

Electrical, Thermoelectrical and PEC Studies of Copper Doped CdSe Thin Films

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ABSTRACT

Copper doped CdSe thin films of various composition (0.1-1.0 mol %) deposited by dip coating technique on clean glass substrate at room temperature. Sample prepared on stainless steel plates have been applied for PEC characterization. The electrical conductance at 300K enhances as the amount of copper raises up to 0.1 mol % and later magnitude shrinks for greater amount. Copper doped samples demonstrates n-kind conductance. As temperature rise conductivity also rises confirming semiconducting nature of sample. Activation energy reduces up to 0.1 mol % and enhances at higher copper amount. Thermoelectric power increases up to 0.1 mol % copper dopant sample and later decreases. The rise in thermoelectric power with rise in temperature confirming the uniform character of the sample. The various performance parameter of PEC were examined with respect to varying dopant amount. Fill factor, ideality factor, short circuit current, open circuit voltage, and solar energy conversion enhances up to 0.1 mol% copper amount then reduces. The utility of this work is in improving the efficiency of PEC cell. The efficiency of doped sample is greater than undoped cadmium selenide.

1. Introduction

CdSe belongs to II-VI family of semiconducting material receiving ever increasing attentions due to its wide variety of applications [1]. One of the greatest significant uses of semiconducting thin samples is in photovoltaic tools as well as solar devices [2-7]. The examination of photoelectrochemical cells invented via crystalline thin samples of II-VI compounds was remarkable due to its outstanding optoelectronic characteristics [8-12]. In PEC cells light generated electron hole couples are applied to produce energy in the identical manner as in solid phase solar devices. Doping with copper, aluminium, Indium improves the properties of semiconducting substance. In current years thin samples were developed as prospective semiconductors⁽³⁸⁶⁻³⁹⁰⁾ [13-17] of high performance and lower manufacturing prices. Monovalent copper ions doped CdSe thin Films will be synthesised by utilizing dip technique [18] onto non conducting amorphous and conducting templates. The varying amount of copper ions have been added as of 0.01 to 1.0 mole %. The several deposition factors will be examined to found out suitable conditions for good quality of samples. The parametric like electrical conductivity, activation, type of semiconductor will be estimated by copper doping. The PEC will be constructed using thin films photoelectrodes. The cell performance of copper doped samples will be examined in terms of various cell parameters such as current voltage, power output curve.

Pawar [19] et al synthesized undoped and iron doped cadmium selenide thin samples using electro deposition technique. The undoped and doped samples were examined using cyclic voltammetry. Photoelectrochemical characteristics indicate that iron doped samples were greater sensitive to light compare to undoped samples. The structural parameters indicate samples were crystalline nature having hexagonal phase. The comprehensive surface topography has been altered after doping.

Ristova [20] et al reported silver insertion cadmium sulphide sample via applying an ion interchange technique. The surge of conductance in addition to simultaneous reduction of the photoconductivity was associated to the Ag rise in the sample.

The electrical conductance of copper doped cadmium selenide sample have been computed via applying two probe technique in temperature 300-500 K. The deviation in conductance with temperature is the most important characteristics in examining the nature of semimetals. The activation energy of all dopant sample is small compared to the undoped Cadmium selenide. The power outcome characteristics as well as various parameters of each dopant photoelectrode have been examined in this paper. The criteria of a good thin films photoelectrode for PEC cell is low resistivity and high grain size. Thermal treatment is necessary for fabrication process of various opto electronic devices and PEC cells Thermoelectrical power became useful to make decision of conduction type of semiconductor .

2. Experimental Details

Every chemical applied in preparation have been analytical level. Ammonia, selenium powder, cadmium sulphate, sodium sulphite and trichloroacetic acid were utilized. Sodium selenosulphate (0.2 M) became applied selenide ion resource for synthesise of cadmium selenide samples. The mixture became ready by heating 3.0g selenium fine particles accompanied by 9.0 g Na₂SO₃ in 100mL two fold purified water for 8 hour on 353 K. Mixtures became cool, filter to take out solid residue and put in storage in flask. [21] For manufacture of CdSe samples, 10 mL of (0.2 M) cadmium sulphate octahydrate have been in use in 100 mL glass vessel, and after that it be chelated by means of trichloroacetic acid. 15 mL (5N) ammonia became mixed this reactive solution. Afterward 10 mL (0.2 M) sodium selenosulphate is further mixed in vessel. 30 mL distilled water become mixed in the bath. By

using pH meter, pH of reactants was measured. It was observed to be 10.20. The glass vessel becomes placed in the ice. The solution was stirred strongly prior to dipping non conducting as well as conducting substrates, which were mounted upright somewhat slanting in reaction mixture. Temperature of reactive solution became formerly allowable to rise to 298 K extremely gradually. Once four hour was completed, templates have been distant. The deposited glass substrate was dried in nature.

3. Result and Discussion

The electrical conductance of copper doped cadmium selenide samples synthesized via dip process have been computed via applying two probe technique in temperature 300 to 525K. Dissimilarity of conductivity in opposition to temperature of samples is represented in fig.1. Conductance of samples will rise with raise in temperature, indicative of semiconducting nature.

The magnitude of specific conductance was calculated to be $1.345 \times 10^{-6} (\Omega \text{ cm})^{-1}$ at 300K and $9.38 \times 10^{-4} (\Omega \text{ cm})^{-1}$ at 525 K for 0.01 mol% of copper. Likewise, specific conductance became turn out to be $2.948 \times 10^{-6} (\Omega \text{ cm})^{-1}$ at 300 K and $1.36 \times 10^{-3} (\Omega \text{ cm})^{-1}$ at 525 K for 1.0 mol% of copper. The electrical conductance at 300 K enhances as the amount of copper raise up to 0.1 mol % and later magnitude shrink for greater amount. This ascribed to get better the crystal phase up to 0.1mol% of copper as well as declining the crystal imperfection and state density. This almost consents with Tall in, who observed that conductance for cadmium selenide boost with growing amount of copper. For samples having amount of copper among 0.1 and 1 mol%, the experimental decline in conductance may be because of interstitial inclusion of copper ions in the cadmium selenide substitute mainly as charge lock in point. [22]

Activation energy is measured applying equation 1.

$$\sigma = \sigma_0 \exp(E_a/kT) \text{-----1}$$

Wherein σ_0 is invariable

There are two stage of conductance during the heating temperature limit. In such situation the first activation energy take place at lower temperature range 300-333K. Conduction process at this step is because of carriers flow to localized states close to valence as well as conduction band. 2nd activation energy takes place at greater temperature range 333-500 K. In this area activation energy is because of transportation of carrier stimulated into the additional states away from mobility edge. 2 conduction processes indicates the Conductance is random with temperature. Change in the imperfection and unbalanced Fermi level invariant of temperature guide to changeable the magnitude of activation energies at this range of temperature.⁵⁵⁶ Activation energy became turn out to reduce up to 0.1mol % and enhance at higher copper amount. This suggests divergence of Fermi level in the direction of valence because of rising of doping level within optical energy. The magnitudes of first activation energy reduce up to 0.1mol% sample. 2nd activation energy also reduce with rising amount of copper up to 0.1mol%. This can be because of altering in localized states, phase, and content of samples. It is also due to the reshuffle of atoms that give up smaller amount of imperfection. [23] 1st activation energy is lesser than 2nd activation energy. This is because of the thermal contamination ionize at acceptor levels required to

least amount energy for movement the carrier. The activation energies for different low temperature region were obtained to 0.099 and 0.248eV at lower and higher temperature region for 0.01mol% copper dopant. Activation energies for different low temperature region were achieved to 0.101 and 0.287eV at lower and higher temperature region for 1.0 mol% copper dopant. The various electrical parameters are enlisted in table .1.

Thermoelectric power estimation became carry out in temperature limit 300-525K. Sample display p-kind conductance for copper inserted CdSe samples. This is ascribed to the availability of copper quantity that operate as acceptor contamination as alternate location for cadmium and this have the same opinion with Ture and Ermolovich [24-25] as they observed that copper atoms as acceptor contamination in cadmium selenide sample. This indicates going up thermoelectric power along with enhancing temperature of every sample suggesting degenerate nature. Fig 2 suggests variation in thermoelectric power with respect to temperature. It changes linearly with working temperature.

Thermoelectric power became turn out to be 21.65 to 40.31 $\mu\text{V}/\text{K}$ in the temperature limit 300- 525 K for 0.01 mol % copper dopant sample. For 1.0 mol% copper dopant sample, thermoelectric power alteration from 26.21 to 48.42 $\mu\text{V}/\text{K}$ became obtained in the temperature 300 to 525K. It is increases up to 0.1mol% copper dopant sample and later decreases. The obtained values of thermoelectric power of all dopant samples were greater than undoped cadmium selenide. Thermoelectric power of p-kind sample enhances quickly than that of n-kind sample.

The amount of carrier [26] with related to temperature is computed utilizing relation 2.

$$\log n = 3/2 \log T - 0.005 P + 15.7198 \text{---} 2$$

For each copper dopant cadmium selenide sample. At opening temperature (300K), the quantity of carrier became found out to be 2.156×10^{19} and 3.957×10^{19} at closing temperature (525K) for 0.01mol% copper dopant. For 1.0mol% dopant, the magnitude of quantity of carrier became found out to be 2.046×10^{19} at 300 K and 3.604×10^{19} at 525 K. As the temperature rise quantities of p-kind carrier enhance. Quantity of carrier decreases with copper dopant amount up to 0.1 mol%, later for higher dopant level it enhances. This may be due to recrystallization of samples via addition of copper and pack every dangling bond. The quantity of carriers that obtained by Sathyalatha and Levey became 2.14×10^{17} and 6×10^{17} correspondingly. The obtained values are superior to reported value.

The relation 3

$$\mu = \sigma/ne \text{-----3}$$

Becomes employed to compute the mobility [27] of hole in copper dopant samples. For 0.01mol% dopant, at initial temperature mobility of carrier became turn out to 0.347 while 132.20 $\text{cm}^2/\text{V} \cdot \text{sec}$ at 525 K. For 1 mol % dopant, at initial temperature mobility of carrier became obtained to be 3.32 at 300 K while 208.10 at 525 K. As temperature rise, mobility too enhances. Mobility enhances for up to 0.1mol% copper dopant. It is observed that mobility surges exponentially by enhancing amount of copper. This is ascribed to decrease the scattering of transporters from the face. This is also because of removal

of imperfections in the dopant sample as well as rise in crystalline character that is because of reduction in the granule boundaries. The grain boundary potential became estimated via applying a chart pattern of $\log \mu T^{1/2}$ with opposite temperature. Potential barrier height at granule border reduces along with copper amount up to 0.1 mol%, however quantity larger than 0.1mol% dopant. The different thermoelectric parameters are enlisted in Table 2.

The representation of constructed cell was p-CdSe:Cu | NaOH (1M) + S (1M) +Na₂S (1M) | C (graphite). The device provides certain potential difference as well as current .Power outcome characteristics as well as various parameters of each dopant photoelectrode have been examined.

Current voltage properties of the cell constructed using copper doped cadmium selenide electrode became studied. The unsymmetrical character of the curvature displays rectification characteristics of the boundary. Subsequently lighting, moving the curve in 2nd quadrant of the chart proposes that holes are mainstream transporters, approving the p-kind conductance of copper doped cadmium selenide thin sample. Surge in the current radiance designated that the copper doped cadmium selenide sample is photoactive.560 Current obtained is highest for 0.1 mol% copper dopant sample.

The junction ideality parameter became computed applying the chart of \log (current) in opposition to potential difference for each dopant samples. Fig.3 shows such chart for different sample. It was alters with dopant amount. Estimated ideality parameters became observed to 2.73 for 0.01mol% dopant and 2.86 for 1.0mol% dopant thin films. The obtained value of junction ideality parameter is greater than one might be due to the series resistance consequence in addition to carrier recombination at the junction. [28] Junction ideality parameter diminishes as the dopant amount enhance upto 0.1mol%. For greater level of copper dopant quantity, the junction ideality parameter raise. [29-30] Fig.4 signifies the photo electrochemical power generation characteristics of each dopant cells were examined using radiation 30 mw/cm². Different parameters such energy output, short circuit current, fill parameters, open circuit voltage rise up to 0.1mol% copper dopant, though deterioration subsequently. The shunts as well as series resistance decline up to 0.1mol% dopant, Photoelectrode of 0.01mol % copper dopant indicates open circuit voltage 290 mV and short circuit current 230mA/cm². Relation 4, 5

$$\%FF = [(I_m \times V_m)] / [(I_{sc} \times V_{oc})] \times 100 \text{ ----4}$$

$$\eta = [(V_{oc} \times I_{sc} \times FF \times 100)] / [(P_{input})] \text{ ----5}$$

Became employed to calculate fill factors and production of device. Calculations designate that solar energy conversation [31-32] productivity is 0.80% as well as fill factor [33] was 38.93% at 0.01mol% dopant .The open circuit voltage

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was obtained to be 278 mV. Short-circuit current is computed to be 215 mA/cm² for sample 1.0mol% dopant. Estimates designate that fill parameter are 37.42% as well as solar energy conversation productivity is 0.76% at 1.0mol% dopant amount.

The output and fill parameters rise because of enhance in open circuit voltage in conjunction with short circuit current. The magnitude of resistance was determined by applying relation 6 and 7.

$$(dI/dV)_{I=0} = (1/R_s) \text{ -----6}$$

$$(dI/dV)_{V=0} = (1/R_{sh}) \text{ -----7}$$

For 0.01mol % dopant the series resistance was found to be 731Ω and 742Ω for 1.0mol% dopant. While 0.01mol % dopant samples the shunt resistance was found to be 523Ω and 532Ω for 1.0mol% dopant. The several photoelectrochemical factors are enlisted in table 3

At 0.1mol% dopant has effective optical gap which consequences in improvement in power output. The electrical conductivity was found maximum and activation energy was least for 0.1mol% copper dopant sample. The mobility of carrier is extreme for 0.1mol% copper dopant sample in the series. Greater short circuit current because of lesser sample resistance in addition to an improved the energy absorption was found for 0.1mol% copper dopant electrode. The highest power output was originated to be 0.1mol% copper dopant electrode.

4. Conclusion

Homogenous and uniform Cu doped CdSe film have been successfully deposited using dip technique. Temperature dependence of electrical resistivity indicates the semiconducting nature of the film.

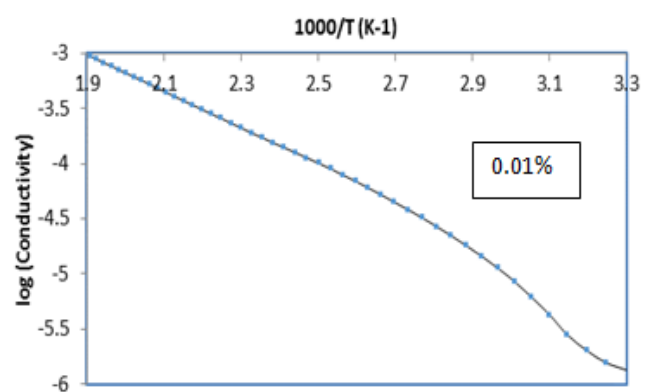
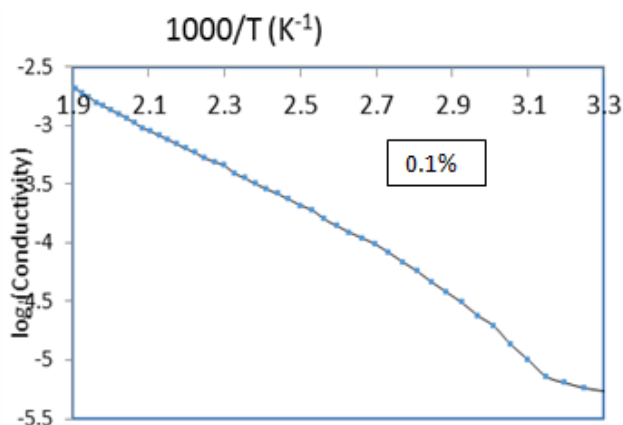
Thermoelectric power measurement shows p type conduction for copper doped CdSe thin film. PEC studies and calculations designate that fill factor is 37.42%. Solar energy conversation productivity is 0.76% at 1.0 mol % dopant amount.

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Appendix



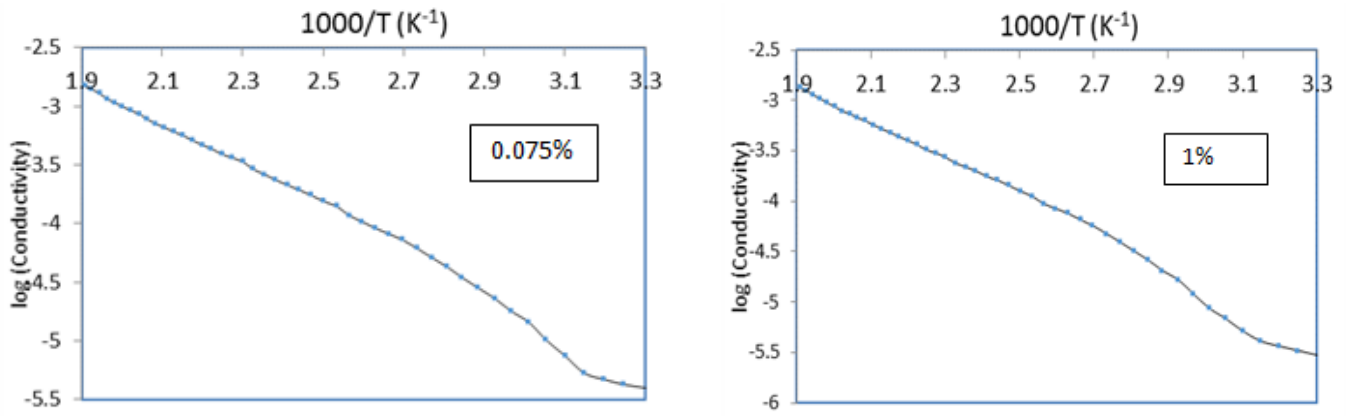


Fig 1. Electrical conductance of 0.1 mol% copper doped cadmium selenide

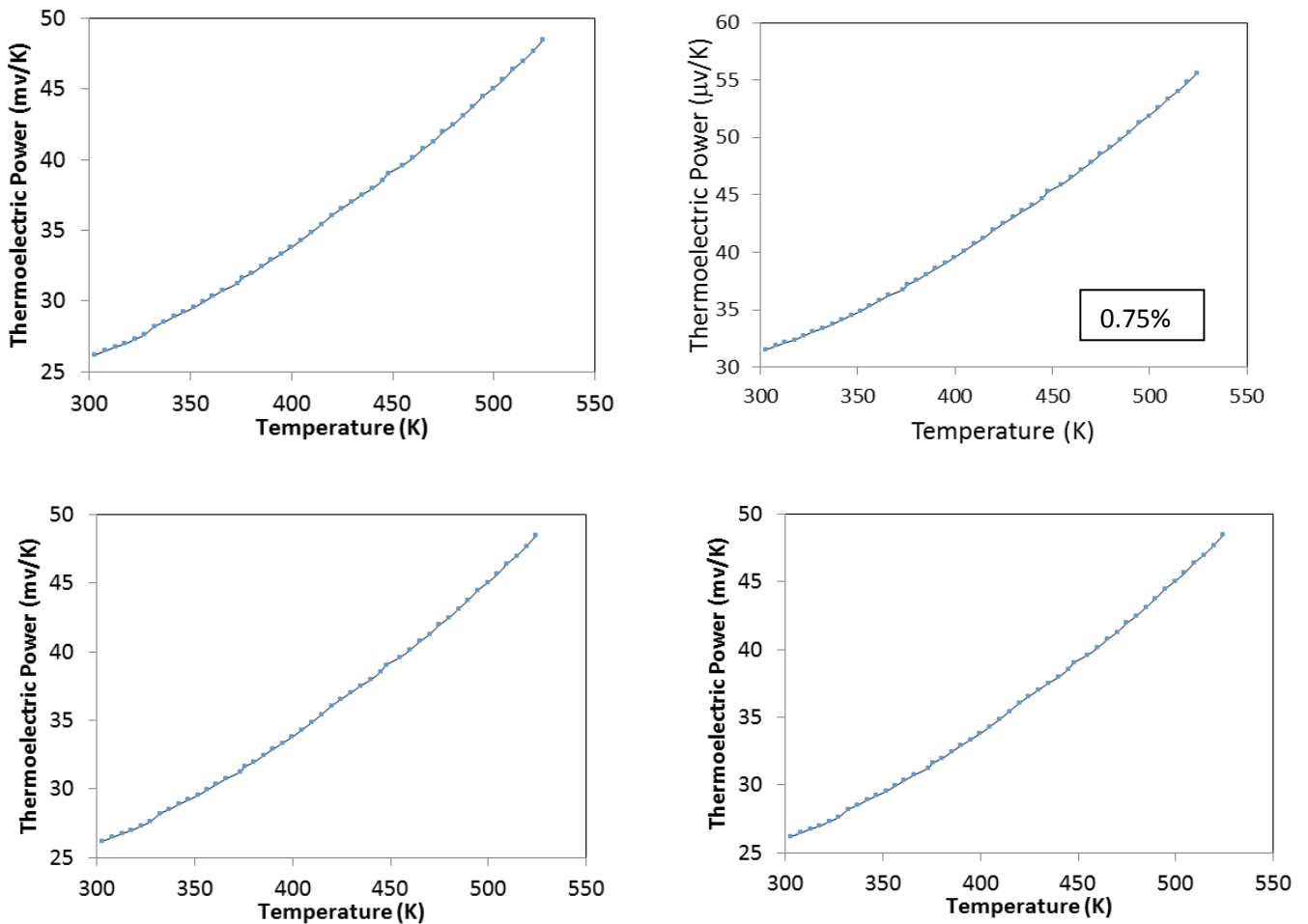


Fig 2 Thermoelectrical Measurement of Copper Doped Cdse

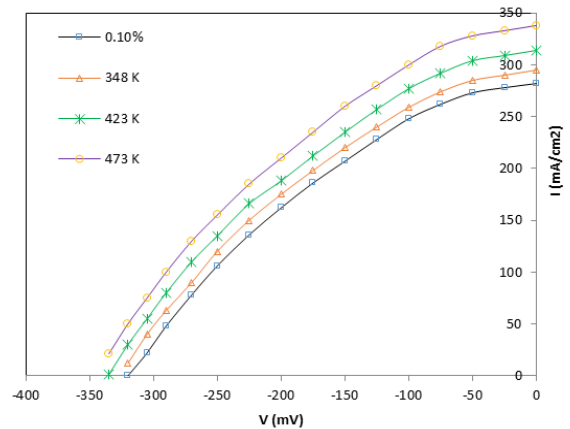
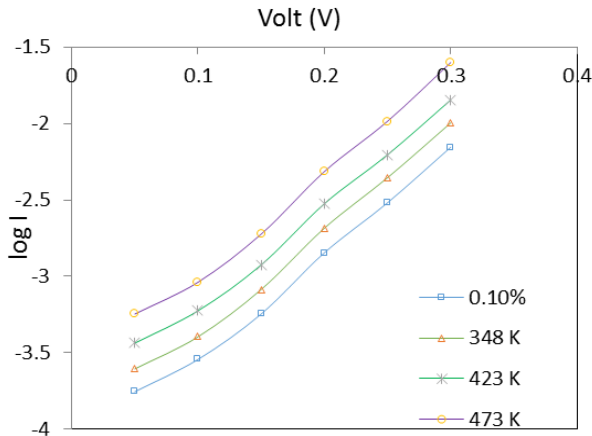
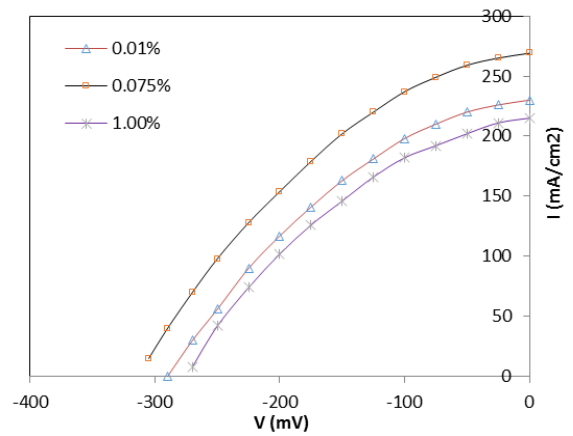
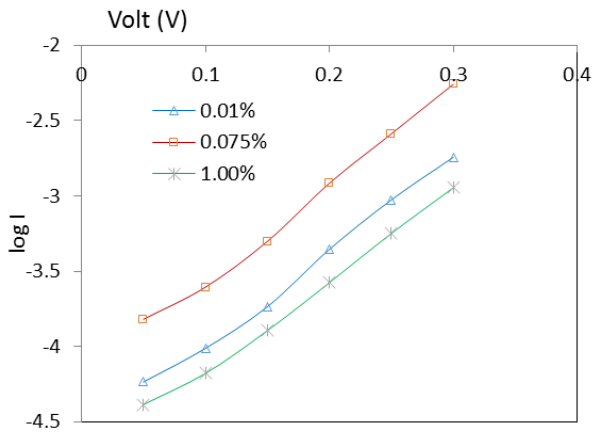


Fig 3. Estimation of Ideality parameter of copper doped CdSe

Fig 4. Photoelectrochemical properties of copper doped CdSe electrode

Tables:

Table-1 Electrical parameters of copper doped CdSe

Composition.	V_{oc} (mV)	I_{sc} (mA)	η %	ff %	R_{sh} (Ω)	R_s (Ω)	n_d
0.01	290	230	0.80	38.93	523	731	2.73
0.025	298	242	0.87	39.66	502	698	2.69
0.05	305	251	0.93	41.02	476	663	2.64
0.075	312	269	1.00	42.78	445	638	2.62
0.1	320	282	1.09	43.67	408	617	2.57
0.25	310	268	0.98	42.03	447	651	2.68
0.5	297	246	0.91	40.87	489	695	2.72
0.75	286	229	0.84	39.04	504	719	2.79
1.0	278	215	0.76	37.42	532	742	2.86

Table 2. Thermoelectric power parameters of copper doped cadmium selenide.

No.	Composition	(P) (μ V/K)		N		μ ($cm^2/V.sec$)		Φ_B (eV)
		300 K	525 K	300 K (10^{19})	525 K (10^{19})	300 K	525 K	
1	0.01	21.65	40.31	2.156	3.957	0.347	132.2	0.372
2	0.025	24.78	45.24	2.080	3.738	0.945	198.5	0.363
3	0.05	28.45	50.55	1.994	3.517	1.896	301.4	0.356
4	0.075	31.57	55.51	1.923	3.319	3.567	419.5	0.352
5	0.1	35.38	62.45	1.830	3.066	5.140	543.0	0.341
6	0.25	33.45	59.15	1.881	3.185	4.678	488.8	0.349
7	0.5	31.79	56.45	1.919	3.286	4.124	395.3	0.355
8	0.75	28.77	52.33	1.986	3.445	3.756	300.6	0.363
9	1.0	26.21	48.42	2.046	3.604	3.320	208.1	0.370

Table 3. Performance parameter of copper doped cadmium selenide photoelectrode

No.	Composition	Specific Conductance ($\Omega \text{ cm}^{-1}$)		Activation Energy (eV)	
		300 K (10^{-6})	525 K (10^{-4})	LT	HT
1	0.01	1.345	9.38	0.099	0.248
2	0.025	2.454	11.57	0.094	0.239
3	0.05	3.434	14.68	0.090	0.231
4	0.075	4.893	17.44	0.086	0.226
5	0.1	5.430	20.2	0.083	0.221
6	0.25	4.964	18.36	0.088	0.239
7	0.5	4.476	16.46	0.093	0.257
8	0.75	3.578	14.69	0.098	0.271
9	1.0	2.948	13.6	0.101	0.287