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EFFECT OF REDOX SOLUTIONS ON OPTOELECTRONIC PROPERTIES OF CADMIUM SELENIDE FILMS

Md. Rashid Tanveer

Chemistry Department, St. Andrew's College, Gorakhpur-273001, UP(INDIA)

Email: rashidtanveer1@gmail.com

Abstract

Cadmiumselenide films of variable composition have been prepared using electrochemical codeposition method. Photoelectroactivityof cadmium acetate solution usingpolysulphide solution, Ce^{3+}/Ce^{4+} and Fe^{2+}/Fe^{3+} redox couples has been studied and compared with its activity in the I_3^-/I_2. Electrochemical impedance measurements have been used to estimate capacitance of the deposited thin films for the calculation of charge carrier density. Current voltage measurements have also been used for the characterization of these films. Dependence of photoelectroactivity of these thin films on light intensity, pH of redox solutions and the externally applied electrical bias has been investigated.

Keywords: Cadmium selenide, thin films, redox solutions, photoelectroactivity, light intensity

Introduction

The capture and conversion of solar energy into electricity is the promising way of generation of non polluting energy. This requires photovoltaic and photoelectrochemical cells consist of semiconducting materials. Recently there has been a great interest in developing inexpensive techniques for preparing large area polycrystalline thin films of binary semiconductors, for their application in photoelectrochemical cells. These cells essentially consist of a semiconductor electrolyte junction. Among binary semiconductor, CdSe is particularly of interest. CdSe is II-VI binary compound semiconductor. The electronic band gap of CdSe is most important parameter which determines the photosensitivity in visible range of electromagnetic spectrum .The high photosensitivity i.e. high absorption coefficient makes them suitable material for thin film photovoltaic device [1]. due to their excellent electrical, optical and structural properties. CdSe is also used in photo conducting, gamma ray detector, optoelectronics,thin film transistor and laser devices [2] The thin film of CdSe exhibits both types of semiconductivity dependingupon the type of vacancies created during deposition of thin films. The electronic behavior of CdSe thin films strongly depends upon method of deposition and source material used for film fabrication because of the non-stiochiometry created in film during deposition. The various vacuum and non-vacuum deposition methods have been used to deposit CdSe thin films. In the area of chemical deposition, the spray pyrolysis [3], electrochemical deposition [4], chemical bath deposition [5] and SILAR method [6,7] have been used to deposit CdSe thin films. The thermal evaporation [8], laser ablation method [9] and electron beam evaporation technique [10] in the area of physical deposition in vacuum have been used to deposit CdSe thin films. The fabrication and characterization of CdSe thin films by different techniques have been studied extensively. They studied their electrical, photo-electrical, structural, optical properties and reported ntypesemiconductivity of these thin films due to Selenium vacancies or excess of Cadmium. Therefore, we planned tocreate controlled amount of non-stiochiometry in CdSe thin films i.e. selenium vacancies orCadmium rich which is responsible for their n-type semiconductivity.

The CdSe thin films of were fabricated on titanium substrate at roomtemperatures by electrochemical codeposition method. These thin films were characterized by electrical and optical measurements.Thedirect band gap was calculated using absorption coefficient which is measured in thewavelength range 400nm to 700nm and found that the direct band gap varies between 1.48 eV to 1.38 eV.

To fulfill the increasing demand of energy mainly fossil fuels are being used worldwide. The excessive burning of fossil fuels have created global warming and air pollution to the alarming level[1-4]. Now there is a need to develop an alternate, sustainable and pollution free source of energy. Solar cells based on solar energy material is such an appropriate and promising alternate. Metal chalcogenides and mixed metal chalcogenides are currently being used as solar energy material in these solar cells for solar energy conversion.

For accomplishing optical conversions in solar cells, photoelectrochemical systems based on polycrystalline semiconductors are extensivelyinvestigated for their suitability[11-14]. In some cases electrosynthesis may be used to advantage for the preparation of such photoelectroactivematerials[15]. Such materials when kept in electrolyte systems containing redox species often undergo corrosion [16].We have prepared CdSe films of variable compositions and examined their corrosion behavior by impedance spectral studies. Electrodeposited thin films were also characterized on the basis of their photoresponse and photoaction spectral studies in different redox solutions. It has been demonstrated that the impairment of their activity due to anodic oxidation under illumination can be overcame to a large extent in aqueous polysulphide solution [17]. Displacement of selenide by sulphide ions in this redox solutions resulting in the formation of a protective cadmium sulphide layer would be responsible for stability of cadmium selenide thin films[18]. Photodecomposition of cadmium selenide occurs [19] as

$$\mathrm{CdSe}+\ 2h^{+} \qquad \mathrm{Cd}^{2+} + \mathrm{Se} \rightarrow$$

It is expected that this decomposition may be obviated to some extent in the presence of excess of Cd^{2+} ions in redox solution. We have chosen to study photoelectroactivity of cadmium selenide in cadmium acetate solution using aqueous polysulphide solution. Ce^{3+}/Ce^{4+} and Fe^{2+}/Fe^{3+} redox systems and compared the results with those obtained using I_3^-/I_2.

Characterization of the electrode in different redox system using capacitance and current voltage measurements has been carried out. Effect of pH and light intensity on photoelectroactivity of deposited thin films has been investigated.

Experimental:

For electrochemical codeposition three electrode cell was used. A flag shaped titanium foil was cleaned with emery paper (john oakey), polished with diamond lapping paste(METSES diamond lapping 1.0 µm and 0.5 µm size) and METESES lubricating oil. 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(Scientific Mes-Technik, India). Cadmium sulphate, potassium iodide, cadmium acetate (all CDH, India) and selenium dioxide (Aldrich) were used for the preparation of solutions. Current voltage studies in appropriate electroplating solution were carried out using rotating disc electrode system (pine instrumental company, USA). Electrochemical impedance measurement was carried out using Model 378 Electrochemical Measurements System (EG &Pricton Applied Research, USA) consisting of a potentiostat (Model 273) and a lock-in amplifier (Model 5208). For the measurement of photopotential a simple experimental arrangement was used[16] in whichwhen the dark potential between the working and counter electrodes became steady, the working electrode whereCdSe thin film was deposited.Illuminated with a beam of light from a 1000 watt tungsten lamp. Change in the potential was then recorded. 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:

For electrosynthesis of CdSe to take place it is essential that the deposition potential be sufficiently negative to discharge selenious acid to selenide ion in concentration high enough to precipitate CdSe in presence of Cd^{2+} ions, without being sufficiently negative to discharge cd^{2+} ions. Thus for electrochemical formation of substance, identification of the optimum deposition potential is essential. To do this current voltage behavior has been examined using rotating disc electrode. The results shows thatrelevent electrochemical activity is confined to about -0.45 V to -0.75 V versus SCE. These results also show that the deposition current increases with increase in disc rotation rate because of increase in reduction rate of constituent ions due to agitation. However it was observed that on variation of the concentration of SeO_2 keeping the cadmium sulphate content constant, the deposition current increases with increase in the concentration of SeO_2 in electroplating solution. Therefore the rate determining step is the deposition of selenium and not the depositon of cadmium. CdSe thin films were prepared using different potentials within this range and tested for their photoactivity in I_3^-/I_2 redox solution in the experimental setup.

CdSe (Ti) | Redox solution | Pt

It has already been demonstrated that CdSe thin films prepared using depositon potential of -0.65 V vs SCE are endowed with maximum photoactivity [20]· Accordingly all subsequent preparations were carried out using this optimal deposition potential. Deposition process were carried out for three hours in all cases.

The influence of concentration of SeO_2 in the electroplating solution was also analysed. For this purpose the concentration of $CdSO_4$ was kept constant and concentration of SeO_2 is varied. Photoactivity data obtained using CdSe thin films of above variable compositions is presented in Table-1. These results show that the thin films obtained using 0.01 M SeO_2 along with 0.05 M $CdSO_4$ in the electroplating solution produce maximum photoresponse. For these electrodeposited thin films of CdSe synthesized with different concentration of $CdSO_4$ in the electroplating solution, capacitance studies were carried out. The data of capacitance parameterssuch as charge carrier density, N_D and flat band potential, E_{fb} were derived from impedence studies at frequency = 1 KHz. The results are presented in Table -2. These results indicate that the CdSe thin film synthesized using electroplating solution consist of 0.05M $CdSO_4$ and 0.01M SeO_2 has lowest charge carrier density and maximum flat band potential. This indicates that the electroplating solution consist of 0.05M $CdSO_4$ and 0.01M SeO_2 is most suitable for electrosynthesis of CdSe thin films.

The capacitance measurements were also carried out at different frequencies. N_D and E_{fb} values were derived from these results.The variation in the values of flat band potential with applied frequency is shown in Fig. 1. The results shows that a very small decrease in photopotential is observed with significant increase in frequency. The flat band potential is practically independent of frequency.Now various CdSe thin films were synthesized using above electroplating solution and deposition potential equal to -0.65V. The results presented in Fig.2. shows that the value of N_D decrease sharply with increase in applied frequency. This is aggreement with the finding of some other workers [21].

The photopotential of the CdSe thin films is measured in different redox solutions. Higher photopotential is obtained in the case of I_3^-/I_2 redox solution. Theroretically the maximum photopotential should approach the difference between the flat band potiential of semiconductor and the redox potential of the electrolyte[22]. However, the experimentally observed photopotential values are of lower magnitude. It appears that existence of dissipative pathways and non-ideal character of the semiconducter-electrolyte interface result in lowering of the photopotential .

When the species in solution do not interact with the semiconductor surface, the changes in E_{redox} will be reflected in identical changes in the expected photopotential[23].Since conduction band and valence band positions are fixed and the band bending at equilibrium depends on the position of E_{redox} ,a linear dependence is expected provided the flat band potentials remains approximately constant . The values of flat band potential given in Table-3 are approximately constant except when polysulphide solution is used.The photopotential, however, do not depend linearly on redox potential (Fig 3).This deviation from the expected behaviour may arised due to significant shifting of potential in the Helmholtz layer on account of adsorption of ionic species on the interface. This result in the alteration of the surface charge distribution[24,25] .

A semiconducter-electrolyte interface treated as a schottky junction, may be used to derive the flat band potentials[26] from current –voltage characteristics.Current-voltage curves obtained under illumination using different redox couples were carried out. It was observed thatthe behaviour of the semiconductor thin film in only I_3^-/I_2 and S^{2-}/S_n^- redox couples is reasonably good; and the flat band potentials respectively are 0.69 V and 0.91V verses SCE. These values are somewhat higher than those derived from the capacitance data.Current-voltage curves in the I_3^-/I_2 redox system at different light intensities are shown in Fig.4. The onset of photocurrent becomes more cathodic with increase in light intensity, consistent with a more powerful oxidising surface at higher light intensities[27]. Under identical conditions significantly different photopotentials were observed.Initial rate of build-up of photopotential was found to be the lowest in polysulphide solution although the system yields maximum photopotential.The observed photopotentials vary with light intensity I_L. At lower intensity of illumination, a linear relationship is observed while tendency towards saturations is clearly indicated at higher I_L values. However, a linear relationship exist between photopotential and logarithm of the light intensity(Fig.5) for almost all the three redox solutions.

The observed photoeffect has also has been found to depend on pH of solution (Table 4).In I_3^-/I_2, the maximum phtoeffect is observed at pH=6,while in Ce^{3+}/Ce^{4-} and Fe^{2+}/Fe^{3+} it is observed at pH = 1.98 and 4 respectively.

The charge distribution in the interfacial region on the semiconductor side equilibrated with a redox system can be altered by the application of an electrical field. The electrical fields act predominantly across the depletion layer because of relatively lower concentration of charge carriers in this region. The semiconductor thus exhibits altered photoelectroactivity. Representative results are shown in Fig.6. Stability of semiconductor electrode in cadmium acetate in the presence of the different redox systems has been tested under uninterrupted illumination. Some impairment in the activity of the electrode has been observed in these redox solutions. However the CdSe thin films were found to be fairly stable in I_3^-/I_2 redox solution.

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Conclusion:

The above investigations clearly shows that the solution consists of 0.05M $CdSO_4$ and 0.01M SeO_2 is the most suitable electroplating solution for the electrosynthesis of CdSe thin films. For electrochemical characterization cadmium acetate containing I_3^- /I_2 redox couple was found to be most suitable.

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Table 1: Photoactivity dataof CdSethin films prepared with different electroplating solutions.

Electroplating solution: 0.05M $CdSO_4$ and variable composition of SeO_2

[SeO_2] (M)	**E_D (mV)**	**E_L (mV)**	**E_P (mV)**
0.005	-102 -66 -84	81 115 111	183 181 195
0.010	-165 39 -153	98 315 128	263 276 281
0.015	-147 111 -78	48 353 124	195 242 202
0.025	-151 -50 -17	44 153 156	195 202 176

Table 2: Flat band potential and charge carrier density valves of CdSe thin films.

Electroplating solution: 0.05M $CdSO_4$ and variable composition of SeO_2

[SeO_2] (M)	**E_{fb} (V)**	**N_D (10^{19} cm^{-3})**
0.005	0.76	6.31
0.010	1.24	0.98
0.015	0.88	4.17
0.025	1.07	2.91

Table 3: Flat band potential values calculated from Mott-Schottky plots in different redox solutions.

Redox solutions	**E_{fb} (V)**
$(CH_3COO)_2Cd/Ce^{3+}/Ce^{2+}$	0.648
$(CH_3COO)_2Cd/I_3^-/ I_2$	0.623
$(CH_3COO)_2Cd/Fe^{2+}/Fe^{3+}$	0.571
$(CH_3COO)_2Cd/S/S_n^-$	0.756

Table 4: Variation of photopotential with pH for different redox solutions

$(CH_3COO)_2Cd/I_3^-/ I_2$		**$(CH_3COO)_2Cd/Ce^{3+}/Ce^{2+}$**		**$(CH_3COO)_2Cd/Fe^{2+}/Fe^{3+}$**	
pH	**E_P (mV)**	**pH**	**E_P (mV)**	**pH**	**E_P (mV)**
4.00	135	1.20	339	1.90	164
4.30	208	1.98	395	4.00	228
5.10	330	4.00	261	5.00	192
6.00	407	5.15	276	6.00	151
7.00	273	6.60	231	6.35	149

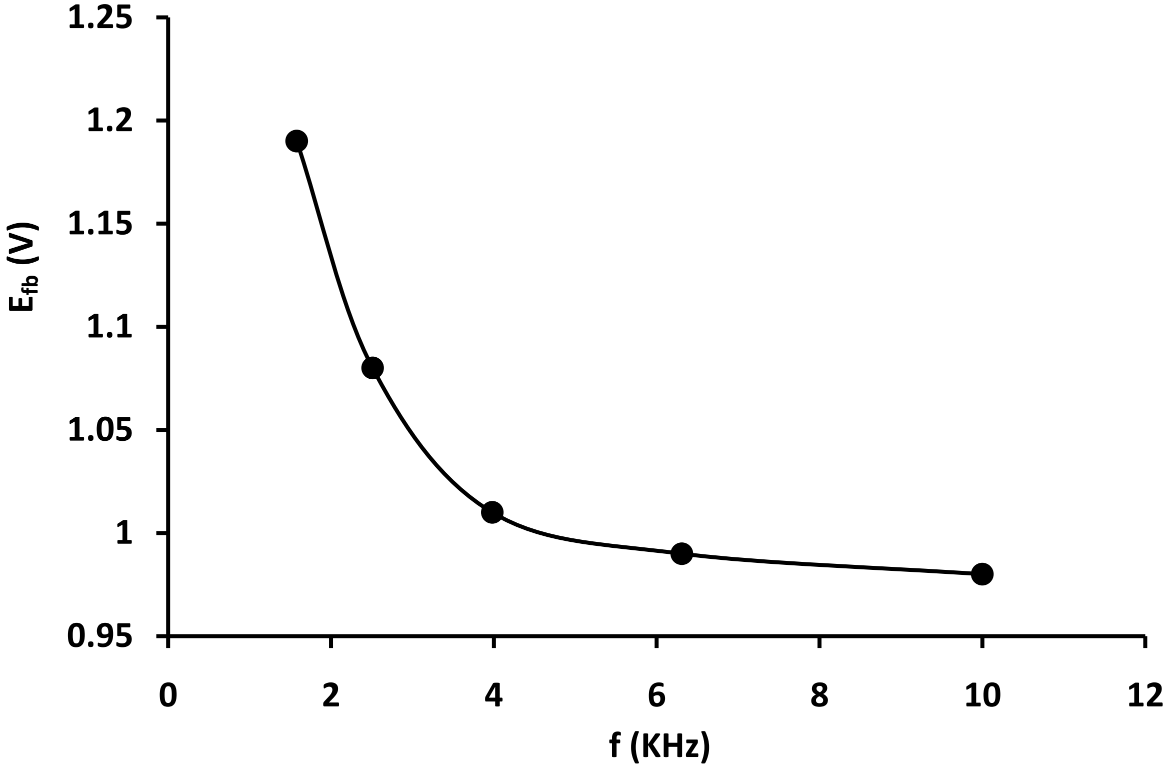

Fig.1. Variation of flat band potential (E_{fb}) with applied frequency.

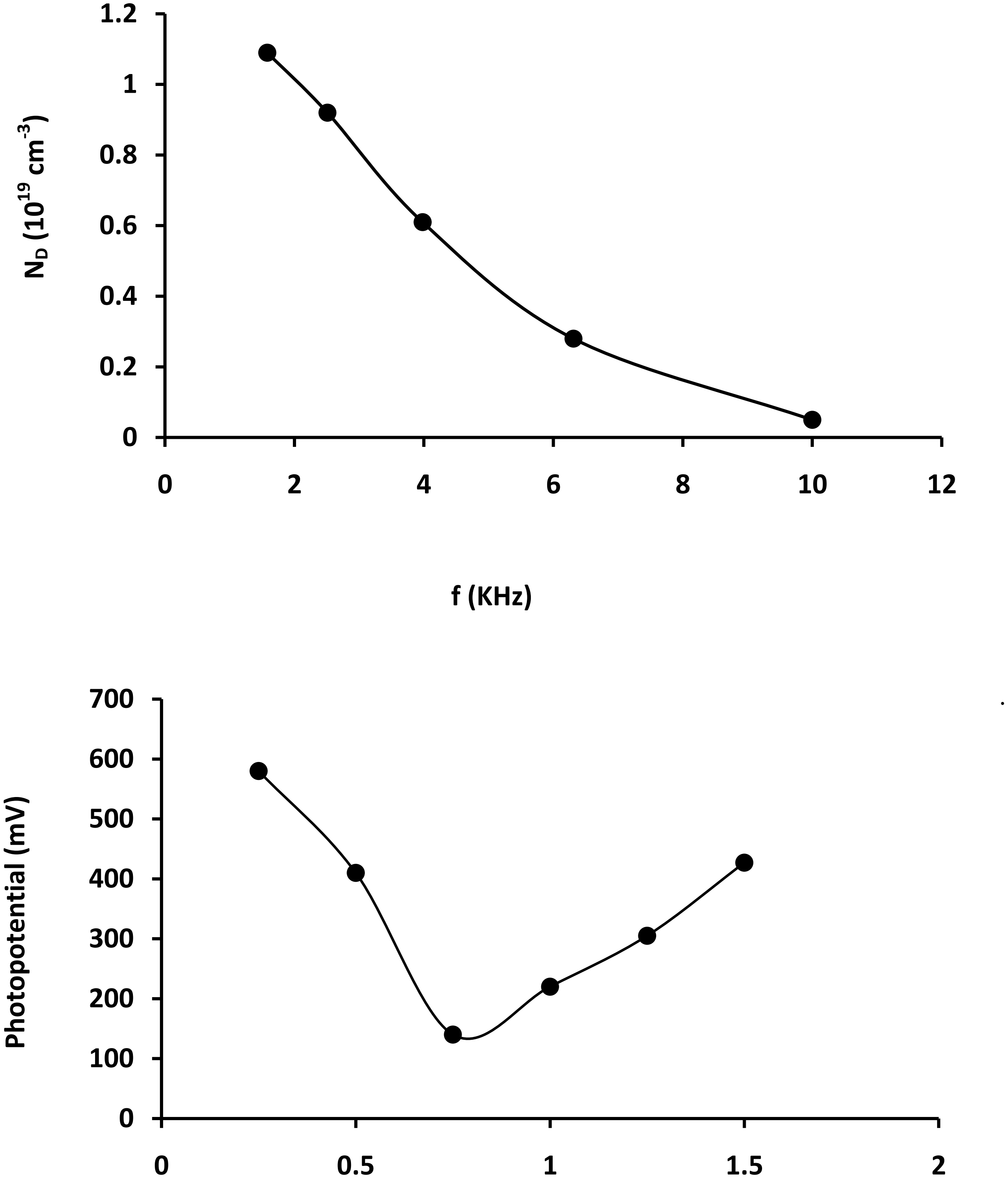

Fig.2. Variation of N_D values with applied frequency

Fig.3. Dependence of photopotential on redox potential.

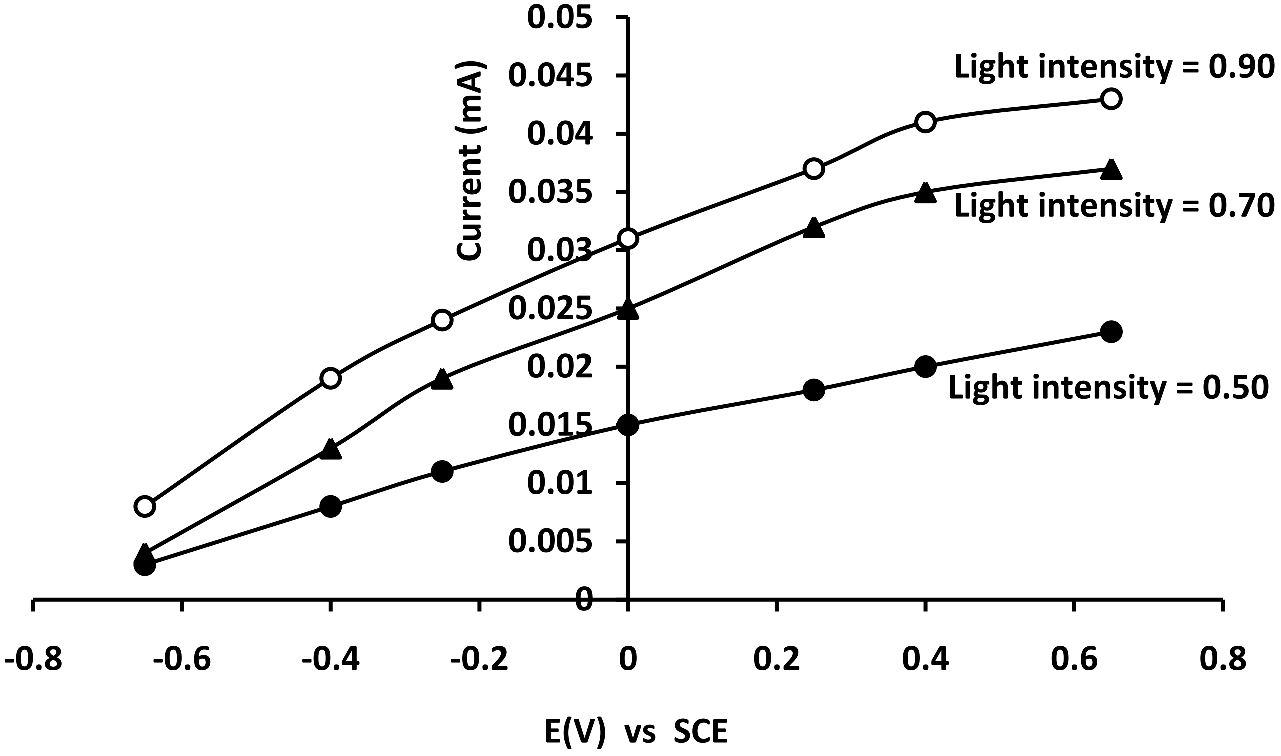

Fig.4. Current voltage behavior for CdSe films at different relative light intensities at different applied potentials in I_3^- /I_2 redox solution.

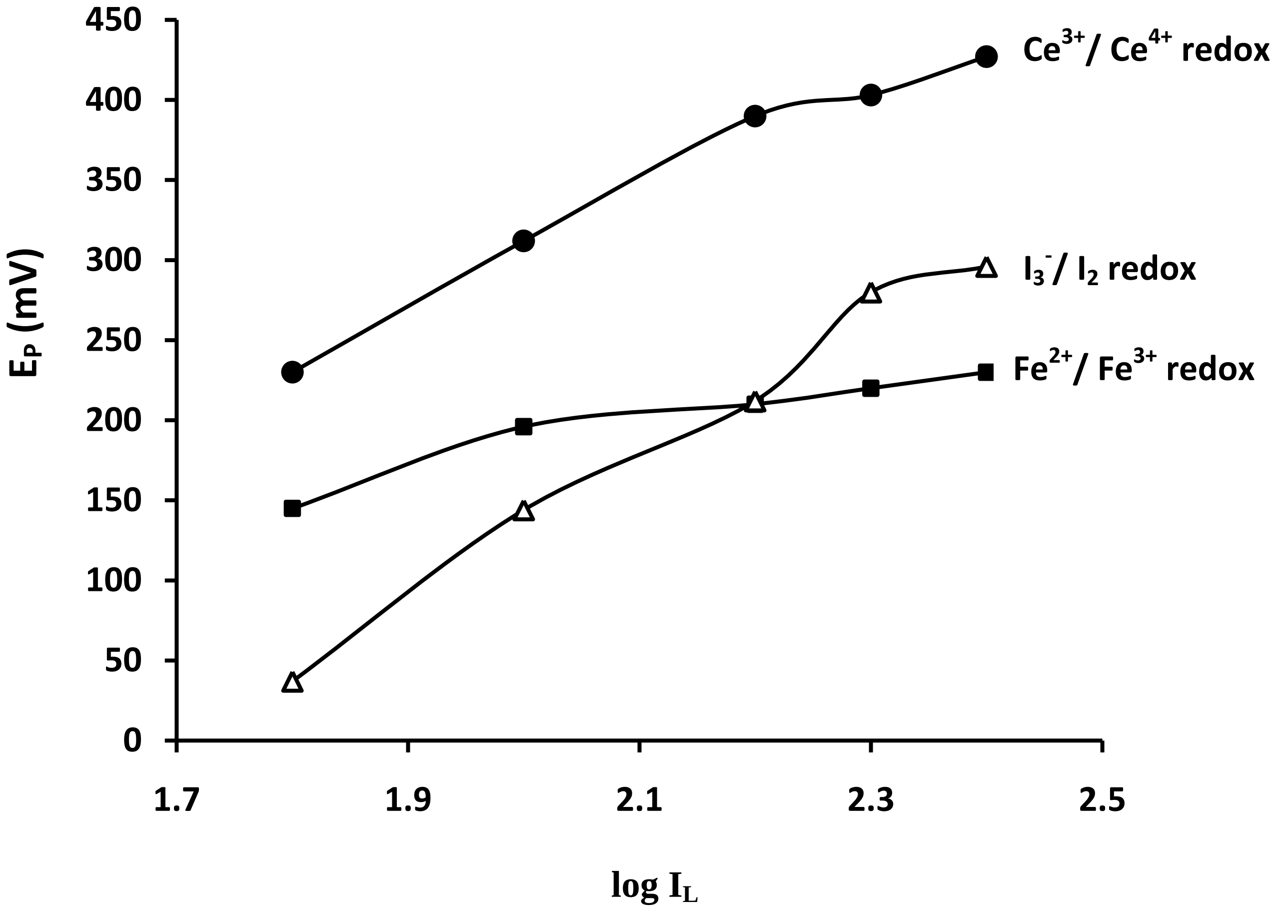

Fig.5. Variation of photopotential with log I_L in different redox solutions

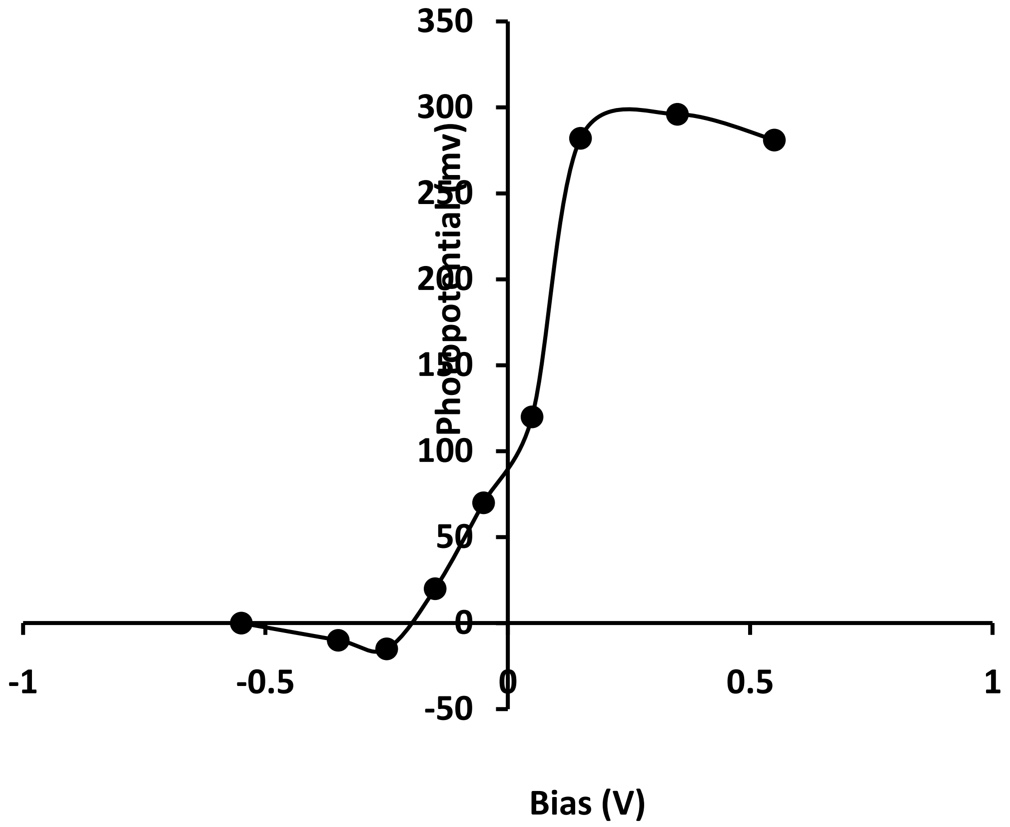

Fig.6. Effect of externally applied bias on photopotentialof CdSe thin films in $(CH_3COO)_2Cd/Ce^{3+}/Ce^{4+}$ redox solution.