Photovoltaic Studies of $Cd_{1-x}Co_xS$ Based Electrochemical Cells

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Abstract

The $Cd_{1-x}Co_xS$ $(0 \leq x \leq 0.5)$ thin films were deposited on chemomechanically and ultrasonically cleaned stainless steel substrates by a liquid phase chemical bath deposition technique. *The preparative parameters, (viz. growth temperature (56 ^0C), deposition time (80 minutes), reaction pH (11±0.2) and the rate of mechanical churning (70±2)) and deposition conditions were used as optimized previously. The electrode/electrolyte interfaces were then set up between the n-type $Cd_{1-x}Co_xS$ $(0 \leq x < 0.5)$ photosensing electrodes and a sulphide/polysulphide (0.25 M) redox electrolyte in H-shaped corning glass cells. A graphite rod treated in a cobalt sulphate solution for 24 hours was employed as a counter electrode. The as- fabricated cells were then characterized through the voltage-current and voltage-capacitance characteristics in dark, photovoltaic power output characteristics under constant illumination, and different responses of the cells to incident light. The PV performance parameters such open-circuit photopotential (V_{ph}), short circuit photocurrent (I_{ph}), series and shunt resistances (R_s & R_{sh}), efficiency (η), form factor (ff), dark ideality factor (n_d), ideality factor under illumination(n_L), built-in potential (Φ_B), dark current (I_D), the flat band potential(V_{fb}), junction capacitance under flat band condition (c_j), cut off wavelength(λ_c) and photogenerated carrier life time(τ) were evaluated for various cells with a special emphasis given to the electrode composition (x). In general, photovoltaic output performance of the $Cd_{1-X}Co_XS$ based electrochemical cell is improved after Co implantation (x=0.1) in CdS.*

Keywords: *Photovoltaics, electrochemical cells, n-$Cd_{1-x}Co_x$ S photosensing electode, efficiency, recombination centres.*

Introduction

Thin film photovoltaics is one of the most promising possible solutions for the present energy crisis and is still immatured and far from the commercial utility[1-6]. Presently, solar cells are mainly made by using bulk silicon wafers. However, due to high cost of silicon wafer based solar cells thin film solar cell is one of the most practical approaches for solar energy conversion in near future[1-3,7-11]. One of the main challenges in solar energy research is to search for new advanced solar materials and to fabricate and develop a new methodology that can produce high quality thin films at low production cost and should yield stable module efficiency. To achieve these goals, a variety of newer solar materials were proposed and many methods and hybrids thereof have been fabricated /developed with a focus on their high performance throughput and lower costs for the thin film solar cells[1-5,12-15]. Metal chalcogenides are proved to be the strong contender and have attracted a considerable attention owing to their efficient energy conversion ratio[1-6, 13, 16, 17]. In the right perspectives, efforts need to be focused on improving the

conversion efficiency and lowering the cost of the metal chalcogenide based solar cell. A device grade metal chalcogenide thin film can be usually obtained by chemical bath deposition, electrodeposition, vacuum depositions, spray pyrolysis, surfactant assisted method, etc.[2,3,16-22]. Deposition using chemical bath is reported to be more advantageous than others[12,16,17,19,23-26]; because it is the conventional method with the advantages of economy, convenience, ease of scaling up to large area deposition and high degree of composition control[12,17,19,23-29]. Cadmium sulfide and cobalt sulfide seems to be very promising among the chalcogenides because they have the direct band gaps of 2.42 eV and 1.10 eV respectively, high photosensitivity in the visible region of the spectrum, high coefficients of optical absorption and excellent stability with its n-type semiconductor characteristics[9,12,17,21,24,30-35]. Further, both the end materials out of the series can be synthesized under the same conditions of preparation procedure and a variety of alloyed/mixed materials of the $Cd_{1-x}Co_xS$ kind with tailor made properties can be generated with ease and without the use of sophisticated instrumentation[16-18,21,22,35]. These materials are therefore, of extremely importance for efficient use in optronic devices, especially in solar cell applications[12,16-18,22,29,30,35]. It was therefore proposed to synthesize CdS, CoS and $Cd_{1-x}Co_xS$ ($0 \leq x \leq 0.5$) thin films under the same conditions of preparation using a liquid phase chemical bath deposition (LPCBD) method and to apply them for photovoltaic conversion through electrochemical photovoltaic cells.

Experimental methods and characterization techniques

Preparation of the $Cd_{1-x}Co_xS$ thin films

CdS and $Cd_{1-x}Co_xS$ thin film samples of varying composition ($0 \leq x \leq 0.5$) were obtained onto the mirror grade polished stainless steel substrates using a liquid phase chemical bath deposition method set by us[13,17,24,34,35]. Cadmium sulphate, cobalt sulphate, and thiourea were used as the sources of materials. Equimolar (1M) volumes of cadmium sulphate, cobalt sulphate and thiourea(in proportion with x value) were taken in a reaction bath and allowed to react in an alkaline medium to produce CdS and $Cd_{1-x}Co_xS$ thin film deposits. The deposition was carried out at a pH value of 11 and the deposition temperature was maintained at 56^0C. The polished and cleaned stainless steel substrates were then positioned vertically on a specially designed substrate holder and rotated with 70±2 rpm speed in the reaction bath. The deposition was continued for 80 minutes and the samples were taken off the reaction bath and detached from the substrate holder, washed with double distilled water, dried and then preserved in a dark desiccator.

Fabrication and characterization of the photoelectrochemical solar cells

The photoelectrochemical cells were then fabricated by employing these thin films as the active photoelectrode and a sulfide/polysulfide electrolyte (0.25 M) as a redox couple in a H-shaped glass cuvette fitted in a suitable copper pot. An impregnated graphite rod was used as a counter electrode. The voltage-current and voltage-capacitance characteristics in dark were recorded at room temperature. The power output curves were obtained under a steady illumination of 13 mW/cm^2.Tungsten–filament lamp (250W / 230V) was used as a source of white light. The photoresponses were also noted for various input light intensities (5 mW / cm^2 to 50 mW / cm^2). The spectral responsivities of the various electrode materials were examined in the range of wavelengths from 400 nm to 750 nm. This has been achieved by interposing filters of different wavelengths in the path way of the incident light and measuring the short circuit current of the cells. The input intensity was measured with a Lutron-101 (Taiwan), lux meter, whereas short circuit photocurrent was recorded with a HP-34401, 6 ½ digit current meter. A saturated calomel electrode (SCE) was used as the reference electrode while measuring the junction capacitance. The potentiometric arrangement was used for the measurement of junction capacitances at various applied reverse bias. A 4 ½ digit, LCR-Q meter (Aplab-4910) was used to measure the junction capacitance, whereas the current–voltage characteristics were obtained as usual. The barrier heights were also measured for these cells by measuring the reverse saturation current at different temperatures. The

Hewlett- Packard-34401, 6 ½ digit and HIL-2665, 4 ½ digit multimeters were used for the measurement of current and voltage, respectively. A ten-turn 1 KΩ helical potentiometer was used to vary the junction potential.

Results and Discussion

An electrochemical conversion of solar radiations into electricity via photovoltaic route is gaining much popularity today and is an extremely important and desirable way out from the present energy crisis. Todays solar cells are fabricated from highly pure and perfectly crystalline materials and active junctions, which are mainly responsible for the energy transformation process, are fabricated that requires cost involving technology. The electrochemical photovoltaic cells based on polycrystalline semiconductor materials provide an economic chemical route for trapping the solar radiations available abundantly and non pollutantly. These cells convert optical energy directly into electrical energy and offer promises of much higher mass specific power at extremely low cost. A 'photoelectrochemical cell' or 'electrochemical photovoltaic cell' is a solid-liquid junction cell where light is absorbed in a thin solid film called a 'semiconductor photoelectrode' immersed in a liquid (redox electrolyte) and connected to a second 'counter electrode' through a load resistance. The core of the photoelectrochemical solar cell is the space charge region, established in a semiconductor electrode due to equilibration of the Fermi levels up on immersion in a liquid electrolyte, which converts incident photons into equivalent electron-hole pairs. The major absorber materials (semiconductor photoelectrodes) of these cells should have optimal electronic structures to maximize the incident solar energy absorption, the process being begins with the photons which have higher energies than the band gap transmitting their energies to the crystal lattice. These energies are able to excite easily the localized valance electrons into the conduction band as the free negative carriers generating equivalent positive carriers termed as holes. Because of the Coulomb attractive forces between them, these photo-generated electron-hole pairs tend to recombine easily. The electric field set up at the interface effectively sweeps out the electrons and holes; the electrons move into the bulk of the semiconductor whereas holes arrive at the electrode/electrolyte interface. The semiconductor /electrolyte junction is generally less sensitive to the form of the semiconductor (viz. less crystallite size, irregular morphology, etc) than conventional solid state junction, reducing the demands on the semiconductor itself. This is the greatest advantage that LPCBD films have often been employed as semiconductor photoelectrodes[12,19,25]. Although technology of solar photovoltaics is well developed, there is a need to search new materials and matchable electrolyte systems or novel structures to enhance the efficiency and stability to an acceptable limit for competing the existing sources of electricity generation. In electrochemical photovoltaic cells, an interface between a semiconductor electrode of fairly high band gap (>2eV) and an electrolyte combines the characteristic features of both phases (semiconductor and an electrolyte). For these Schottky type barriers, typically 1 μm thick, densely packed space charge of ionised donors or acceptors ions is formed within the semiconductor wherein minority carriers are present in too low concentration[5].To get deep insight about the behavior of a semiconductor / electrolyte interface, a series of electrochemical photovoltaic cells were fabricated with n-Cd_{1-x} Co_xS (0≤x≤0.5) as the photosensing electrode and sulphide/polysulphide (0.25M) as an electrolyte redox couple in a glass cell as described earlier[34]. The interfaces were then characterized in dark and under illuminated conditions.

Electrode / electrolyte interface properties in dark

As a typical example, we have characterized the interfaces of the various cells through the dynamic voltage-current and voltage-capacitance characteristics in dark at 300K and barrier potentials at the interface were determined. The voltage- current characteristics were therefore obtained for a whole series of the cells under study and figure1 shows few of its representative plots under forward and reverse biases. It has been seen that there is a high degree of rectification for the current in dark and the conventional direction of the current flow is negative towards the $Cd_{1-x}Co_xS$ semiconductor electrode[5].The reverse saturation current densities(I_o) at high applied bias depart from their saturation values and this is the case normally observed with the thin polycrystalline film semiconductor/electrolyte interfaces[4,8].The I-V curves were analyzed to understand the charge transport mechanism at the interface. To follow, the plots of V vs log I (figure 2) were plotted and the junction ideality factors (n_d) were determined from the linear regions at relatively high applied forward bias. The linear regions of V vs log I for various cells have different slopes comparable to the fact that each cell possess different barrier height[4,8].The ideality factors are listed in table-1 and indicate that the electrode /electrolyte interfaces have been much affected by the recombination mechanism effects[4,5,8]. The dark current densities (I_o) at zero applied bias were also determined for all the cells from V vs log I variation. It is seen that dark saturation current density (I_o) decreased considerable with incorporation of Co into CdS lattice.
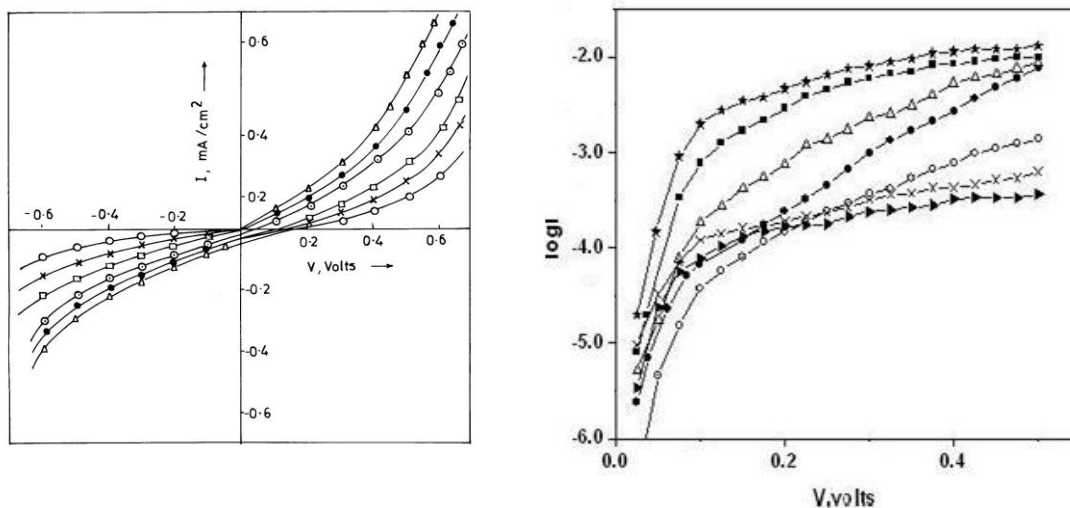

Figure 1 (left): *V-I characteristic in dark for six representative electrochemical photovoltaic cells formed with $Cd_{1-x}Co_xS$ photoelectrodes: □ - x = 0, ⊙ - x = 0.01, ● - x = 0.075, △ - x = 0.1, x - x = 0.35, and o - x = 0.5.* ***Figure 2 (right):*** *Variation of V vs log I for different $Cd_{1-x}Co_xS$ thin film photo electrodes: ⊙ - x = 0, ● - x = 0.01, △- x = 0.05, ■ - x = 0.075, ★ - x = 0.1, x − x = 0.2, and ▶- x = 0.35*

A second important characteristic of an electrode /electrolyte interface is it's voltage dependent space charge layer capacitance that gives useful informations pertaining to the donor concentration, the extent of band bending at the interface and type of conductivity exhibited by the semiconductor material in the photovoltaic process. The interface space charge capacitance was therefore measured for all the cells for various values of the applied voltage (0 to –0.7 vs SCE,at $1v_{pp}$-1KH$_2$). The C^{-2}-V plots were then constructed from these measurements and are shown in figure 3.The plots were extrapolated to the voltage axis to give v_{fb}, the flat band potentials of the various cells. The variation of the electrode composition (x) and flat band potential (v_{fb}) is shown in figure 4. It appears that v_{fb} varies over a range of approximately 232 mV, being maximum for a cell with electrode composition of 0.1. At this moment, the enhancement in v_{fb} can be correlated to: (i) decreased electron affinity of CdS due to incorporation of Co and (ii) an increased amount of surface adsorption and creation of new donor levels in the band gap of CdS and hence the amount of band bending at the interface[4,5,8]. Figure 4 also shows decrease in v_{fb} with x and can be ascribed to the Fermi level pinning[4,5,8]. The enhancement in v_{fb} can further be supported by the measurements on the built-in-potential (Φ_B) at the interface. The built-in-potentials were therefore measured for all the cells under study. For this purpose reverse saturation current was measured as a function of the cell temperature at a constant value of applied electrode potential. The built-in-potentials for various cells were then determined from the variation log (I_0/T^2) vs 1/T (figure.5) and it is found that Φ_B increased with x up 0.1 and then decreased. The enhancement in (Φ_B) can be attributed to the enhanced crystallite size and decreased dislocation density associated with the electrode material as reported earlier[13].The decrease in Φ_B with x can be correlated to the decreased grain size and dislocation density.
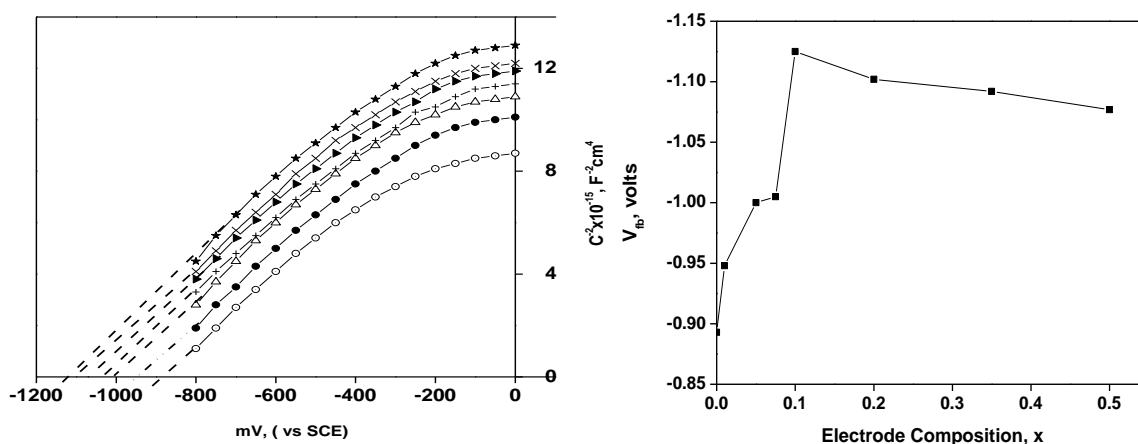

Figure 3 (left): Mott-Schottky plots for determination of the flat band potentials, (V_{fb}) for different photovoltaic cells devised with photoelectrodes of various compostions: ⊙ - x = 0, ● - x = 0.01, △- x = 0.05, ★ - x = 0.1, x – x = 0.2, ▶- x = 0.35, and + - x = 0.5. Figure 4 (right): Variation in V_{fb} with the electrode composition, x.
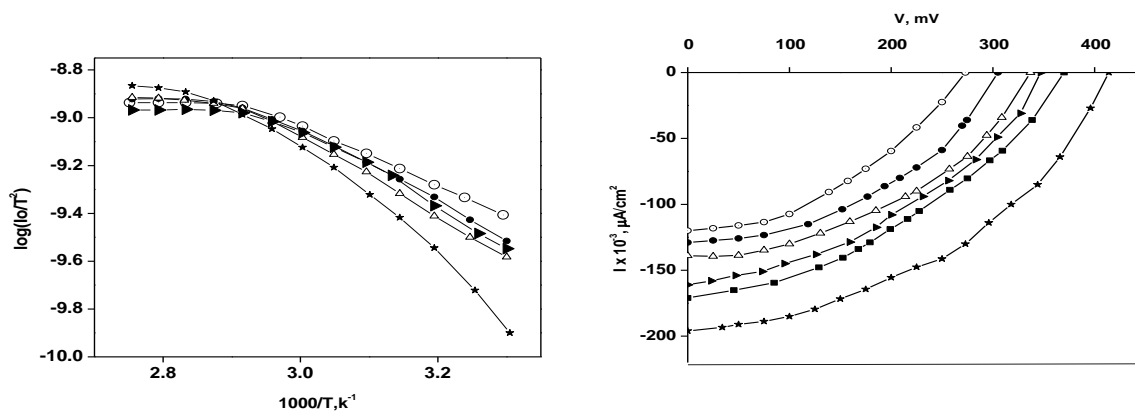
Figure 5 (***left***): *Variation of 1/T versus log I_o / T^2 for different photovoltaic cells of different electrode composition:* $\odot$ *- x = 0,* $\bullet$ *- x = 0.01,* $\triangle$*- x = 0.05,* $\star$ *- x = 0.1, and* $\blacktriangleright$*- x = 0.35.* ***Figure 6*** (***right***): *Power output curves for different cells of different photoelectrode composition:* $\odot$ *- x = 0,* $\bullet$ *- x = 0.01,* $\triangle$*- x = 0.05,* $\blacksquare$ *- x = 0.075,* $\star$ *- x = 0.1,* $\blacktriangleright$*- x = 0.35.*

Table1: *Photovoltaic performance of the electrochemical cells formed with Cd $_{1-x}$Co $_x$S electrode (0 ≤ x ≤ 0.5) and electrolyte.*

Electrode composition x	V_{oc} mV	I_{sc} μA /cm^2	R_s KΩ	R_{sh} KΩ	η %	ff %	n_d	Φ_B eV
0	273	120	1.15	4.24	0.98	38.9	3.73	0.24
0.01	305	129	0.920	4.75	1.23	40.8	3.55	0.27
0.05	337	139	0.860	4.91	1.52	42.4	3.42	0.32
0.075	370	171	0.790	5.28	2.26	46.5	3.30	0.35
0.1	**414**	**196**	**0.750**	**5.50**	**2.94**	**47.1**	**3.12**	**0.42**
0.2	379	188	0.820	4.73	2.20	40.2	3.40	0.29
0.3	347	161	0.860	4.26	1.68	39.0	3.45	0.26
0.5	311	154	1.10	3.66	1.92	28.4	3.37	0.28

Another useful technique to determine the properties of the semiconductor / electrolyte interface is its illumination with a light of suitable wavelength that shows photovoltaic effect. The photo- current (I_{ph}), photo-voltage (V_{ph}) characteristic was then recorded for all the cells under a white light illumination of 13.4 mW/cm^2. It is seen that both I_{ph} and V_{ph} have been enhanced up to a value of x equal to 0.1 and then decreased for higher x values. The power output curves were obtained for all the cells under a constant illumination of 13.4mw/cm^2 and are shown in figure.6. The cell characteristics viz. photocurrent (I_{ph}) and photovoltage (V_{ph}), efficiency (η%), fill factor (ff%), series and shunt resistances (R_s & R_{sh}) were then determined from these curves and are cited in table-1. A maximum energy conversion efficiency (η%) and fill factor (ff%) of 2.94 % and 47.1% , respectively have been found at x=0.1. Table-1shows that the performance of a electrochemical photovoltaic cell is found to be improved and is optimum for a cell whose electrode composition is 0.1. We attribute the observed improvements to the increased photocurrent, photovoltage, flatband potential, grain size and decreased energy band gap, electrode resistance and dislocation density(surface states).

Conclusions

1. Semiconductor / Liquid Junction photovoltaic cell can be easily deviced with just immersion of photo-electrode in a liquid electrolyte.
2. A maximum energy conversion efficiency of 2.94 % has been made feasible with these cells.
3. For the performance improvements, it needs further electrode processing.

Acknowledgments

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