



Optical Response of $Hg_x Zn_{1-x} S$ Electrode For PEC Cell

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Abstract: The polycrystalline Hg-doped ZnS thin films semiconductor photoelectrodes of various compositions were prepared by chemical bath deposition technique. The deposition conditions and preparation parameters are optimized to have good quality of films. As-deposited films were made use as an active photoelectrodes in a photoelectrochemical cell with polysulfide (1M) as an electrolyte and impregnated graphite as the counter electrode. As fabricated photoelectrochemical (PEC) cells are then used to study their optical characteristics. The spectral response characteristics of the films at room temperature were studied under the constant illumination of light of intensity 20 mWcm^{-2} . Mott-Schottky plots were also studied and the flat band potential (V_{fb}) is found to be increased with electrode composition x and reached to its maximum value at $x = 0.1$. Transient response times of as-deposited photoelectrodes of different compositions were studied.

Keywords: pseudo-binary MZS, CBD, PEC cells, flat band.

I. INTRODUCTION

A binary and ternary compounds of II-VI, IV-VI or II-IV-VI are most dominant semiconductor groups in thin films for photo-voltaic and detector configurations. Many researchers have been working on the development of semiconductor materials by forming solid solutions of different compositions to obtain variation in flat band potential and optical energy gap of alloyed materials, which capture a large fraction of the ultraviolet, visible and near infrared regions of the electromagnetic spectrum and for the electrolytes, which are suitable for better stability. Enhancement in photo-potential and photo-current have been observed in such systems which are being attributed to the shift in flat band potential which increases the barrier height at a junction.

Chalcogenides, in general because of their potential as efficient absorbers in the visible and near IR regions of solar radiations, have attracted more and more researchers in the field of detection and photoelectrochemical conversion. These materials show a good deal of a wide range of photon energy. Low fabrication cost, ease in operation and relatively no lattice mismatch, are the great advantages of PEC cells over the thin films solid solar cells. They have better and efficient solar energy conversion devices [1]-[5].

To understand the importance of solid state parameter we deposited the $Hg_x Zn_{1-x} S$ thin films by inexpensive, simple and easy to operate chemical bath deposition method. The photoelectrochemical performance of these cells has been studied and presented in this paper.

II. EXPERIMENTAL PROCEDURE

A. Preparation of thin film electrodes

$Hg_x Zn_{1-x} S$ ($0 \leq x \leq 1$) thin films were deposited on thoroughly cleaned glass substrate (Blue Star, Mumbai) and high quality stainless steel substrate using chemical bath deposition method. For this purpose, $HgCl_2$ (1M), $ZnSO_4 \cdot 7H_2O$ (1M) and $CS(NH_2)_2$ in stoichiometric proportions were taken in a reaction vessel. Triethanolamine was added to form a bound complex. Sodium hydroxide and aqueous ammonia were added to this reaction mixture to adjust the pH of the reaction and to increase the film adherence to the substrates. The deposition parameters viz. temperature, speed of mechanical churning, time of deposition, pH etc. was kept constant at their optimized values of $60^\circ C$, 60 ± 2 rpm, 90 minutes and 10 ± 0.2 as reported earlier [6]-[7].

B. Fabrication of $Hg_x Zn_{1-x} S$ photoelectrochemical cells

The photoelectrochemical (PEC) cells were fabricated for different electrode material compositions, as an active photoelectrode and polysulfide as a suitable redox couple in an H-shaped corning glass corvette set. An impregnated graphite rod acts as a counter electrode which is placed behind the active photoelectrode at a distance of 2mm. The current-voltage characteristics in dark and under illumination were studied and examined at room temperature. The



cells are illuminated by the light of 20 mW/cm² intensity and photo-voltaic power output curves were obtained for all these cells. A potentiometric arrangement was used for measurement of current – voltage capacitor-voltage at various applied bias potentials for dark conditions. The spectral response of the various cells was examined in the range of wavelength from 350 to 950 nm. Digital picometer of 3¹/₂ digits, SES Instrumentation Pvt. Ltd., classic (999N1) digital Multimeter and Apla’s Autocoupler LCR-Q meter were used for the measurement of current, voltage and capacitor respectively.

III. RESULTS AND DISCUSSION

A. Physical properties

Hg_xZn_{1-x}S thin films of various compositions are deposited onto the well-polished stainless steel substrate at by chemical bath deposition process. For this purpose, the preoperative parameters such as temperature, deposition time, pH, and speed of the substrate of rotation were kept constant at their optimized value. The as-grown films are thin, uniform, mechanically hard and adherent to the substrate support. It is seen that the layer thickness decreased monotonically with composition parameter. The thin film properties of these films viz. structural, optical and electrical transport properties have studied and reported earlier [6]-[7].

B. Photoelectrochemical (PEC) Studies

The photoelectrochemical cell was prepared by using thin films of Hg_xZn_{1-x}S as an active photoelectrode for current – voltage, capacitance-voltage, power output and optical characterization. The cell performance, junction ideality was determined from forward and reverse leakage I-V characteristics under the dark condition. It is seen that considerable recombination at the electrode/electrolyte interface and its values are cited in the table. In order to determine the flat band potentials for different cell, Mott-Schottky plots were constructed and the flat band potentials were determined by extrapolating the steep portion of the curves on voltage –axis and its values are cited in the table. It is observed that the flat

Table: Some of the photoelectrochemical performances parameters of Hg_xZn_{1-x}S thin films.

X	λ nm	C _j μF	τ μs	R _s Ω	n _d	n _L	V _{fb} mV
0	348.69	9.713	0.544	56	6.15	2.46	357
0.01	341.65	8.805	0.431	49	5.98	2.22	421
0.02	351.30	8.805	0.379	43	5.64	1.92	506
0.04	372.37	8.528	0.333	39	5.18	1.66	543
0.06	394.69	8.248	0.289	35	4.56	1.55	584
0.08	402.59	8.151	0.269	33	4.07	1.46	599
0.10	475.69	8.085	0.274	33.9	4.45	1.38	616
0.20	476.92	8.392	0.504	60	5.25	1.51	581
0.40	506.86	8.482	0.577	68	5.70	1.86	546
0.60	525.42	8.687	0.660	76	5.87	1.98	496
0.80	576.74	8.980	0.799	89	5.99	2.10	446
1.00	626.46	9.325	0.951	102	6.15	2.34	408

band potential was maximum at composition x= 0.1 and then decreased as composition x increases. The increase in flat band potential is due to increase in surface deposition and formation of new donor levels in the band gap of the semiconductor electrode, Which shift the Fermi level in an upward direction causing an increase in built in potential of the cell. The generation of scattering centers in the electrode material, is as a result of excess incorporation of Hg content and surface states at the interfacing of electrode and electrolyte. [3],[8]-[11]

C. Spectral Response

To study the spectral response of the material the PEC cells were illuminated by incident light at constant intensity (20mW/cm²) for the different wavelength from 250 to 800 nm. The corresponding photocurrents were measured as



shown in the fig. 1. The graph shows that the photocurrent increased with incident wavelength and maximum at the cut-off frequency (λ_c) equals to 348.69nm and 626.46 nm for cells of composition $x = 0$ and $x = 0.1$ respectively. There after photocurrent decreased for higher wavelengths. The longer wavelength cut-off is not sharp which is in accordance with its theoretical model of the low pass filter circuit as shown in the fig. 2 [3],[12]-[15].

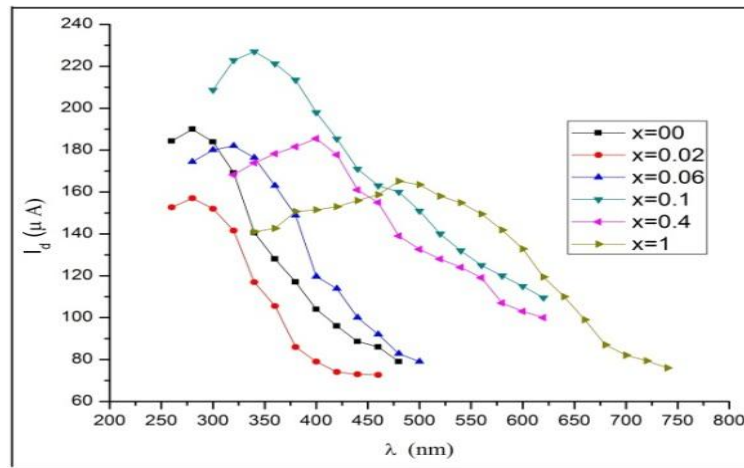


Figure 1: Variation of photocurrent with wavelength of the incident light for various compositions.

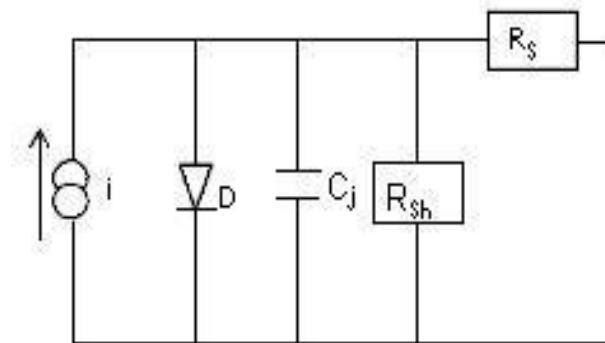


Figure 2: An electric analog of an electrochemical cell
 I = constant current source, D = ideal diode
 R_s = series resistance, R_{sh} = shunt resistance
 C_j = junction capacitance of the diode.

The cut-off frequency (f_c) and response time (τ) of this low-pass filter is given by,

$$f_c = \frac{1}{2\pi\tau} \quad (1)$$

$$\tau = R_s C_j \quad (2)$$

D. Photoresponse

To study the photoresponsivity of as-deposited electrodes for different composition, electrodes were illuminated by light of wavelength ($\lambda_c = 810$ nm). Photo-potential (V_{ph}) and photocurrent (I_{ph}) were recorded by varying intensity of incident light from 5 to 20 mWatts/cm². The photo-response of these cells were studied by constructing plots of $\ln(I_{ph})$ vs V_{ph} as shown in fig. 3 to calculate the lighted quality factor

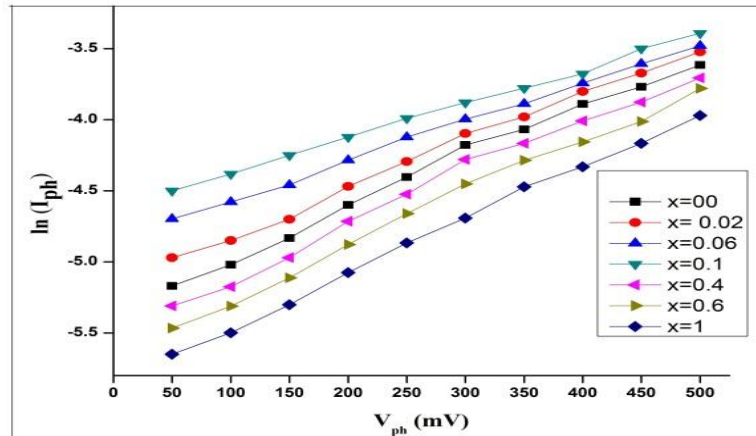


Figure 3: Variation of photo current vs photo potentials

(n_L) of the junction and their values are cited in the table. From the fig. 3 it is observed that (V_{ph}) and (I_{ph}) increased with the composition x and reached to its maximum value at $x = 0.1$. This behaviour of electrodes is mainly due to increase in the flat band potential and decrease in electric resistivity, an optical energy gap of the photoelectrochemical cells. [13]-[14].

E. Transient Time

To understand the photo response of cells, the electrodes of different composition were illuminated by light of suitable wavelength. The photo-potentials were measured as a function of ON and OFF time for all these cells. Fig. 4 shows the variation of photo potential with ON and OFF times for few selected configurations. From these plots, it is clear that the transient response is exponential in nature, when the light source is ON photo potential increases exponentially with time, this is a clear indication of something analogous to the charging of a capacitor when connected across the battery. Similarly when light source is cut (OFF), the decrease in photo potential behaves as if the discharging of a capacitor.

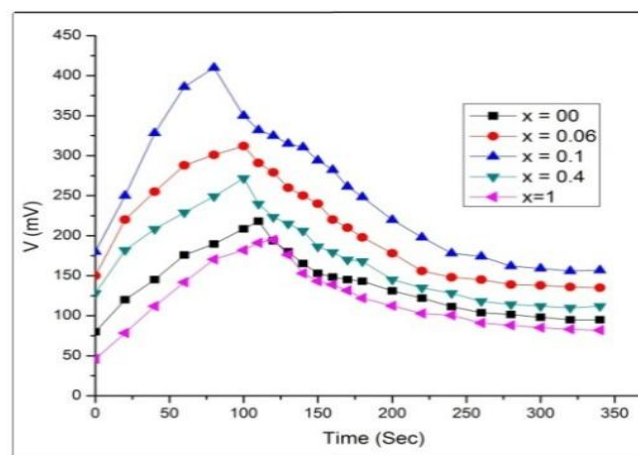


Figure 4: Transient responses of electrochemical cells for some electrode compositions.

Thus the three main factors which limit the switching speed (response time) of photo electrodes in photoelectrochemical cells, are as follows [12]-[13].

1. Diffusion time of photo carriers to the depletion region. Carrier diffusion is inherently a slow process; the time taken for carrier to diffuse is given by $\tau_{diff} = \frac{d^2}{2D_c}$ where (d) distance and D_c minority carrier diffusion coefficient. At wavelengths near the band gap and at low reverse bias speed of some optically generated carriers limit the diffusion. The carriers generated within the depletion region responses rapidly, which gives to slow decrease of photo potential.



2. Drift time of carriers through the depletion region. The carriers which are generated near to the one edge of depletion region has to spend longest transit time, so it can travel full depletion region.
3. Junction capacitor effect. The bandwidth may improve by reducing junction capacitor and it can be done by reducing area (A) and doping level (N_d) or increasing the reverse bias voltage. This leads to increases in the depletion width and the drift transit time.

IV. CONCLUSION

Thin films of $Hg_x Zn_{1-x} S$ of various composition x were deposited by chemical bath deposition. As deposited electrodes of different composition are in conjunction with polysulfide electrolyte can be used as photovoltaic cell. Spectral response study of shows electrochemical cells are of analogous to a low pass filter. The response time of a cell shows similarnature to its solid –solid junction counterpart and response time depends on electrodes composition and it is optimized at $x=0.1$.

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