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STUDIES ON ELECTROSYNTHESIS AND PHOTORESPONSE OF THALLIUM DOPED CdSe FILMS

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ABSTRACT

The doping of thallium in cadmium selenide thin films have been carried out using a simple electrochemical codeposition method with the objective to study its effect on the photoelectrochemical properties of cadmium selenide thin films and identification of optimal deposition potential at which thin films of highest photoresponse and greatest stability is obtained. Electro synthesized these thallium doped CdSe films deposited at different deposition potential have been characterized by current voltage behavior, capacitance and photo action spectral studies. The doping of thallium lowers the band gap of the elctrodeposited material of thin films. Corrosion measurements revealed that the thin films were endowed with lowest corrosion rate when synthesis was carried out at optimal deposition potential.

Keywords: Thallium doped cadmium selenide, electro synthesis, deposition potential, band gap, capacitance, corrosion

INTRODUCTION

Industrialization and urbanization has taken a toll on the environment. The air is polluted, the water resources are getting depleted and the climate is being unpredictable [1-3]. Environmental degradation is now one of the greatest challenges before us.

We are dependent on the environment for all our needs. The uncontrolled exploitation of natural resources is continued from long period. Many natural resources, such as fossil fuels cannot be replenished. If this exploitation continues, there will soon be a time when there will be no natural resource left. Thus the protection of earth and environment and to save them for our future generation should be our prime duty [4].

As the non renewable resources of energy are in limited quantity on earth, it is important to conserve their current supply and to use renewable resources of energy so that natural resources of energy will be available for future use [5-7]. The most suitable renewable resource of energy is solar energy. It is nonpolluting and safe source of energy [8-10]. For conversion of solar energy into electricity solar cells are used. Currently these are the best sources of electric power in satellites.

In the solar cells various types of semiconducting materials are being used. Among them mixed metal chalcogenides are currently attracting attention because of their importance from the view of a variety of optoelectronic and photovoltaic applications [11-13]. Some such materials having variable band gaps have been investigated [14-16].

We have carried out electro synthesis of thallium doped cadmium selenide in the form of titanium supported thin films with the objective of determination of their photo electrochemical characteristics. In electro synthetic work the deposition potential as well as the composition of electroplating solution play a vital role in controlling the quality of the electrodeposited thin films. Corrosion behavior, capacitance measurement and current-voltage studies in the dark and under illumination along with photo action spectral studies have been used for the characterization of the electrodeposited thin films.

EXPERIMENTAL

For electrochemical codeposition three electrode cells was used. A flag shaped titanium plate was cleaned with emery paper (john oakey), polished with diamond lapping paste (METSES diamond lapping 1.0 µm and 0.5 µm size) and Hifin Fluid-'OS' (Madras Metallurgical Services Pvt. Ltd.). It is then washed successively with acetone and deionized water. Its surface except the portion where material deposition was intended was covered with insulating tape. The electrode was then allowed to soak in an electroplating solution for an hour. Titanium foil was also used as counter electrode. The potential of working electrode was varied with respect to a saturated calomel electrode and the current between working and counter electrodes was measured using a digital multimeter (MASTECH, India Model MS 8220R). Cadmium sulphate, potassium iodide, cadmium acetate (all CDH, India) and selenium dioxide and thallium nitrate (Aldrich) were used for the preparation of solutions. Current voltage studies in appropriate electroplating solution were carried out using indigenously made power supply. For the measurement of photopotential a simple experimental arrangement was used in which when the dark potential between the working and counter electrodes became steady, the working electrode where CdSe thin film was deposited was illuminated with a beam of light from a 1000 watt tungsten lamp. Change in the potential was then recorded with a digital multimeter (Scientific Mes-Technik, India). Intensity of illumination was varied using a Dimmerstat (Automatic Electric Private Limited, Mumbai) to study the dependence of photopotential on relative light intensity.

RESULTS AND DISCUSSION

In order to identify the potential domain within which the deposition may take place, current voltage behavior is examined. The results show that the relevant electrochemical activity is expected within -0.5 V to -0.85 V versus saturated calomel electrode.

The thallium doped cadmium selenide films were prepared using electroplating solution containing 0.05 M $CdSO_4$, 0.01 M SeO_2 and 10^{-3} M Tl NO_3 by applying different deposition potential within -0.50 V to – 0.85 V range. The deposition condition of these thin films are presented in Table I. The film thickness values, h are calculated from current time plots using relationship [17]

$$h = Q\,(EW) / F\,A\,d$$

Where Q = charge in coulomb

(EW) = equivalent weight of deposited material

A = area of electrode and d = density

In the case of electroplating solution containing $TlNO_3$, the deposition current was fairly high. It was observed that in the case of deposition of (CdTl)Se films, the deposition current first decreases sharply, after few minutes it increases to certain value and again decreases. But steady current was always sufficiently higher than that in the case when $TlNO_3$, was not added in the electroplating solution deposited. A representative current time plot is shown in Fig. 1.

These films were tested for their optoelectronic behavior in 1.0 M cadmium acetate solution containing 0.01 M KI and 50 mM I_2 solution. The result is summarized in Table 2. These results show that a deposition potential of -0.70V is most suitable for obtaining the electrodeposited thin films of thallium doped cadmium selenide of better photo response.. The electrodeposited films at this potential shows maximum photo activity. Build up of photo potential and its decay was much faster in almost all cases. Further photo activity data shows that the electrodeposited films become anodic upon illumination indicating their p-type semiconducting nature. When deposition was carried out at -0.82V, the current measured between working and counter electrodes was very high.

The initial current was – 1.80 mA and steady current was – 0.79 mA. Due to very high current the deposited films were amorphous in nature and a little part of it was dropped into the solution during electro synthesis.

The value of dark potential E_D gives valuable information about the quality of the electrodeposited films. The dark potential E_D of electrodeposited film first decreases rapidly and then attains constant value. This happens in almost all cases. A representative plot is given in Fig. 2. It is observed in almost all cases that if E_D has low positive value then the electrodeposited film exhibit better photo response

Current voltage behavior of the thallium doped cadmium selenide thin film semiconductor electrodes in dark and under illumination was also studied to obtain the information concerning the nature of the semiconducting material. This clearly shows that the thallium doped cadmium selenide films are endowed with p-type semiconductivity.

Thallium doped cadmium selenide deposited films are likely to be susceptible to corrosion. With a view to ascertain ability of these films to withstand photocorrosion, the thin films were subjected to uninterrupted illumination in I_3^-/ I_2 redox solution. The results show that the electrodeposited films are resistant towards photocorrosion in substantial measure.

With a view to study the influence of thallium inclusion on band gap, photo action spectra in 300 nm to 1000 nm range were employed. A representative plot is shown in Fig.3. Band gap values were obtained from Ep^2 versus λ curves in accordance to the equation

$$Eg = \frac{hc}{\lambda \tau e}$$

Where Eg = band gap
c = velocity of light
e = electronic charge.
h = Plank constant

Cadmium selenide has a band gap of 1.7 eV. Whereas in the case of thallium selenide it is 0.75 eV. A lowering of band gap is expected with inclusion of thallium in the cadmium selenide lattice. It was indeed found experimently the band gap values of thallium doped CdSe thin films were found to be close to 1.39 eV.

Light intensity dependence of photopotential has been examined in Fig.4. The photopotential initially increases with light intensity but at higher light intensity, a stage of saturation is observed. On the other hand the photocurrent increases with increase in light intensity (Fig. 5.). However a linear relation exist between photopotential and ln(Light Intensity). The result is presented in Fig. 6. This behaviour indicates semiconducting nature of these thin films. The data are also consistent with equation.

$$Ep = \underline{2.303AKT} \quad \log I_L + Be$$

In this equation B is a constant and A is ideality factor. I_L denotes light intensity.

Examination of these results reveals that thallium doped cadmium selenide film under consideration is endowed with ideality factor 1.22. This shows that the above preparation was not ideal. For ideal systems this factor should be unity.

In order to investigate electrochemical corrosion behavior of the thin films variation of current with potential was studied to obtain Tafel plots. The anodic and cathodic Tafel plots are described by

$$\eta = \beta \, log \frac{i}{icorr}$$

Where $\eta =$ overvoltage of the thim film electrode with respect to its value at equilibrium, the so called corrosion polential E_{corr}

$i = current\ at\ applied\ polential$

i_{corr} = corrosion current

E_{corr} and i_{corr} were obtained using paralac data analysis technique [18]. Cathodic and anodic Tafels β_c and β_A are obtained from the slopes of Tafel plots .The corrosion rate is generally expressed is g/s and is measured using equation.

$$\mathcal{R}corr = \frac{icorr \ \chi \, (E.W)}{\mathcal{F}}$$

Where EW = equivalent weight of the deposited film . F = Faraday constant .

The values of corrosion current, corrosion rate, β_c and β_A for (CdTl)Se thin films deposited at different deposition potential were calculated from Tafel plots. The results are presented in Table.3.These results show that the thin films deposited at depositon potential -0.70 V versus saturated calomel electrode exhibit lowest corrosion rate.

A semiconductor when kept in a redox system behaves as a capacitor because of the formation of depletion layer. This capacitance varies with the potential to which the electrode is subjected and this variation is given by the Mott-Schottky relationship

$$1/C^2 = 2\,(E - E_{fb}\,) \,/\, e\ \varepsilon\ \varepsilon_0\ N_A$$

Where C is the capacitance of space charge region, e is the electronic charge, ε is the semiconductor dielectric constant, ε_0 is the 8.85 x 10^{-14} C/V cm, E is the applied voltage and E_{fb} is the potential at which the semiconductor bands are flat.

The charge carrier density, N_A and the flat band potential E_{fb} may be obtained by plotting $1/C^2$ against E vs SCE in the form of Mott-Schottky plots [19]. A representative Mott-Schottky plot is presented in the Fig.7. The slope of the plot is given by

$$Slope = 2 \,/\, [e\varepsilon\varepsilon_0\ N_A]$$

So that

$$N_A = 2 \,/\, [\ e\varepsilon\varepsilon_0 \ slope]$$

The capacitance behavior of (CdTl)Se thin films prepared in the electroplating solution containing 0.05 M $CdSO_4$, 0.01 M $Se0_2$ and 10^{-3} M $TlNO_3$

using different deposition potentials was studied. The results are presented in Table 4. These results show that highest flat band potential and charge carrier density is obtained for the thin films which were deposited at -0.70 V. The positive value of E_{fb} in all cases show that the deposited (CdTl)Se thin films are endowed with p-type of semiconductivity, the result already derived on the basis of photoactivity and current voltage behavior in dark and under illumination.

With the knowledge of flat band potential E_{fb}, the band bending and hence the depletion layer width, W_D, can be calculated [20-21]. We know that

$$E_b = E_{F,\,redox} - E_f \quad \text{and}$$

$$W_D = [2\, \epsilon_{SC}\, \epsilon_o\, E_b / e\, N_A]^{1/2}$$

Value of $E_{F,redox}$, the redox potential of I_3^-/I_2 redox couple is 0.295 V vs SCE. Results are also included in Table 4.

CONCLUSION

The above studies illustrate the possibility of doping of thallium in cadmium selenide thin films. The preparation of (CdTl)Se thin films may be carried out by electrochemical codeposition technique. The doping of thallium improves the quality of thin films in terms of their photoresponse and corrosion characteristics. Further the doping of thallium lowers the band gap of the deposited semiconducting material.

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Table 1. Deposition conditions of (CdTl)Se thin films obtained at different deposition potentials

Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and 10^{-3}M $TlNO_3$

Deposition Time = 2 hours

Deposition Potential (V)	**Initial current (mA)**	**Steady current (mA)**	**Film thickness (10^{-5}cm)**
-0.55	0.68	0.34	2.36
-0.60	0.83	0.42	2.98
-0.65	1.07	0.49	5.82
-0.70	1.01	0.50	6.53
-0.75	1.15	0.54	8.25
-0.80	2.24	0.58	9.97

Table 2. Variation of photoactivity of (CdTl)Se thin films with deposition potential

Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and 10^{-3}M $TlNO_3$

Deposition Potential(V)	**E_D (mV)**	**E_L (mV)**	**E_P (mV)**
-0.55	-616 -599 -537	-406 -356 -267	210 243 250
-0.60	-565 -521 -484	-369 -314 -266	196 207 218
-0.65	-575 -522 -440	-402 -302 -216	173 220 224
-0.70	-498 -519 44	-206 -218 370	292 301 326
-0.75	-460 -423 -512	-239 -220 -218	221 196 204
-0.80	-635 -525 -570	-402 -405 -466	233 220 204

Table 3. Corrosion characteristics obtained from Tafel plots

Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and 10^{-3} M $TlNO_3$

Testing solution: 1.0M $(CH_3COO)_2Cd$, 0.1M KI and 50mM I_2

Deposition potential (V)	E_{corr} (i = 0) (mV)	Cathodic Tafel β_C(mV)	Anodic Tafel β_A(mV)	i_{corr} (μ_A cm^{-2})	Corrosion rate (10^{-9} g/s)
-0.55	-202.96	277.77	312.50	2.65	2.92
-0.60	-83.54	166.66	385.05	2.75	2.72
-0.65	-55.47	300.01	454.24	2.45	2.42
-0.70	-50.88	449.39	375.12	1.97	1.95
-0.75	-136.47	100.65	212.78	2.29	2.26
-0.80	-253.63	249.61	167.31	2.88	2.85

Table 4. Capacitance characteristics of (CdTl)Se films of synthesized at different deposition Potentials.

Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and 10^{-3} M $TlNO_3$

Testing solution: 1.0M $(CH_3COO)_2$ Cd, 0.1M KI and 50mM I_2

Deposition potential(V)	E_{fb} (V)	N_A ($10^{17}cm^{-3}$)	E_b (V)	W_D (10^{-12}cm)
-0.55	1.12	1.10	0.825	1.91
-0.60	1.21	1.36	0.915	1.81
-0.65	1.32	2.11	1.025	1.54
-0.70	1.55	5.36	1.255	1.07
-0.75	1.39	2.82	1.095	1.37

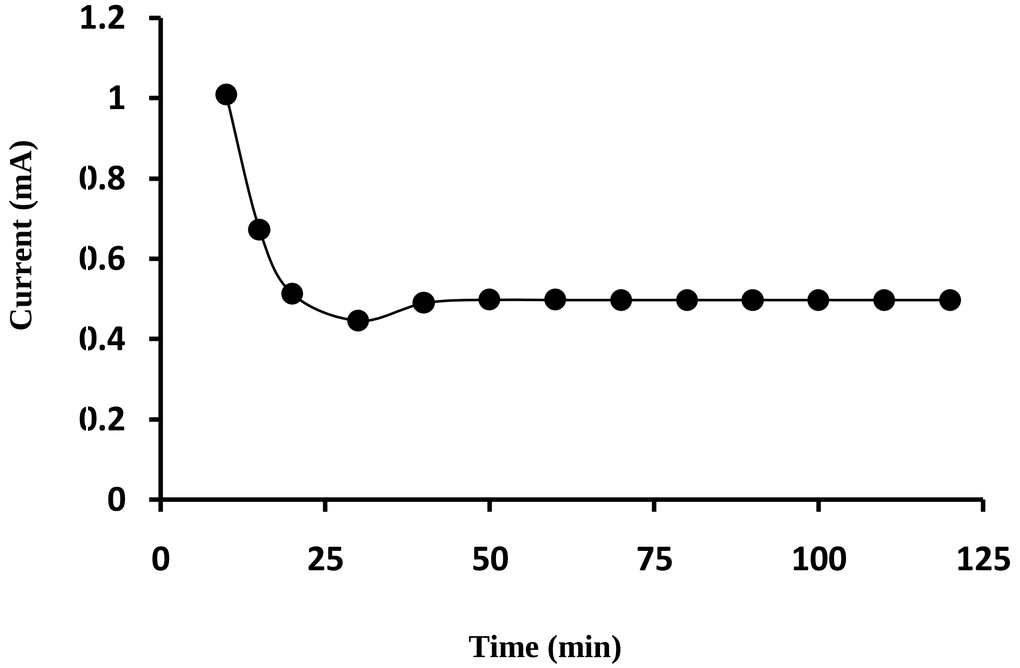

Fig.1. A representative current time curve

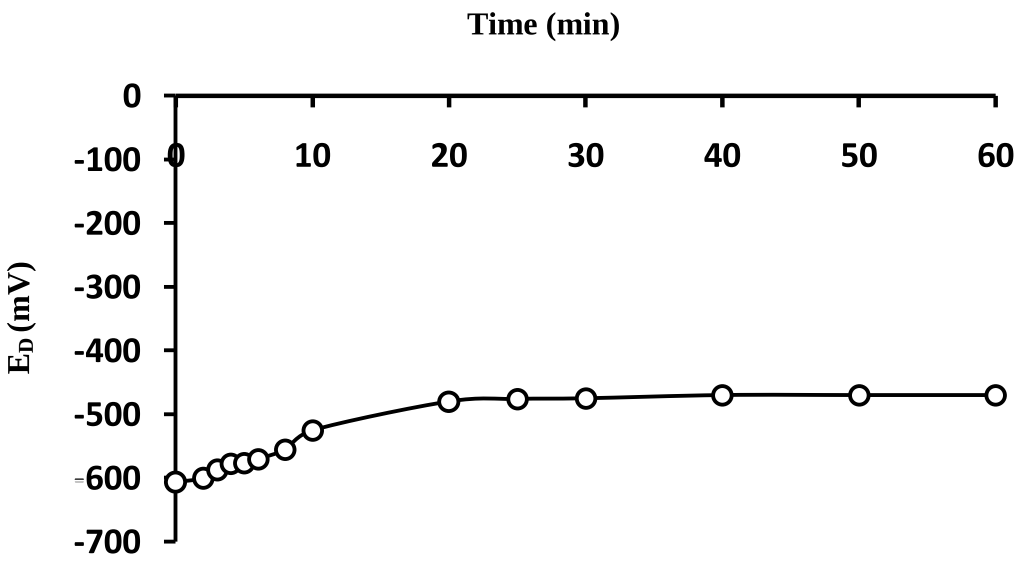

Fig. 2. Variation of dark potential with time

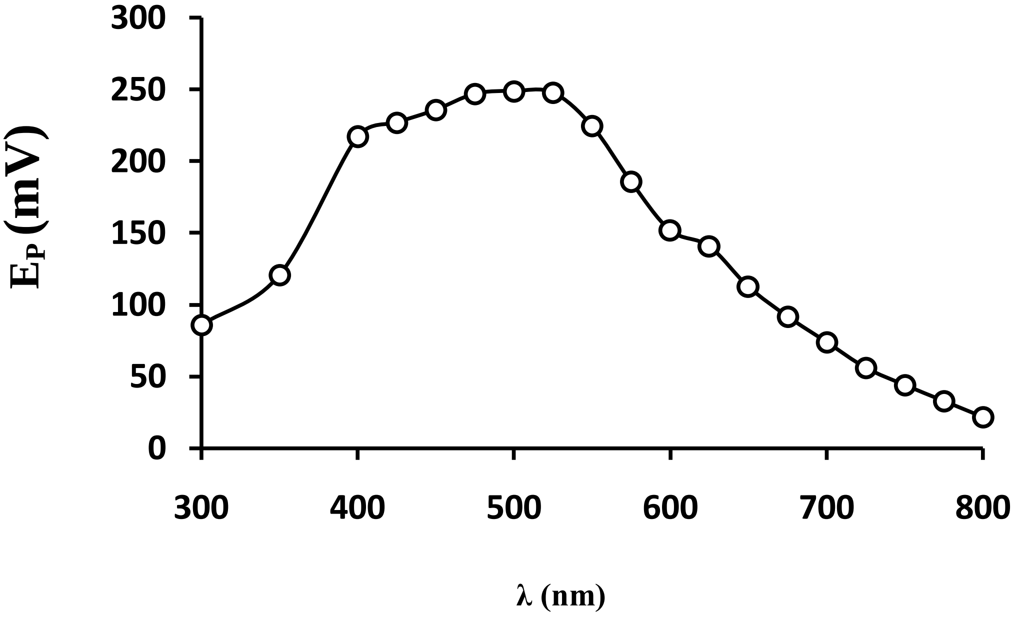

Fig. 3. Photoaction spectrum of a typical thallium doped cadmium selenide thin film

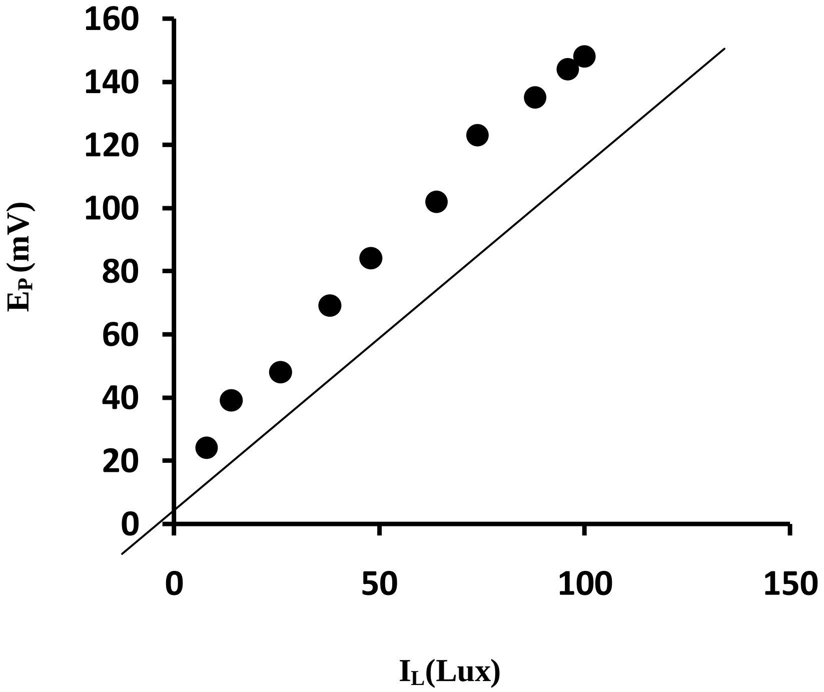

Fig. 4. Variation of photopotential E_P, with light intensity

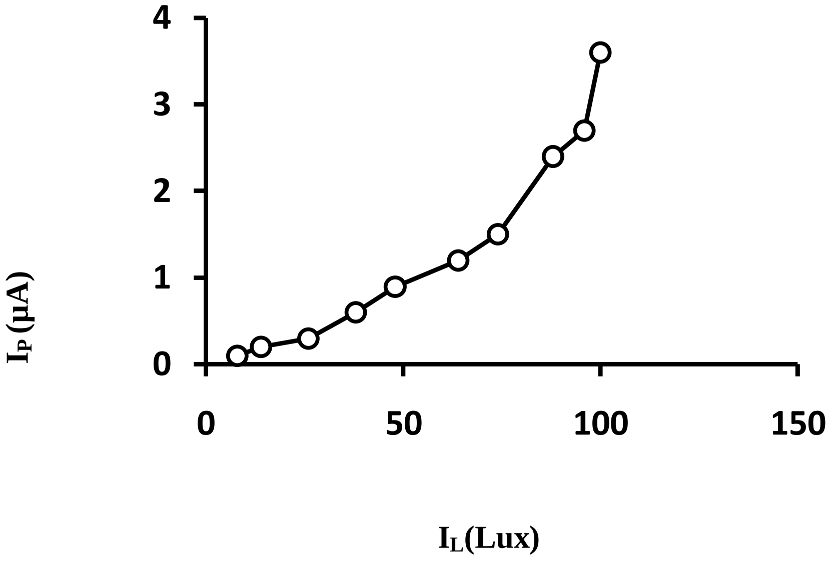

Fig. 5. Variation of photocurrent with light intensity

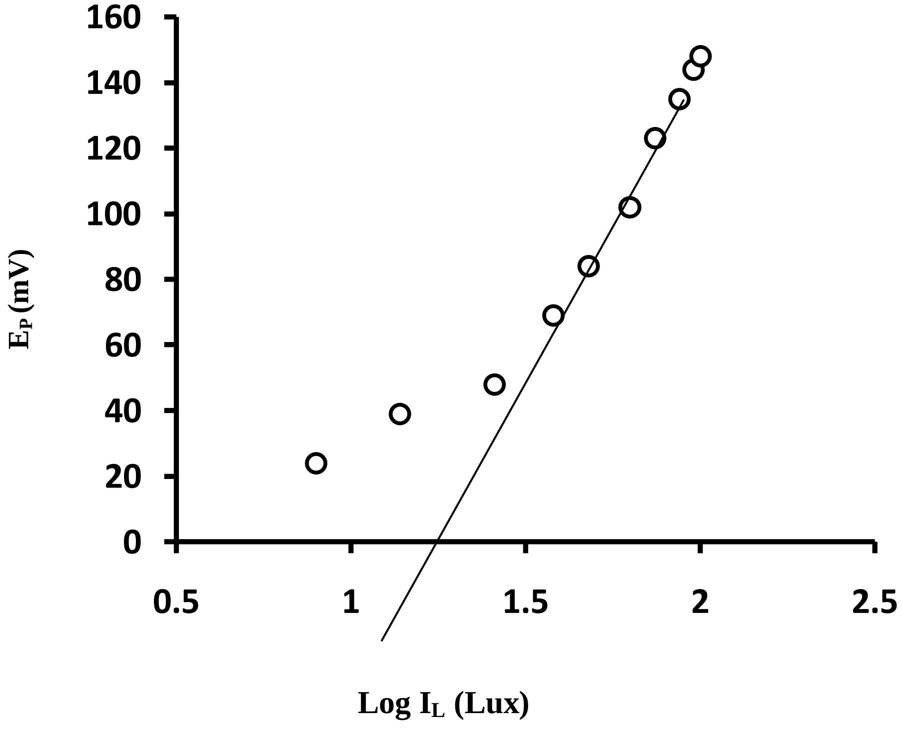

Fig.6. Variation of photopotential with log(light intensity)

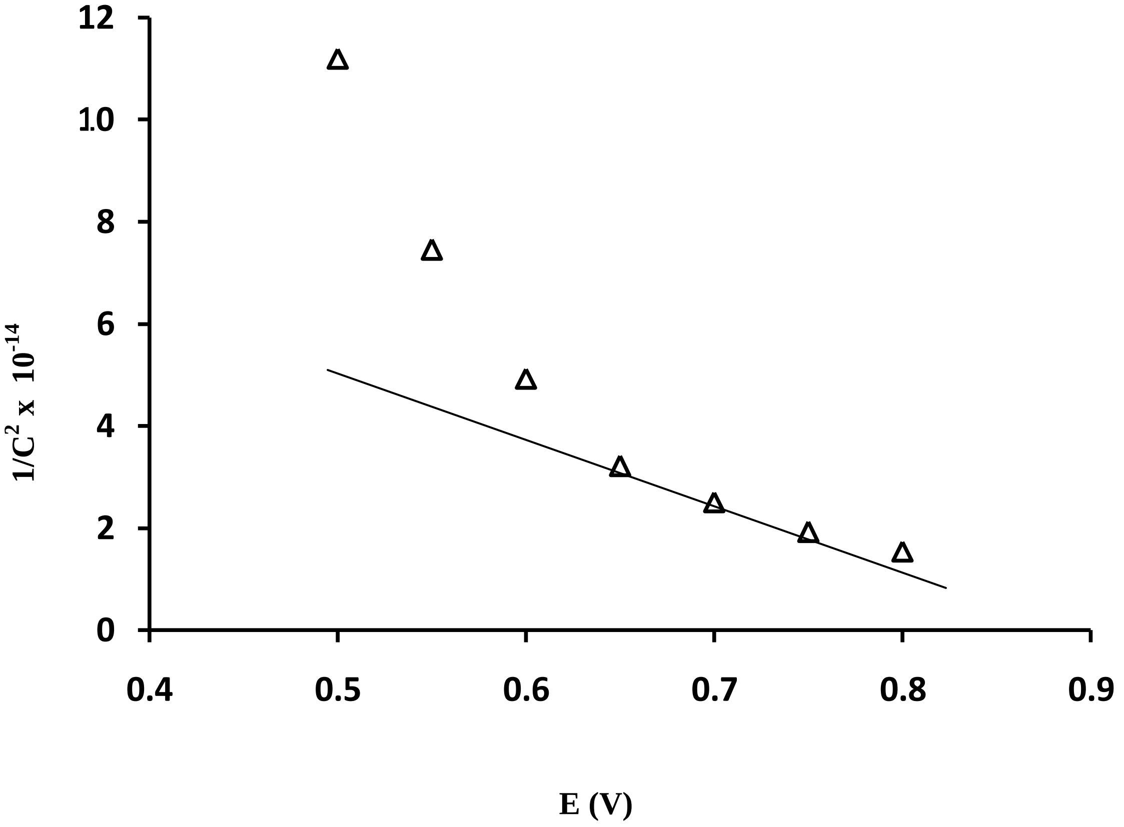

Fig. 7 A representative Mott-Schottky plot