$CdS_{1-x}Te_x$ thin film photo electrodes for electrode/electrolyte interfaces

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ABSTRACT

The electrical properties and optical responses of an active photo electrode ($CdS_{1-x}Te_x$) / electrolyte interfaces have been studied. The active photo electrode material was deposited using a chemical bath technique. The basic ingredients used were cadmium sulphate, thiourea and refluxed sodium tellurosulphite. The composition parameter, x was varied from 0 to 1. The various photoelectrochemical (PEC) cells have been fabricated and then characterized through their electrical and optical properties. These properties were evaluated through their performance parameters such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), series and shunt resistances (R_s and R_{sh}), fill factor (ff %), efficiency (η %), junction ideality factor (n_d), lighted quality factor (n_L) and band bending potential (V_{fb}). The calculated values of these parameters revealed that the conversion efficiency and fill factor were enhanced from 0.056 % to 0.48% and 31% to 52% respectively for materials composition, x = 0.1. The incremental changes in the performance parameters and consequently enhancement in the cell performance have been explained on the basis of alterations in the electrode properties.

Keywords: Solution grown, Cd (S, Te), electrode/eletrolyte interfaces

1. INTRODUCTION

Now days, the energy crisis has created the enormous interest in the field of research for non-conventional energy sources. One of the best alternatives is the conversion of solar energy (since it is abundant, clean and exhaustive in nature) into its electrical counterpart with the help of photoelectrochemical cells [1]. Binary and ternary compounds of II-VI and IV-VI class semiconductors, especially cadmium chalcogenides are currently becoming the focus of intensive research since they exhibit potential as efficient absorbers in the visible and near visible regions of solar spectrum [2] - [5].

The action spectra of such materials show a good deal of enhancement in optical absorbance over a wide range of photon energies. Cadmium sulphide is such a semiconductor material, which has shown great promise as a material for PEC conversion [2], [3]. With this material, a relatively large fraction of the solar spectrum could be utilized and it is, therefore, reasonable to expect a considerable improvement in the conversion efficiency. The conversion efficiencies so far reported are low as compared with other materials such as $CuInS_2$, $CuInSe_2$ etc., and one of the major reasons pointed out many researchers is the unmatched electrode resistivity [2] – [5]. The active electrode materials resistivity could be made to match by incorporation of proper impurities in the host lattice [2] – [8]. We have therefore, attempted to deposit mixed $CdS_{1-x}Te_x$ thin films with $0 \leq x \leq 1$ by employing a simple and inexpensive scalable chemical bath deposition technique. The photo electrochemical solar cells are then formed and various cell properties are investigated as a function of photo electrode materials composition.

2. EXPERIMENTAL PROCEDURE

Thin films of CdS1-xTex of varying composition parameter, x from 0 to 1 were deposited onto the quality stainless steel substrates. Cadmium sulphate, thiourea and sodium tellurosulphite were used as the basic ingredients. Triethanolamine was added to form a bound complex. The appropriate quantities of Sodium hydroxide and aqueous ammonia were added to adjust the pH of the reaction mixture and film adherence to the substrate support. The volume stoichiometric quantities of thiourea and sodium tellurosulphite were added to the reaction container. The preparative parameters and deposition conditions were optimized (pH = 10.2 ± 0.2, speed of rotation = 70 ± 2 rpm, deposition time = 75 min and deposition temperature = 55°C).

Photoelectrochemical cell was then devised in H-shaped glass cuvette using one of these samples as an active photo electrode, sulphide / polysulphide redox couple as an electrolyte and impregnated graphite rod as a counter electrode.

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The power output characteristics were obtained for all the cell configurations under a constant illumination of 20 mW/cm^2 (tungsten filament lamp, 250 W). The photocurrents and photo potentials were also measured for various illumination intensities (5 to 35 mW/cm^2). The spectral response of the various cells was examined in the wavelength range of 400 to 900 nm. The dynamic current – voltage and capacitance – voltage characteristics in dark were obtained potentiometrically for all these cells. A three-electrode system was used for C-V measurements. A standard calomel electrode was used as a reference electrode. The reverse saturation current of the various cells was noted in the 373 to 300 K temperature range to calculate the built-in-potentials of the various cells. The various currents and potentials were measured by 6 ½ digit HP and 4 ½ digit HIL 2665 multimeters. Illumination intensities were recorded by a Lutron-101 (Taiwan) luxmeter.

3. RESULTS AND DISCUSSION

3.1 Physical observations

The as- grown $CdS_{1-x}Te_x$ film deposits are thin, uniform, smooth, diffusely reflecting and well adherent to the substrate support. The samples develop a changing colour from yellow through yellowish orange and finally to milky white, as the electrode materials composition parameter, x increased from 0 to 1, which indicates the substitution of S^{2-} ions by Te^{2-} ions in the host CdS lattice. Thin film thickness was measured and is found to be decreased nonlinearly with the composition parameter, x. The dependence of the film thickness on x can easily be understood from the relative rates of reactions of CdS and CdTe. The rate of film formation of CdS is relatively faster than that of CdTe at these experimental conditions thereby decreasing the film thickness.

3.2 $CdS_{1-x}Te_x$ photoelectrodes for electrode/electrolyte interface studies

The photoelectrochemical cells, set in a glass cuvette with these active electrodes and sulphide / polysulphide as an electrolyte, have been illuminated by a light of photon energy greater than the optical gaps of these semiconductors. The excess charge carriers which are generated as a result of the photon absorption are separated at the space charge region, the electrons move deep into the bulk, while the holes move to the surface of the semiconductor causing redox reactions to occur. The charge separation process continues until it results in a counter field which is maximized at the open circuit conditions [5], [9] – [11].

The photo responsiveness of these cells was studied under a variable input light intensity from 5 to 35 mW/cm2. The open-circuit voltages (Voc) and short-circuit currents (Isc) were recorded as a function of the input intensity. The short-circuit photocurrent is approximately a linear function of input intensity and this is shown in Figure 1 for some of the typical cell configurations.
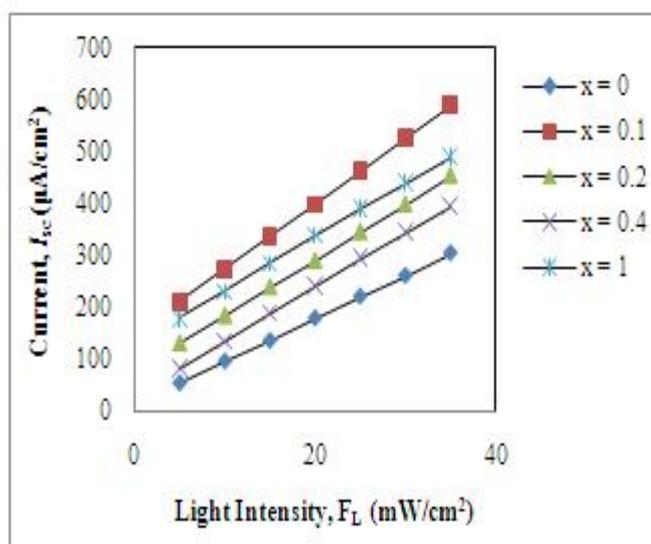

Figure 1 Plots of V_{oc} versus log I_{sc} for five representative cells: a) x = 0 (♦), b) x = 0.1 (■), c) x = 0.2 (▲), d) x = 0.4 (×) and e) x = 1 (*)

The linear dependence of short-circuit current demonstrates that the transport of electro active species to the electrode/ electrolyte interface does not limit the rate of the overall charge transfer reaction [9] – [11].

Thus a plot of V_{oc} versus ln I_{sc} would be a straight line and n_L may be calculated from its slope. The lighted quality factors (n_L) of the junctions may then be computed by plotting V_{oc} versus ln I_{sc}. The values of n_L are cited in the Table.

Table Various performance parameters of $CdS_{1-x}Te_x$ photo electrochemical interfaces

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x	V_{fb} mV	V_{oc} mV	I_{sc} μA/ cm^2	n_d	n_L	R_s Ω	R_{sh} kΩ	ϕ_B eV
0	- 624	286	198	3.37	2.42	983	1.98	0.37
.05	-686	378	245	2.98	2.58	795	2.34	0.39
.10	-742	523	396	2.63	2.87	647	3.05	0.49
.20	-630	412	289	2.81	2.69	810	2.67	0.45
.40	-649	329	246	3.02	2.48	873	2.38	0.43
.60	-564	210	197	3.14	2.37	934	2.24	0.41
.80	-512	267	223	3.17	2.23	981	2.43	0.42
1.0	-537	319	257	3.26	2.17	975	2.51	0.46

The power output curves have been obtained for all the cell configurations, and Figure 2 shows few such curves for the cells of different compositions.
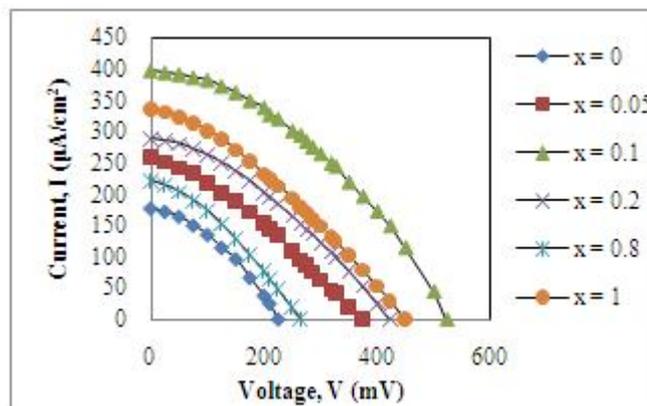

Figure 2 Power output curves: a) x = 0 (♦),b) x = 0.05 (■), c) x = 0.1 (▲),d) x = 0.2 (×), e) x = 0.8 (*) and f) x = 1(•)

The cell parameters, viz. open circuit potential (V_{oc}), short circuit current (I_{sc}), efficiency (η %) and fill factor (*ff* %), series and shunt resistances R_s and R_{sh} have been determined. Both the open-circuit voltage and short-circuit current have been found to be boosted from 225 mV and 178 μA/cm^2 to 523 mV and 398 μA/cm^2 for the photo electrode of material composition, x = 0.1 and decreased thereafter for higher values of electrode materials composition, *x*. We attribute the observed improvement in V_{oc} and I_{sc} mainly to the decreased series resistance, increased photosensitivity, improved grain structure and decreased band gap of these films [5], [9], [11] – [12]. The values of fill factor (*ff* %), series and shunt resistances R_s and R_{sh} are cited in the Table. The variation of quantum conversion efficiency (η %) with the composition parameter, *x* is shown in Figure 3.

In general, to explain the variation ofη, we should consider the materials characteristics such as band gap energy (E_g) and flat-band potential (V_{fb}). Quantum conversion efficiency has a direct relation to the flat-band potential, whereas, it varies reciprocally with the band gap energy [11], [12].
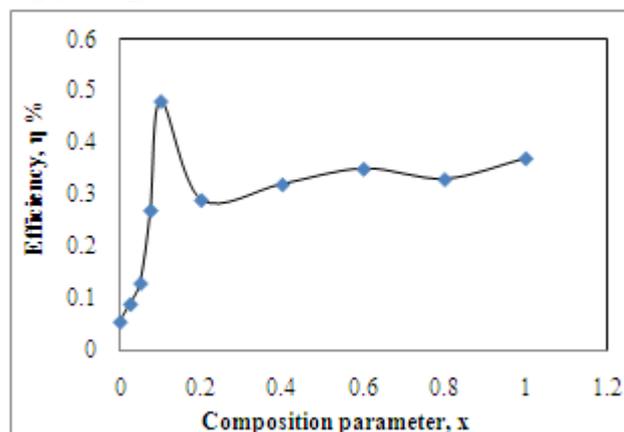

Figure 3 Variation of efficiency η % on composition parameter, x.

The spectral response were examined for the selected cells and it has been found that a PEC cell devised of photo electrode of optimum composition (x = 0.1) has comparatively broader response with a response edge on the higher wavelength side shifted towards still higher wavelength side. From the action spectra, it is clear that the photocurrent increased with the incident wavelength and maximized at the cut-off wavelength (λ_c) and thereafter the photocurrent decreased for higher wavelengths. However the longer wavelength cut-off is not sharp which is in accordance with its theoretical model (Fig. 4) which suggests that the PEC cell under such circumstances is analogous to a low-pass filter circuit [13] – [16].
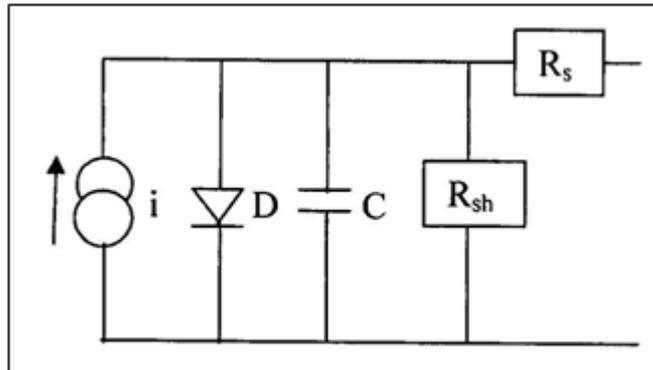

Figure 4 Electrical analog of a PEC cell: i - constant current source, D-ideal diode, R_s – series resistance, R_{sh} – shunt resistance and C- junction capacitor.

4. CONCLUSIONS

The results so obtained suggest that the addition of a trace amount of Te^{2-} ions into host CdS lattice considerably improves the efficiency, η and fill factor. The PEC cell performance is found to be optimum at $x = 0.1$ and is ascribed to the increased flat band potential, decreased band gap and electron affinity, increased photoelectrode absorption and improved grain structure. The increase in photocurrent, I_{sc}, is mainly due to the decrease in the photo electrode resistance and band gap of the material and increased absorption of the incident light by the photo electrode material. The behavior of the photoelectrochemical cell is analogous to that of a low-pass filter circuit with no sharp longer wavelength cut-off.

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