

Photoelectrochemical Properties of CdSe:Sb Thin Film based Solar Cells: Influence of Electrode Thickness

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Abstract

CdSe:Sb (0.1 mol%) thin films of varying thicknesses (423–1838 nm) have been deposited onto the glass and stainless steel substrates in an alkaline medium ($\text{pH} = 10$) using a solution growth technique. The photoelectrochemical activities of these films have been examined using CdSe:Sb (0.1 mol%)/0.25 M NaOH - 0.25M Na₂S- 0.25M S/graphite cell configuration. The films were characterized under illumination of 20 mW/cm² intensity to evaluate various cell parameters such as η , ff , R_s , R_{sh} etc. It is found that the efficiency η and fill factor ff increased from 0.24% to 0.45%, and 51% to 52.9%, respectively, with increase in the film thickness from 423 nm to 1826 nm. The I-V characteristics in dark revealed that the junctions formed in these cells are of rectifying nature. The magnitude of flat band potentials V_{fb} were determined from the C-V characteristics in dark and found to increase from 1080 mV to 1370 mV. The improvement in the cell performance has been explained in terms of the modified crystal size, surface features and film transport characteristics.

1. Introduction

The II-VI semiconducting compounds, especially the cadmium chalcogenides, have been extensively studied due to their potential applications in semiconductor devices and solar cells [1–3]. It is worth mentioning that cadmium selenide has an intense potential in solar cells. We have already seen that the CdSe thin films with appropriate Sb doping are promising in photoelectrochemical solar cells [2], with the most favorable results obtained at 0.1 mol% Sb³⁺ concentration in CdSe [4]. The doping concentration considerably reduces the electrode resistivity and, in turn enhances, the cell conversion efficiency [3]. Another technical parameter that has key role in cell performance is the electrode materials thickness [3]. The electrode thickness has much influence and, therefore, has a great impact on the conversion efficiency. In general, for higher solar conversion efficiency, photo electrode materials with larger crystallite sizes are preferred [5].

This paper describes an attempt to increase the film thickness and its effect on the electrochemical photovoltaic conversion efficiency of a solar cell.

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2. Experimental Techniques

CdSe:Sb (0.1 mol% Sb) thin films with varying thicknesses were deposited onto glass and stainless steel substrates using a simple, inexpensive and very economical chemical bath deposition process reported elsewhere [2, 4, 6]. For deposition of the film samples, cadmium sulphate, and sodium selenosulphite (refluxed) were mixed together in a stoichiometric proportion. AR grade antimony trichloride was used as the source material for doping. Triethanolamine was used as a complexing agent. Sodium hydroxide and aqueous ammonia were used to adjust the pH to 10 ± 0.2 , and to increase the film adherence, respectively. The deposition was carried out at temperature 60° over a period of 90 min with a substrate speed of rotation of 70 rpm. The film thickness was increased by repeating the number of depositions. Each time the layers were exposed to fresh quantities of the reactants. The layer surface was cleaned after every successive deposition by double distilled water. The film thickness was measured by an interference fringes technique. The surface morphological features were examined through a Cameca SU-30 (France) scanning electron microscope, and the crystal structure was studied with Philips-PW-1710 diffractometer [Cu k_α Line] in the range of 2θ values from 20° to 80° . The dc electrical conductivity in the samples was measured over the temperature range 300–500 K. A two-probe press contact technique was used for this purpose. Using the integral method, the thermo emf generated by the samples was also measured, in the temperature range 300–550 K.

To characterize the I-V and C-V relationships in darkness and under varying degrees of illumination, built-in potential and power output characteristics CdSe:Sb thin film samples on stainless steel substrates were employed as active photoelectrodes in photoelectrochemical cells. A graphite rod was employed as a counter electrode and sulphide/polysulphide [0.25 M] as an electrolyte and all this was assembled in a specially designed glass cuvette.

3. Results and Discussion

The growth mechanism and kinetics of CdSe:Sb thin film formation is now fairly well understood and is reported elsewhere [2, 4, 6]. The photoelectrochemical studies on these films show that CdSe with 0.1 mol% Sb^{3+} gives higher short circuit current and open circuit photo voltage with an electrochemical conversion efficiency of 0.24% [4]. The open circuit photopotential V_{oc} and short circuit current I_{sc} can further be boosted by increasing the film electrode thickness. The film electrode thickness was therefore increased from 423 nm to 1838 nm by repeating the number of depositions. Each time fresh quantities of reactants were used for deposition. Figure 1 shows the variation of electrode thickness with the number of depositions. It is seen that initial variation in the thickness (up to 1727 nm) is linear, after which the thickness remained more or less the same. This behavior can be explained as follows: The kinetics of film growth suggests film grows either by ion-by-ion condensation, or by adsorption of the colloidal particles from the solution [7, 8]. For the first few layers, we observed thin, adherent, relatively less uniform and specularly reflecting films, showing the film growth as by an ion-by-ion condensation on the substrate surface [7, 8]. For later successive depositions, the earlier layer provides enough nucleating centers and/or the foreign impurities of the same kind and the film growth proceeds further. With the increase in the number of depositions, rate of adsorption of the colloidal particles on the substrate surface ceases and the film thickness tends towards saturation [7, 8].

The photoelectrochemical solar cells were then fabricated with these photoelectrodes of various thicknesses and their I-V and C-V characteristics in dark were studied. It is found that the forward current increased rapidly with increase in the electrode thickness, whereas reverse saturation current I_o decreased [3, 9]. This is partly attributed to: i) reduced surface traps with increase in the thickness; and ii) reduction in path shortening through the micropores in the electrode structure [3, 9]. The reverse saturation current I_o for each of the cells was then determined from these studies. It is observed that I_o decreased with increase in photoelectrode thickness. The junction ideality factors (n_d 's) were also then determined from the slopes of log I-V plots (see Fig. 2) and are cited in Table 1. It is seen that n_d decreased with increased electrode thickness. The capacitance voltage measurements were done on these cells of different thicknesses to evaluate the flat band potentials V_{fb} (see Fig. 3) and are cited in Table 1. It is seen that flat band potential V_{fb} varied considerably, from 1080 mV to 1370 mV as the electrode thickness increased from 423 nm to 1838 nm. This variation can be attributed to the reduced reverse saturation current I_o of a cell [3–5, 7]. To

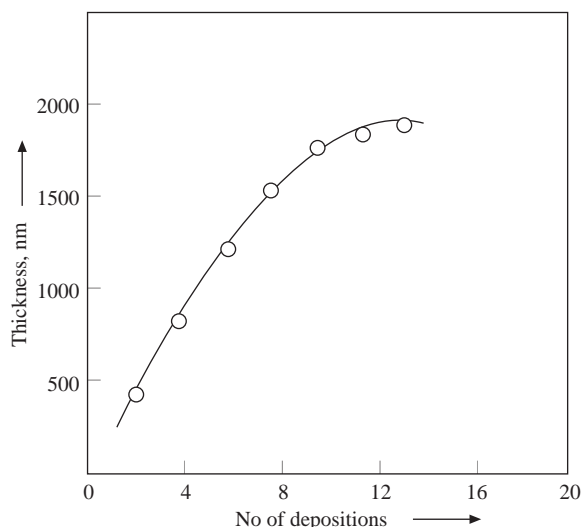


Figure 1. Variation of film thickness versus no. of depositions.

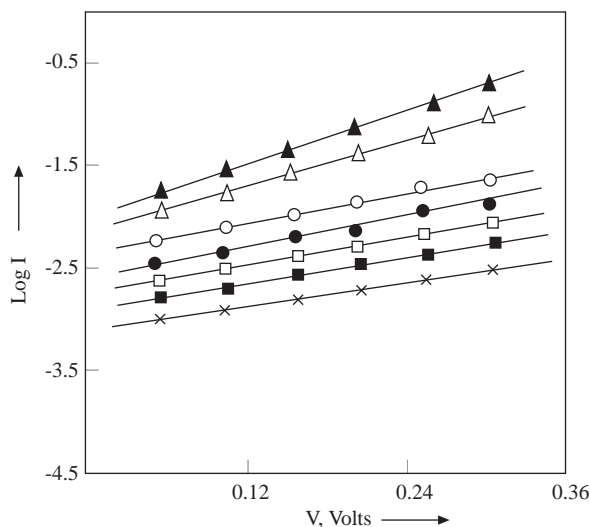


Figure 2. Plots of $\log I$ vs V for seven typical cells of CdSe: Sb (0.1 mol%) photoelectrodes of varying thicknesses. 423 nm(▲), 811 nm (Δ), 1201 nm (\circ), 1493 nm(\bullet), 1727 nm (\square), 1826 nm (\blacksquare) and 1838 nm (\times).

determine the built-in potentials Φ_B of the cells, the temperature dependence of the reverse saturation current I_0 was measured. It was found that the reverse saturation current has an exponential dependence on the temperature. From the slopes of the plots of variation of $\log (I_0/T^2)$ vs. $1/T$, the Φ_B 's were determined and are documented in Table 1. It is seen that Φ_B increased with electrode thickness, which may be attributed to improved grain structure of the film electrode material [9]. The above cells were then illuminated with white light at 20 mW/cm^2 and the power output curves were recorded and are shown in Fig. 4. The cell performance parameters, such as η , ff , R_s and R_{sh} were computed from these curves. These parameters are tabulated in Table 1. It is seen that η and ff increased from 0.24% to 0.45% and 51% to 52.9%, respectively, as the film thickness increased from 423 to 1826 nm. Shunt resistance R_{sh} was found to increase with film thickness. Furthermore, it can be seen that there is considerable reduction in the series resistance R_s of a cell with increase in the electrode thickness. The short circuit current I_{sc} and open circuit voltage V_{oc} are found to increase almost linearly with the thickness, showing slight deviation for higher values of thickness. The enhancement in I_{sc} from $205 \mu\text{A/cm}^2$ to $302 \mu\text{A/cm}^2$ is solely due to 1) increased solar photon absorption volume [9, 10] and 2) due to decreased series resistance in the cell [9, 11]. The increase in V_{oc} from 465 mV to 560 mV can be correlated to the increased flat band potential and

reduced reverse saturation current of a cell [9, 10]. Enhancement in the efficiency and fill factor are direct consequences of improvement in the short circuit current I_{sc} and open circuit voltage V_{oc} . The improved cell performance can also be explained and supported by modifications in the film properties.

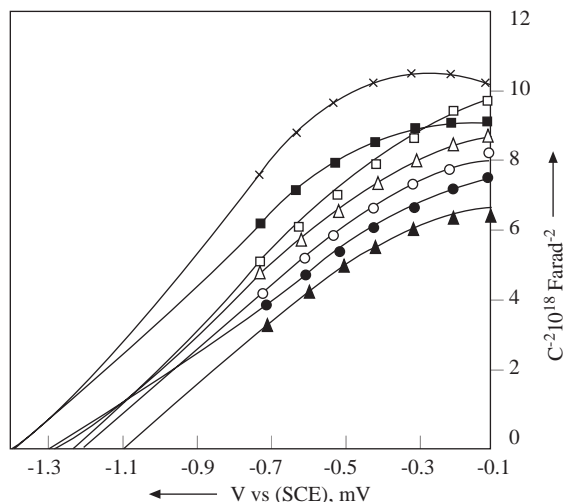


Figure 3. Mott-Schottky plots of CdSe:Sb (0.1 mol%) photoelectrodes of varying thicknesses. 423 nm (▲), 811 nm (Δ), 1201 nm (○), 1493 nm (●), 1727 nm (□), 1826 nm (■) and 1838 nm (x).

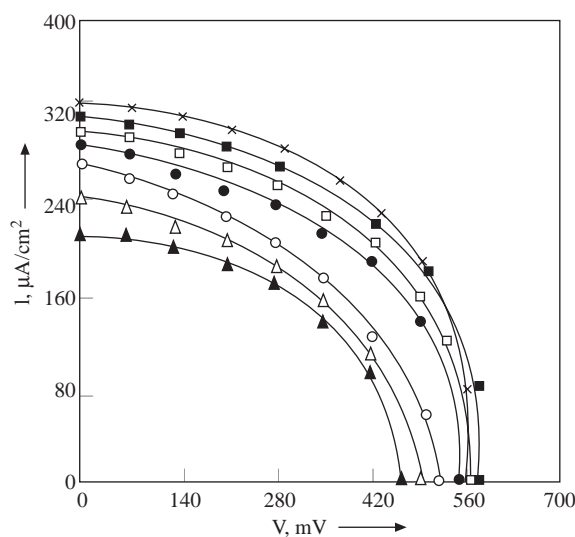


Figure 4. Power output curves for seven typical cells of CdSe:Sb (0.1 mol%) photoelectrodes of varying thicknesses. 423nm (▲), 811 nm (Δ), 1201 nm (○), 1493 nm (●), 1727 nm (□), 1826 nm (■) and 1838 nm (x).

Table 1. Dependence of cell performance parameters on the film thickness.

| Thickness nm | V_{oc} mV | I_{sc} $\mu\text{A}/\text{cm}^2$ | η (%) | ff (%) | R_s Ω | R_{sh} k Ω | n_d | Φ_B eV | V_{fb} mV |
|-----------------|----------------|---------------------------------------|---------------|-------------|-------------------|------------------------|-------|----------------|----------------|
| 423 | 465 | 205 | 0.240 | 51.0 | 300 | 12.0 | 4.0 | 0.63 | 1280 |
| 811 | 490 | 225 | 0.280 | 51.1 | 306 | 11.8 | 3.6 | 0.70 | 1240 |
| 1201 | 511 | 260 | 0.308 | 46.3 | 295 | 12.2 | 3.0 | 0.76 | 1180 |
| 1493 | 545 | 281 | 0.385 | 51.8 | 281 | 12.4 | 2.6 | 0.82 | 1250 |
| 1727 | 552 | 292 | 0.420 | 52.1 | 262 | 12.8 | 2.5 | 0.90 | 1250 |
| 1826 | 560 | 301 | 0.450 | 52.9 | 233 | 13.0 | 2.1 | 0.95 | 1370 |
| 1838 | 563 | 302 | 0.440 | 53.3 | 233 | 12.0 | 2.0 | 0.95 | 1370 |

The X-ray diffractograms of five different film electrodes were obtained (see Fig. 5). The diffraction peaks occur at the same positions with modifications in the peak intensities. This shows improvement in the crystallite size. The average crystallite size \bar{D} was determined by the Debye-Scherrer relation [3]:

$$D = 0.9 \lambda / B \cos(\theta),$$

where λ is the wavelength of incident X-rays, B is the full width at half maxima and θ is the angle of diffraction. Various crystal sizes are documented in Table 2. Typically, the average crystallite size varied from 231 Å to 408 Å as the thickness changed from 423–1826 nm. Figure 6 shows SEM micrographs for five different film electrodes. It is clearly seen that there is significant improvement in the grain structure with the increase in film thickness. The crystallite sizes were also measured and are shown in Table 2. This improvement in grain structure is mainly responsible for boosting the conversion efficiency.

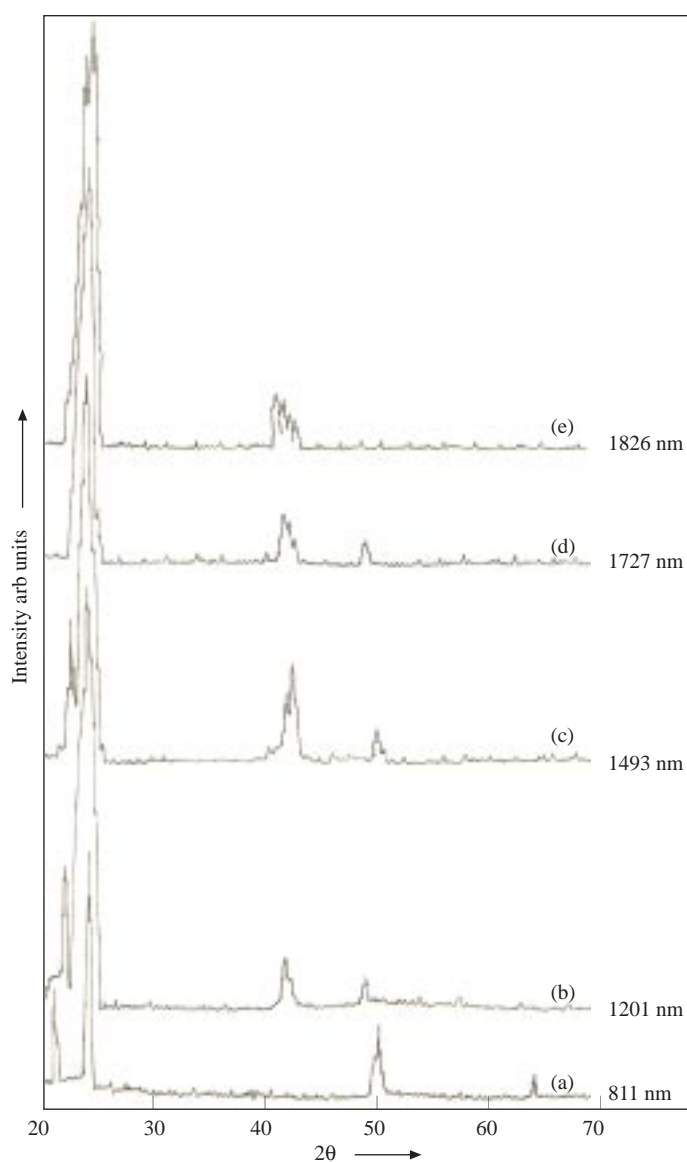


Figure 5. X-ray diffractograms of five typical samples CdSe:Sb (0.1 mol%) photoelectrodes of varying thicknesses. (a) 811 nm, (b) 1201 nm, (c) 1493 nm, (d) 1727 nm, and (e) 1826 nm.

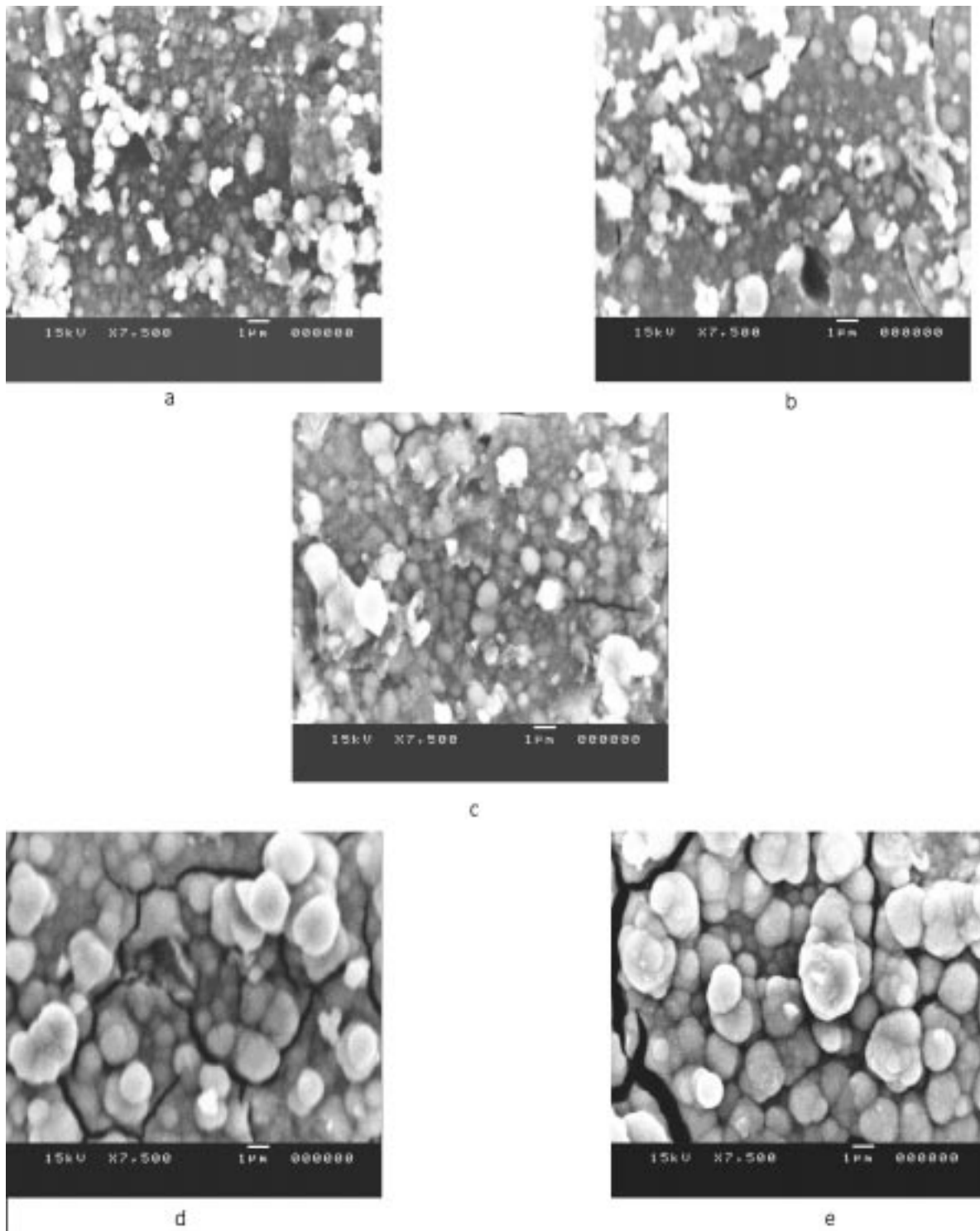


Figure 6. SEM micrographs for five thin film samples of CdSe:Sb(0.1 mol%) photoelectrodes of varying thicknesses. (a) 811 nm, (b) 1201 nm, (c) 1493 nm, (d) 1727 nm, and (e) 1826 nm.

Table 2. Enhancement in the various film characteristics.

| Thickness nm | Grain Size, Å | | $E_{a\sigma}$, eV | | Carrier Concentration $n \times 10^{19} \text{cm}^{-3}$ | Φ_B , eV |
|-----------------|---------------|-----|--------------------|------|---|---------------|
| | XRD | SEM | H.T | L.T | | |
| 423 | 231 | - | 0.57 | 0.17 | 1.5 | 0.47 |
| 811 | 283 | 312 | 0.55 | 0.17 | 3.0 | 0.47 |
| 1201 | 322 | 355 | 0.52 | 0.15 | 3.9 | 0.45 |
| 1493 | 357 | 371 | 0.49 | 0.14 | 5.2 | 0.44 |
| 1727 | 388 | 404 | 0.45 | 0.12 | 7.4 | 0.42 |
| 1826 | 408 | 428 | 0.42 | 0.10 | 9.2 | 0.40 |
| 1838 | - | - | 0.37 | 0.09 | 9.3 | 0.40 |

The dark dc electrical conductivities were measured for these films over the temperature range 300–500 K. The activation energies of electrical conduction were determined from the plots of $\log\sigma$ vs $1000/T$ in both temperature regions and are listed in Table 2. It is found that activation energies are thickness-dependent and found to decrease with increase in thickness. This can be attributed to the reduced intercrystalline barrier height, as explained via Seto’s model [13]. Further, it is found that room temperature electrical conductivity increased with increase in the film thickness. This type of behavior is also reported by Das et al. [14, 15] for $(\text{Bi}_{0.6}\text{Sb}_{0.4})_2\text{Te}_3$ and $\text{Pb}_{0.5}\text{Sn}_{0.5}\text{Fe}$ thin films and Shahane et al. for $\text{CdS}_{0.9}\text{Se}_{0.1}\text{In}$ films [3]. The thermo power properties were measured on the samples over 300–550 K temperature range. These studies were carried out to determine carrier concentration n , mobility μ and intercrystalline barrier heights Φ_B . The variation of thermoelectric power (TEP) with temperature is shown in Fig. 7. The carrier concentration and mobility were determined from these studies. The temperature dependence of mobility was further employed to calculate intercrystalline barrier heights for various film thicknesses and are listed in Table 2. This explains why room temperature electrical conductivity and, in turn, the photoelectrochemical activity of the cell increases with film electrode thickness and is maximum at 1826 nm.

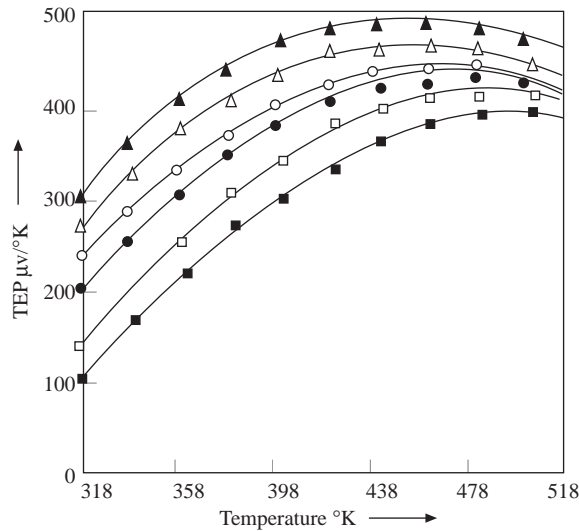


Figure 7. Variation of thermo power with temperature for CdSe:Sb(0.1 mol%) photoelectrodes of varying thicknesses. 423nm(▲), 811 nm(Δ), 1201 nm (○),1493 nm(●),1727 nm (□), 1826 nm (■) and 1838nm (x).

4. Conclusions

The electrode thickness was varied from 423 nm to 1838 nm by repeating the number of depositions with simple, inexpensive solution growth technique. The following are the salient features of our studies.

1. As regards, CdSe:Sb (0.1 mol %) films, the layer thickness went on increasing with number of depositions and was eventually saturated.
2. Photoelectrochemical behaviour is found to be greatly influenced by the increased electrode thickness. Since,
 - a) Both I_{sc} and V_{oc} increased from $205 \mu\text{A}/\text{cm}^2$ to $302 \mu\text{A}/\text{cm}^2$ and 465 mV to 563 mV, respectively.
 - b) Series resistance R_s decreased from 300 to 233 Ω .
 - c) Flat band potential V_{fb} enhanced from 1280 mV to 1370 mV
 - d) Conversion efficiency boosted from 0.24% to 0.45%.
3. This improved cell performance has been ascribed to
 - a) Increased grain size from 231 Å to 408 Å;
 - b) Decreased activation energies and intercrystalline barrier potential; and
 - c) Increased carrier concentration and carrier mobility.

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