for different temperatures are 0.45 V and 0.55 V at 350°C and 400°C. These values of band gap were in good agreement with the value reported by others. These results also suggest that the chemical bath deposition method is quite appropriate to produce CdS<sub>1-x</sub>Se<sub>x</sub> thin films solar cell. Photocurrent increased with applied voltage and showed ohmic behavior in nature for both temperatures. The dark current and photocurrents were measured at -5 to +5 V and the plot showed diode characteristic. Annealing temperatures were fairly influence on photoconductive properties of the films. CdS<sub>1-x</sub>Se<sub>x</sub> thin films with different composition of Se at different annealing temperatures will be investigated in future research. The investigation of CdS<sub>1-x</sub>Se<sub>x</sub> thin films will be focused on the other applications such as optical filters, signal memory devices, optoelectronic switches and radiation protection field.

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## References

1. Abhijit, A., Yadav et al 2011 Journal of Electrochimica Acta
2. Hassanien, A.S., & Akl, A.A., 2015. Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films, Super lattices and Microstructures, doi: 10.1016/j.spmi.2015.10.044
3. Patil, L. A. & Rane, D. S., et al, 2015. International Journal of Engineering, Science and research Technology 4(7) 2277-9655
4. Pujari V B et al 2013 International Journal of application or Innovation in Engineering and Management (IJAIEEM) 2 4847
5. Rui Xie, Jinzhan Su, Ya Liu, Liejin Guo et al, 2013. International Journal of hydrogen energy xxx (2013) I-II