

## Chemical Bath Deposition of CdS layer for Thin Film Solar Cell

T. Kamal<sup>1</sup>, S. Parvez<sup>1</sup>, K. M. Khabir<sup>1</sup>, R. Matin<sup>2</sup>, T. Hossain<sup>3</sup>, H. Sarwar<sup>4</sup>, M. S. Bashar<sup>2</sup>, M. J. Rashid<sup>1</sup>

<sup>1</sup>Dept. of Electrical and Electronic Engineering, University of Dhaka, Bangladesh,

<sup>2</sup>Institute of Fuel Research and Development, BCSIR, Dhaka, Bangladesh,

<sup>3</sup>Dept. of Electrical and Electronic Engineering, University of Asia Pacific, Dhaka, Bangladesh,

<sup>4</sup>Dept. of Computer Science and Engineering, United International University, Dhaka, Bangladesh

---

**Abstract:** Cadmium sulfide (CdS) is the n-type buffer layer with band gap of 2.42 eV. Cadmium sulfide (CdS) buffer layer of CZTS solar cell was deposited on soda-lime glass substrates by the Chemical Bath Deposition (CBD) method, using anhydrous Cadmium chloride (CdCl<sub>2</sub>) and Thiourea (CS(NH<sub>2</sub>)<sub>2</sub>). Deposition of CdS using CBD is based on the slow release of Cd<sup>2+</sup> ions and S<sup>2-</sup> ions in an alkaline bath which is achieved by adding complexing agent ammonia (NH<sub>3</sub>). The influence of bath deposition time on the structural, morphological, and optical properties of these films are investigated. The deposited films are studied by means of XRD, SEM, and UV-Vis spectrometry. The films deposited under optimum conditions (deposition time, t<sub>d</sub> = 70 min [S]/[Cd] = 3.5) shows good structural and optical properties.

---

**Keywords—** Cadmium Sulfide; Chemical bath deposition; Absorbance; XRD; SEM.

---

---

## I. INTRODUCTION

The sustainable and clean energy source sun has a very high potential to cover the electricity demand of the world, as it can convert the sunlight directly into electricity known as photovoltaic (PV) effect. Most of the PV systems currently available are based on silicon materials. Silicon based solar cell exhibits high conversion efficiency (up to 25% at lab)<sup>1</sup>. Though silicon has several advantages but it still suffers from low throughput and cost, thus could not affect the world's energy market. So researchers give effort to develop thin film solar cell such as CdTe, CuIn<sub>x</sub>Ga<sub>1-x</sub>S(Se)<sub>2</sub> (CIGS) and Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS)<sup>2</sup>. But the issues related to silicon solar cell still remains for the thin film solar cell. One major issue related to this thin film solar cell is the choice of appropriate buffer layer. The buffer layer or window layer's role is to absorb the light energy from the high-energy end of the spectrum. It must be thin enough and have a wide enough band gap (2.8 eV or more) to let all available light through the interface (hetero-junction) to the absorbing layer<sup>3</sup>. Different materials can be used as a thin film solar cell buffer layer, such as ZnO, ZnS, CdS and many more. The ZnO and ZnS buffer layer have wide band gap thus they can enhance the generation of electron hole pair in the absorber layer. However these buffer layers suffer from complicated reaction mechanism and light soaking effects, presenting a potential cell reliability problem<sup>4</sup>. In addition ZnS layer exhibit poor electrical properties<sup>5</sup>. On the other hand in the case of CdS, it has high transparency, direct band gap transition (Eg~2.42 eV), high electron affinity and good n-type conductivity<sup>6</sup>. The CdS buffer layer used in CIGS thin film solar cell exhibit an efficiency of 9.8%. In a study it has been found that when a buffer layer comprised of both ZnS and CdS it has much higher efficiency than both individual layers. However, the major disadvantages of CdS are parasitic absorption in the blue part of the solar spectrum and that it is quite toxic<sup>7</sup>.

The deposition of buffer layers are performed through different techniques such as E-beam evaporation, thermal evaporation, sputtering, chemical vapor deposition (CVD) and chemical bath deposition (CBD). Most of the techniques are very complex and hard to control, and thus costly. Some of the techniques are slow and laborious and can exhibit non uniform film with poor film density<sup>8</sup>. In this experiment chemical bath deposition (CBD) processes is presented because it is a relatively simple process to carry out, costs low, doesn't require any vacuum environment and is capable to yield films with good quality. The main objective of this study is to find the best suitable growth condition in order to achieve a thickness of 100-200 nm CdS, which can be used in different types of solar cell. Afterwards the deposited CdS layers are characterized using Scanning Electron Microscopy (SEM), Profilometer, X-ray Diffraction (XRD), Energy Dispersive

Spectroscopy (EDS), UV-visible spectrophotometer and Hall Effect measurement.

## II. EXPERIMENTAL DETAILS

In this experiment soda lime glass substrates of 6 cm × 4 cm is used. The glass substrates are cleaned by a five step procedures. In the first step, the glass substrate is scrubbed for 2-3 minutes with methanol and then rinsed with deionized water. This step is repeated 4 times. In second step, the substrate is immersed in a beaker containing methanol and the beaker is treated in an ultrasonic bath for 10 minutes. Next in the third step, the substrate is immersed in a beaker containing acetone and the beaker is treated again in an ultrasonic bath for 10 minutes. Afterwards in the step four, the substrate is dipped into methanol and the beaker is treated in an ultrasonic bath for 10 minutes. Then in last step, the substrate is immersed in a beaker containing DI water and the beaker is treated in an ultrasonic bath for 15 minutes. Afterwards we used acetone to remove the organic impurities from the glass substrates, particularly for dissolving oily or greasy contaminants<sup>9</sup>.

The concentrations of the components of the solution bath for CdS can be varied over a working range and each group use its own specific recipe. The chemical reactive salts are generally of low cost and in general it is necessary to use small quantities. Chemical components required to deposit the CdS film on soda lime glass substrate are Cadmium Chloride (0.1M), Ammonium Chloride (0.2M), Ammonia (2M) and Thiourea (0.3M). In this experiment thiourea concentration and deposition time are varied to produce four samples which is represented in Table 1.

In each bath soda lime glass substrate of 4×4 cm<sup>2</sup> has been immersed into a 120 ml de-ionized water with a magnetic stirrer. With the help of Teflon holder, all substrates are kept vertically in the solutions. Single dip deposition for each sample is carried out. The initial temperature is 25°C and hot plate temperature is fixed at 70°C. When the temperature is raised to 60°C with a ramp of 1.17°C/min, Cadmium Chloride (CdCl<sub>2</sub>), Ammonium Chloride (NH<sub>4</sub>) are added into the solution. Afterwards the solution is reached to 70°C and Ammonia (NH<sub>3</sub>) is added as a complexing agent. Ammonia (NH<sub>3</sub>) as complexing agent helps to prevent the undesirable homogeneous precipitation by forming complexes with Cd<sup>2+</sup> ions, showing thus the surface reaction on the substrate<sup>10</sup>. At this stage the temperature is dropped to around 60°C. Next the temperature is again raised to 68°C and Thiourea is added at this temperature. After that when the sample is turned into yellow color we take out the sample and rinse it with DI water for one minute to remove loosely adhered particles. Then they are dried out to get rid of the excess moisture. After drying out the samples the rear side of the samples are removed with the help of concentrated hydrochloric acid (HCl).

---

**Table 1:** Parameters that are varied in the deposition process.

No.	Thiourea Concentration (gm)	Deposition time (min)
Sample 1	1.03	54
Sample 2	0.8	40
Sample 3	0.9	45
Sample 4	2.74	50

Note that after adding the Ammonia (NH<sub>3</sub>) we repeatedly check the pH of the solutions. And the pH of all the sample sets are maintained at 10.8-11 by adding 30% aqueous solution of NH<sub>3</sub>. Also pH meter is cleaned before each reading to prevent contamination. Figure 1 shows the chemical bath deposition process and the deposited CdS film.

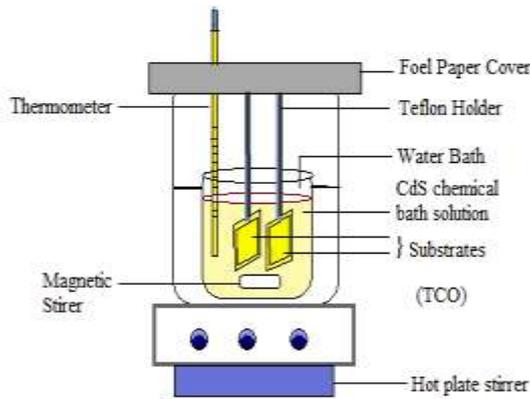


Figure 1(a): Chemical Bath Deposition process



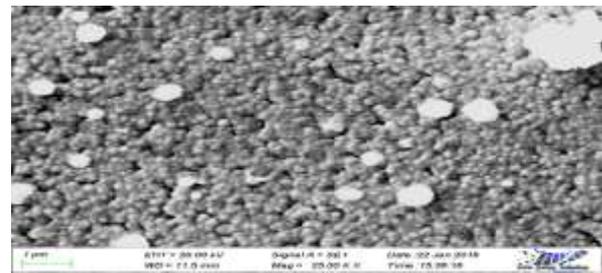
Figure 1(b): Deposited Cadmium Sulphide

### III. Results and Discussion

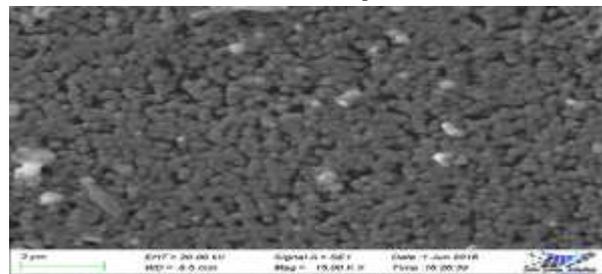
#### A. Morphological Characteristics

Scanning Electron Microscopy (SEM) of Zeiss VPSEM EV018 is used to take the surface images. The four SEM image micrographs of deposited CdS thin films are shown in Figure 2. Each sample shows different topographical pattern as their growth condition is different as mentioned in Table 1.

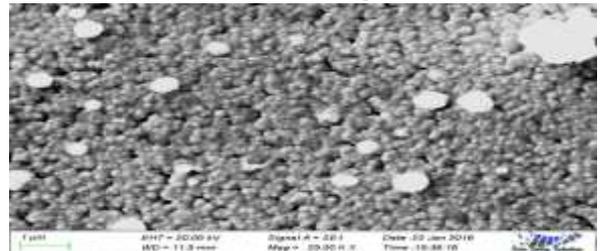
It is observed that Sample 1 shows uniform distribution of agglomerated particles with well-defined boundaries with very few pinholes in it. In sample 2 we do observe more pinholes than sample 1 and with less white particles. Note that sample 3 shows almost similar topographical pattern as sample 1, this is because their growth condition is quite similar. Among all the samples, sample 4 exhibits most number of pinholes associated with white particles. Generally we can say that the grown layers are neither compact nor a 2D layer, rather it confirms that they are polycrystalline.



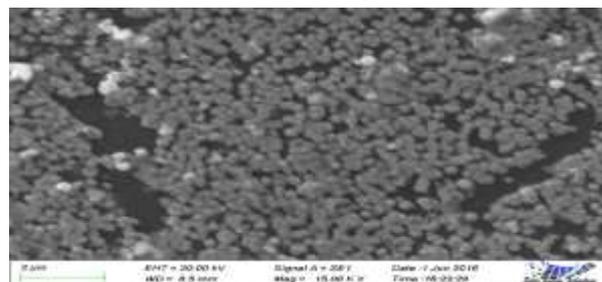
(a) Sample 1



(b) Sample 2



(c) Sample 3



(d) Sample 4

Figure 2: Scanning electron microscopy images of deposited CdS films at different conditions.

### B. Thickness

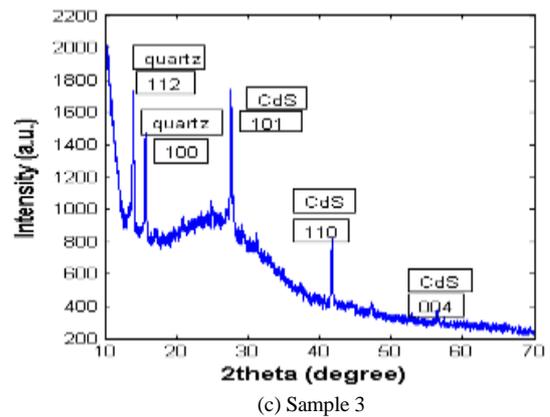
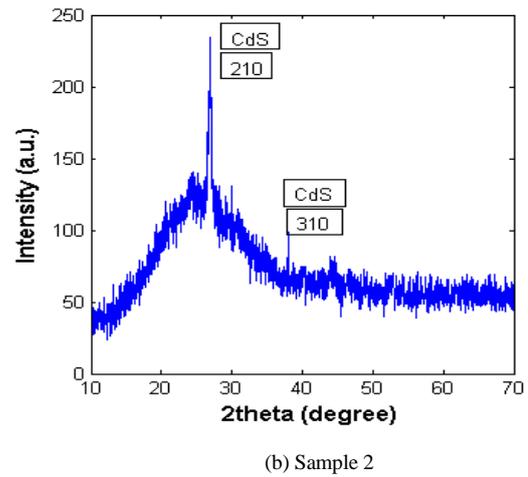
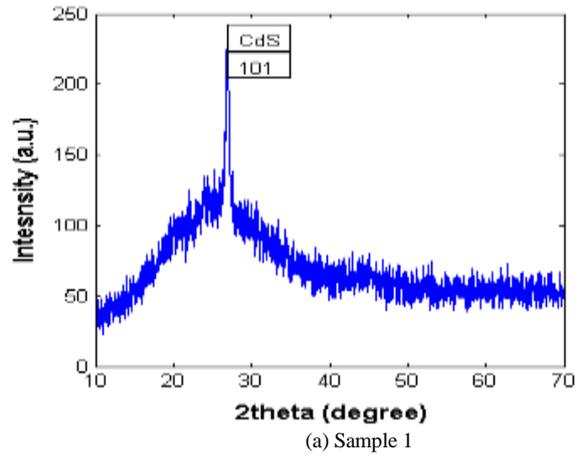
The thickness of the samples are measured using BRUKER DekTak XT system. In the case of sample 1 and 2 the deposited thicknesses are found 50 nm and 20 nm, respectively that is shown in Table 2. However in the case of sample 3 and 4, the obtained thicknesses of 137 nm and 157 nm, respectively are within the optimum range. This is due to the increased concentration of thiourea and more deposition time, shown in Table 1.

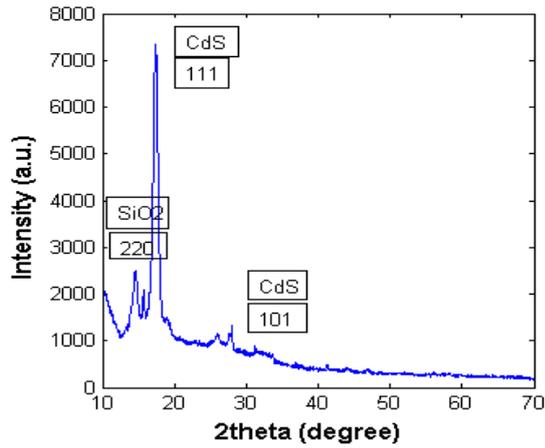
**Table 2:** Thickness of the deposited CdS thin films.

Sample No.	Thickness (nm)
Sample 1	50
Sample 2	20
Sample 3	137
Sample 4	157

### C. Structural Analysis

X-ray diffraction is performed by a GBC Mtrix SSD XRD system with Cu-K $\alpha$  radiation using the wavelength of 0.15418 nm, operated at 36 KV and 28 mA at room temperature with the scanning angular range  $20^\circ \leq 2\theta \leq 70^\circ$  to get possible fundamental peaks for each sample. From Figure 3 it can be seen that in the XRD of sample 1 we do observe only one peak at angle  $26.9^\circ$  of (101) plane which is the preferred orientation of CdS, confirming single crystalline layer<sup>11</sup>. However in the case of sample 2, planes (210) and (310) of CdS are obtained at angle  $27.2^\circ$  and  $38^\circ$ , respectively, suggesting that multiple crystallographic planes are available<sup>12</sup>. In sample 3, it has three different planes of CdS such as (101), (110) and (004) appeared at angles  $27.8^\circ$ ,  $42^\circ$  and  $56^\circ$ , respectively. The appearance of many number of planes is an indication of polycrystalline layers<sup>13</sup>. Also the presence of preferred (101) plane would be an added advantage of this layer. Note that this (101) plane is appeared in sample 4 however with low intensity. In sample 4, an additional plane (111) corresponding to CdS is observed. All this appeared planes in our four samples of CdS are reported that they have hexagonal structure<sup>14</sup>. The reason for getting different planes for different samples is their different growth condition (Table 1).





(d) Sample 4

Figure 3: XRD patterns of four different samples

#### D. Energy Dispersive Analysis of X-rays (EDAX)

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used here for the elemental analysis or chemical characterization of a sample. We performed EDX only on sample-3 as this sample exhibited better crystallinity in the preferred orientation by XRD. In Figure 4(a) the red rectangular of area  $1180 \mu\text{m} \times 570 \mu\text{m}$  in the SEM image shows the place where EDX is carried out. The results are listed in Table 3. It can be seen that the deposited CdS film contains 24.3% of sulphur (S) and 75.7% of cadmium (Cd) of the total weight percentage, whereas in terms of atomic weight sulphur consists 52.9% and cadmium consists 47.1%. The agglomerated white particles with well-defined boundaries present in the SEM image indicate the presence of sulphur<sup>15</sup>.

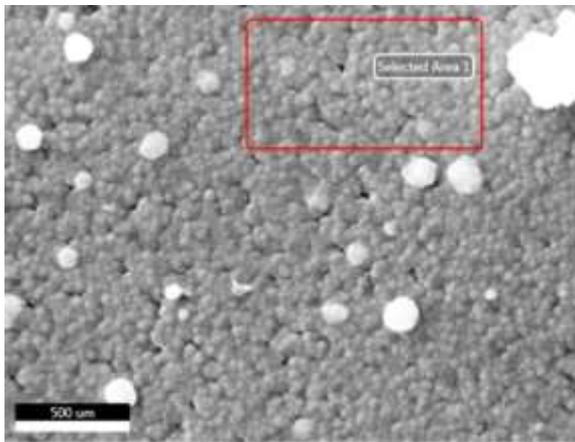


Figure 4: SEM Image of sample 3. Energy dispersive spectroscopy is performed on the red rectangular area.

Table 3: Elemental Properties found from EDS graph.

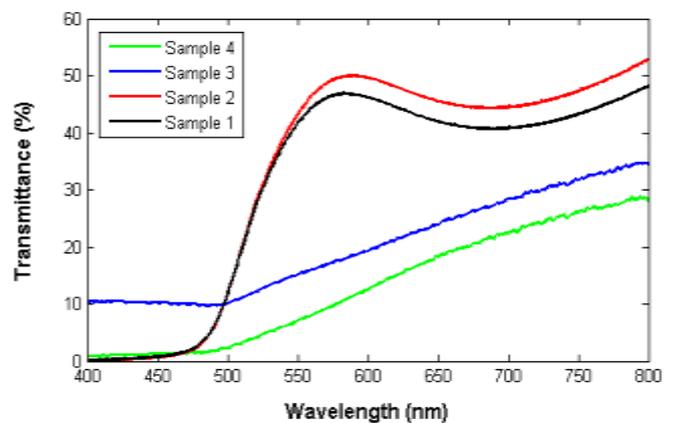
Element	Weight (%)	Atomic (%)	Net Int.	Error (%)	K-ratio
S K	24.3	52.9	34.6	9.4	0.2304
CdL	75.7	47.1	43.3	5.1	0.6631

#### E. Optical Characterization of CdS Thin Film

All optical characterization is carried out by UH4150 Spectrophotometer. For characterization the starting and end wavelengths are set at 260 nm and 1200 nm, respectively. The data is taken for the range of 400 nm to 800 nm. The scan speed is 600 nm/min and scanning interval is 2 nm. The slit width is 1 nm and path length is 10 nm.

##### Transmittance Measurement

The variation of transmittance,  $T$  (in percentage) with wavelength,  $\lambda$  (nm) for the wavelength range of 400-800 nm of deposited CdS films for various growth condition is shown in Figure 5. In the case of sample 1 and sample 2 there is a sharp rise in the transmission spectra near the band edge of 450 nm to 550 nm. Afterwards, for the rest of the wavelengths both sample show transmittance more than 40%<sup>16</sup>. However, in sample 3 and 4, we do observe a gradual increase in the transmittance for the wavelength range of 550 nm to 800 nm. The high transmittance of first two samples is likely due to the less light scattering by their almost smoothest surfaces<sup>17,18</sup>. Also the increase in transmittance of these two samples (1 and 2) with wavelength is possibly caused by the absorption of carrier in the degenerate films<sup>19</sup>. The decrease in transmission for the two other samples (3 and 4) is due to the increase in



crystallinity of films leads to higher scattering of light<sup>20</sup>.

Figure 5: Transmittance spectra of deposited Samples.

Figure 7: Absorbance spectra of deposited Samples

### Reflectance Measurement:

Figure 6 shows the optical reflectance spectra of deposited CdS thin films for different growth conditions. Sample 1 and 2 show low reflectance for the wavelength of 400 nm to 500 nm, and then a sharp transition is observed for the wavelength 500 nm to 560 nm. Afterwards a stable reflectance of above 0.7 is obtained for the wavelength more than 560 nm. However, the samples 3 and 4 exhibit high reflectance of more than 0.8. The variation in reflectance is due to the stoichiometry deviation arises by the sulphur (S) vacancies and excess of cadmium (Cd). The high values of reflectances are typical case of cadmium sulphide thin films depending on the thicknesses<sup>21</sup>.

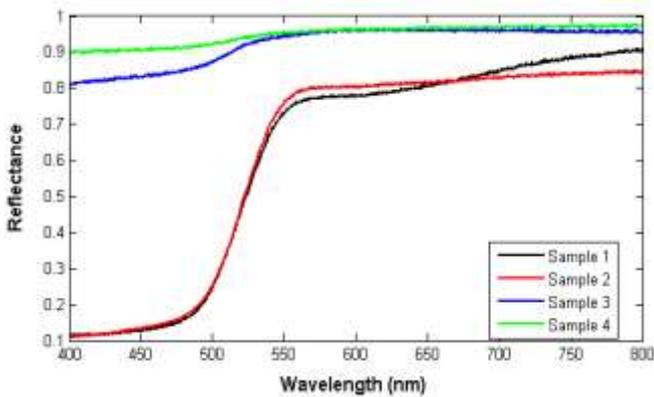
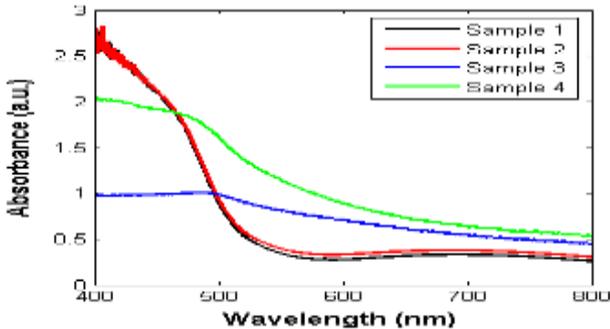


Figure 6: Reflectance spectra of deposited samples.

### Absorbance Measurement

Figure 7 shows the variation of absorbance with wavelength,  $\lambda$  (nm) at wavelength range of 400-800 nm for deposited CdS films having various thickness grown at different conditions. The absorbance of sample 1 and sample 2 is high for the wavelength of 400-500 nm. Afterwards this spectra reveal low absorbance above 500 nm. In the case of sample 3 and sample 4, absorbance shows a decreasing trend for wavelength 500-800 nm because of low absorption coefficient. Note that the thickness of sample 3 and 4 is higher than the sample 1 and 2, and they exhibit high absorbance in the shorter wavelength region.

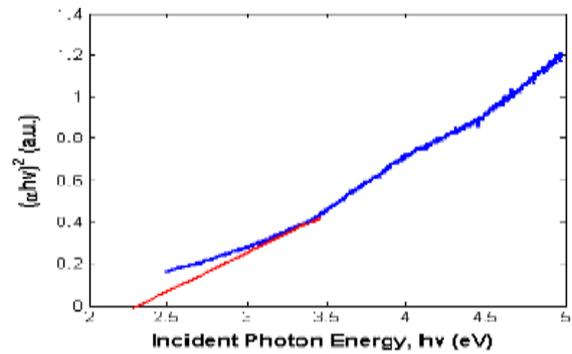


### F. Band gap Measurement

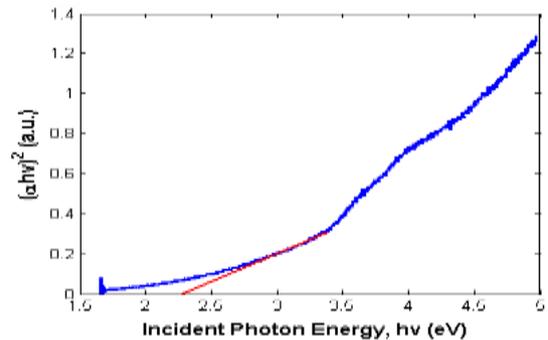
The band gap energy ( $E_g$ ) for CdS films is determined by plotting  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ), where  $\alpha$  is the coefficient of absorption<sup>22</sup>. Here the value of  $\alpha$  is measured using absorbance data. Band gap is estimated by assuming the allowed transition between valence band and conduction bands using the Tauc equation:

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

where,  $B$  is a constant,  $\alpha$  is the absorption coefficient,  $h\nu$  is the incident photon energy, and  $r$  is constant, and for indirect transition  $r$  equals 2. From the plot of  $(\alpha h\nu)^2$  vs  $h\nu$ ,  $E_g$  is determined by extrapolating the straight line portion of the spectrum to  $\alpha h\nu = 0$ . The Tauc plot for the deposited CdS films are shown in Figure 8 below<sup>23</sup>. From this plot both sample 1 and sample 2 exhibit band gap of 2.43 eV that is almost closed to the preferred band gap of CdS (2.42 eV)<sup>24</sup>. Similarly the band gap of sample 3 and sample 4 are determined to 2.18 eV and 2.20 eV.



(a) Sample 1



(b) Sample 2

Figure 8: Variation of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ) for CBD deposited CdS thin films.

### G. Electrical Properties

Electrical properties of the deposited CdS films are obtained by an Ecopia Corp HT55T3 (Korea – 0.545T) Hall Effect system. A Hall effect measurement system can actually be used to determine material parameters, such as carrier mobility(U), carrier concentration (n), Hall coefficient ( $R_H$ ), resistivity, magneto resistance (R), and the conductivity type (N or P), and these parameters are all derived from the Hall voltage measurement<sup>25</sup>. Table 4 shows the Hall Effect measurements conducted for four samples. We can see that sample 4 exhibits highest mobility, sample 3 shows highest resistivity, sample 1 gives highest n-type sheet concentration, and sample 3 present highest magneto resistance. The conductivity of all samples are found n-type (Table 5).

**Table 4:** Electrical properties using Hall probe

Characteristics	Sample 1	Sample 2	Sample 3	Sample 4
Mobility (U)	$5.102 \times 10^0$	$1.254 \times 10^2$	$7.7443 \times 10^0$	$5.854 \times 10^2$
Resistivity (RHO)	$1.149 \times 10^4$	$1.287 \times 10^3$	$2.310 \times 10^4$	$6.414 \times 10^3$
Sheet Concentration (NS)	$-5.322 \times 10^8$	$-7.735 \times 10^7$	$-4.937 \times 10^8$	$-2.593 \times 10^7$
Magneto Resistance ( $\Delta$ )	$2.239 \times 10^8$	$7.671 \times 10^8$	$2.174 \times 10^8$	$3.670 \times 10^8$

**Table 5:** Conductivity of deposited CdS films

Sample No.	Conductivity, $\sigma(1/\Omega\text{-cm})$	Results of conductivity
Sample 1	$1.559 \times 10^{-4}$	n-type
Sample 2	$7.831 \times 10^{-5}$	n-type
Sample 3	$4.328 \times 10^{-5}$	n-type
Sample 4	$1.559 \times 10^{-4}$	n-type

### IV. Conclusion

In this experiment, the deposition conditions have been optimized for getting the better quality layers for using it as a buffer layer in solar cells. From SEM images it can be said that the grown layers of CdS are neither compact nor a 2D layer, rather it confirms that they are polycrystalline. Different thickness is obtained because of varied thiourea concentration and deposition time. XRD patterns reveal that the reason for getting different planes for different samples is their different growth condition. Transmittance shows increasing values for sample 1 and sample 2 whereas low reflectance values are observed for the same samples for wavelength longer than 500 nm. Sample 1 and sample 2 have low absorbance and high transmittance in the visible to infrared range, which is suitable for act this as buffer layer in hetero-junction solar cell application. Both sample 1 and sample 2 exhibit band gap of

2.43 eV that is almost closed to the preferred band gap of CdS (2.42 eV)<sup>26</sup>. Hall Effect measurement exhibits that sample 4 shows highest mobility and the conductivity of all samples are found n-type.

### References

- [1] P. D. Maycock, *Photovoltaic News*, 22 (2003) 2.
- [2] M. Z. Jacobson, *Energy & Environmental Science*, 2 (2009) 148.
- [3]<http://science.howstuffworks.com/environmental/green-science/thin-film-solar-cell2.html>
- [4] <http://ieeexplore.ieee.org/document/1305348/>
- [5]<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4630620/>
- [6] F. Ouachtari, A. Rmili, S. E. B. Elidrissi, A. Bouaouad, H. Erguig, P. Elies, *Journal of Modern Physics*, 2 (2011) 1073-1082.
- [7] K. Kim, L. Larina, J. H. Yun, K. H. Yoon, H. S. Kwon and B. T. Ahn, *Physical Chemistry Chemical Physics*, 15 (2013) 9239-9244.
- [8] V. P. Balema, *Material Matters*, 1.3 (2006) 3.
- [9] P.K Nair, M.T.S Nair, V.M Garcia, O.L Arenas, Y Peña, A. Castillo, I.T Ayala, O Gomezdaza, A Sánchez, J Campos, H Hu, R Suárez, M.E Rincón, *Solar Energy Materials and Solar Cells*, Vol. 52, Issues 3-4, 30, 31 (April 1998) 313-344.
- [10] S. W. N. and Slot L., *Handbook of Photovoltaic Science & Engineering*, (2003) 567-616.
- [11] X-ray Diffraction Pattern: JCPDS card: 26-0243.
- [12] M. B. Rabeh, R. Touatti, M. Kanzari, *International Journal of Engineering Practical research (IJEPR)*, 2(2) (2013) 71.
- [13] J. J. Scragg, P. J. Dale, L.M. Peter, *Thin Solid Films*, 517 (2009) 2481.
- [14] Y Wang, J. Ma, P. Liu, Y. Chen, R. Li, J. Lu, S. Yang, X. Gao, *Material letters*, 77 (2012).
- [15] C. D. Lokhande, S. H. Pawar, *Material Chemistry and Physics*, 11 (1984) 201.
- [16] P. A. Nwofe, P. E. Agbo, *Int. J. Thin. Fil. Sci. Tec.* 4, No. 2 (2015) 63-67.
- [17] X. Zhang, X. Shi, W. Ye, C. Ma, C. Wang, *Applied Physics*, 94 (2009) 381.
- [18] V. D. Vanker, S. R. Das, P. Nath, K. L. Chopra, *Physics Status Solidi (A)*, 45 (1978) 665.
- [19] [https://en.wikipedia.org/wiki/Cadmium\\_sulfide](https://en.wikipedia.org/wiki/Cadmium_sulfide) [20] H. Khallaf, I. O. Oladeji, G. Chai, L. Chow, *Thin Solid Films*, 516 (2008) 7306-7312.
- [21] M. E. Calixto, M. L. A. Aguilera, M. T. Velazquez, G. C. Puente, A. M. Acevedo, *Solar Cells – Thin Film Technologies, In Tech*, (2011) 456.
- [22] F. Y. Liu, Y. Q. Lai, J. Liu, B. Wang, S. S. Kuang, Z. A. Zhang, J. Li, Y. X. Liu, *Journal of Alloys and Compounds*, Vol. 493, No. 1-2 (2010) 305-308.

---

[23] K. S. RAMAIAH, R. D. PILKINGTON, A. E. HILL, R. D. TOMLINSON, A. K.,  
*MATERIAL CHEMISTRY AND PHYSICS*, VOL. 68, NO. 1-3 (2001) 22-30.

[24] [HTTP://WWW.CIRCUITSTODAY.COM/THIN-FILM-SOLAR-CELL](http://www.circuitstoday.com/thin-film-solar-cell)

[25] [EN.WIKIPEDIA.ORG/WIKI/HALL EFFECT](http://en.wikipedia.org/wiki/Hall_effect)

[26] H. YOO, J. KIM, L. ZHANG, *CURRENT APPLIED PHYSICS*, 12 (2012) 1052.