IJASE

INTERNATIONAL JOURNAL OF
APPLIED SCIENCE AND ENGINEERING

Study on Photoelectrochemical Properties of Ternary Doped $Cd_{1-x}Zn_xS$ thin Film Deposited by Chemical Bath Deposition

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ABSTRACT

The photoelectrochemical properties of $Cd_{1-x}Zn_xS$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) thin film, prepared by Chemical bath deposition technique on simple glass and fluorine doped tin oxide(FTO) coated glass substrate were studied. The X-ray diffraction (XRD) studies indicate that film was hexagonal with polycrystalline in nature. The current-voltage (I–V) curve for PEC cell of configuration n-$Cd_{1-x}Zn_xS$//1M polysulphide//C under illumination for film deposited on FTO coated glass substrate, respectively. I–V curve characterizes the semiconductor/ electrolyte junction which acts like a diode. The interface shows a rectifying behavior with a cathodic current (direct) much greater than the anodic current (reverse), which is typical of a Schottky junction formed between an n-type semiconducting material and a metal or an electrolyte. Various PEC parameters such as the junction ideality factor under illumination, series and shunt resistances, efficiency and, fill factor have been calculated for the PEC cells formed. The efficiency and fill factor of these PEC cells are found to be increased as increasing X=0.4 and further, it decreases as X increases.

Keywords: Photoelectrochemical cell (PEC), Thin films, CBD technique, Structural Properties, Optical properties

Global warming, environmental contamination, and impending lack of fossil fuel sources are factors that force modern society towards an increase in the utilization of renewable sources of energy. One of the most abundant resources on the surface of the earth is sunlight. Sunlight reaches the earth in a quantity that is sufficient to supply the total global energy consumption[1]. The use of solar energy has many advantages such as Solar energy is free and abundant. Solar energy has the low environmental impact.

Solar energy does not require large centralized supplies or expensive distribution networks. Solar energy has high public acceptance as a natural form of energy[2].

The conversion of solar energy into the usable form is the potential challenge to the scientists. Now day solar cell devices play the vital role in converting solar energy into usable form. The science and technology of photovoltaic devices (solar cells) and systems have undergone revolutionary developments. Many types of thin film solar cells exist today[3]. To generate chemical energy in a form that can be put away from solar energy is in this way a vital objective for the improvement of clean energy. One strategy for accomplishing this objective is the utilization of a photoelectrochemical (PEC) solar cell. Semiconductor liquid junction solar cells have pulled in a lot of ongoing years because of the developing enthusiasm for solar energy transformation[4]. For a photoelectrochemical solar cell, the prime prerequisite is that the photocathode/photoanode ought to have band gap near the most extreme in the visible spectrum and second the semiconductor-electrolyte framework must be steady[5]. $Cd_{1-x}Zn_xS$ is an II-VI ternary semiconductor with a wide range of band gaps (CdS = 2.45 eV and ZnS = 3.50 eV)[6] and is used in applications in the various optoelectronic device. To reduce the resistivity as well as the bandgap of this material and raise the efficiency of the PEC cells, the material has to be doped with appropriate dopants. a lot of groups have reported the properties of the undoped and doped II-VI thin films arranged by a variety of techniques[4], like Chemical bath deposition[5], Spray pyrolysis technique[7], Anodization and dip-calcination method[8], SILAR Technique[9], Co-precipitation[10], Aqueous and non-aqueous (ethylene glycol) baths[11], hydrothermal process[12], Electrochemical deposition[13]. Among these techniques, chemical bath deposition (CBD) is the most good-looking because of its useful features over other deposition techniques because it is simple, gives high-quality films at low temperatures, requires slow evaporation temperatures and easily coats very large surfaces[14].

In this paper, we focused on the Electrochemical study of $Cd_{1-x}Zn_xS$ thin film deposited on FTO coated glass plate. And calculate the various parameter of it such as open-circuit voltage (V_{oc}), short circuit current (I_{sc}), efficiency (η), fill factor (FF), Series resistance (R_s), Shant resistance (R_{sh}) etc. And also reported the structural, optical and characterization of $Cd_{1-x}Zn_xS$ thin film using chemical bath deposition technique.

EXPERIMENTAL WORK

Preparation of $Cd_{1-x}Zn_xS$ thin films on FTO Coated glass

We prepare the film on Glass slides and FTO (Florin dopped tin oxide) Coated glass substrate (purchases from technistro Nagpur). Glass slides were washed with detergent and rinsed in acetone before the deposition of the films. The cleaned substrate was kept dipped in deionized water before use. The well-cleaned glass substrates were slowly introduced into the bath vertically after obtaining the homogeneous solution. Experimental detail reported elsewhere[6]. The desired pH value 11 was achieved by the addition of aqueous ammonia solution proportionally into the mixture in the chemical bath. The temperature of the mixed solution was maintained at 75°C using a constant temperature under continuous stirring. The films were prepared under continuous stirring for 1 h. The deposited films were cleaned several times with de-ionized water. After that film was dried in sun and air.

Fabrication of Photoelectrochemical (PEC) solar cells

The photoelectrochemical solar cell was fabricated using $Cd_{1-x}Zn_xS$ thin film on FTO (Fluorine doped

tin oxide) coated glass substrate as an active photoelectrode, graphite rod as a counter electrode and the saturated calomel electrode (SCE) as a reference electrode. The aqueous 1 M polysulfide (Na$_2$S+S+NaOH) was used as a redox electrolyte. A 100W tungsten filament lamp (intensity 25 mW/cm^2) was used as a light source. To avoid direct heating of cell, water lens was interposed between the lamp and the cell. The distance between the photoelectrode and counter electrode was 0.2 cm. The area of the semiconducting thin film other than that in contact with electrolyte was covered by epoxy resin to annul any contribution due to the contact of the base contact oxide material with the electrolyte and its interference in the measured values of the net photocurrent density. For measurement of the power output characteristics, a two-electrode configuration consisting of the thin film photoelectrode and graphite as the counter electrode was used. Measurements for the power output characteristics and I–V plots were made at fixed intervals after waiting for sufficient time to equilibrate the system at that setting.

Preparation of polysulphide electrolyte

The polysulphide electrolyte solution was prepared in an aqueous medium. The basic ingredients used for the preparation of solution were as follows:

1. A. R. Grade Sodium sulfide (Na$_2$S) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.
2. A. R. Grade Sulphur powder (S) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.
3. A. R. Grade Sodium hydroxide (NaOH) supplied by S. d. fine Chem. Ltd., Boisar, Mumbai.

One molar polysulphide electrolyte was made in double distilled water by adding appropriate amounts of sodium hydroxide and sodium sulfide at room temperature. In this solution, sulphur was added and the mixture was stirred vigorously. Then the mixture was filtered and stored in an air sealed bottle. The color of the final solution was yellowish pink "As shown in Fig. 1."
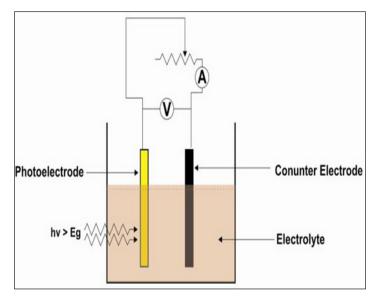

Fig. 1: Experimental arrangement for photovoltaic output characteristic of PEC cell formed with Cd$_{1-x}$Zn$_x$S (0.0<×<1.0) thin film photoelectrode
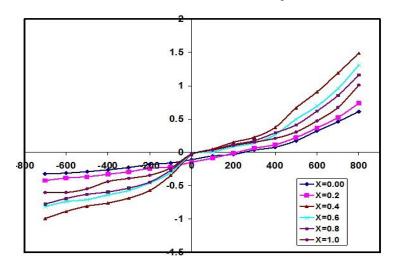
RESULT AND DISCUSSION

XRD Measurement

The XRD pattern of the $Cd_{(1-x)}Zn_xS$ "As shown in Fig. 4", diffraction indicate the presence of CdS and ZnS peke material show cubic and hexagonal in structure. The standard crystallographic data for CdS and ZnS were taken from JCPDS card no. 80-0006 and 36-1450 respectively which shows a good agreement with the graph. "As shown in Table 2", the lattice parameters a and c value for hexagonal and cubic structure calculated have been reported elsewhere[6]. The grain size 'D' of the samples was obtained by using 'Scherrer's formula.
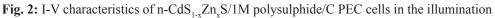
Optical properties:

The optical analysis of the $Cd_{1-x}Zn_xS$ thin films for x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1. The optical studies revealed that the films were the direct type of transition thin film are highly absorptive, which concern the optical band gap. Estimated values of the energy gap reported elsewhere[6]. Energy Band gap of the $Cd_{1-x}Zn_xS$ compound increased upon increasing the Zn content "As shown in Fig. 5". The optical band gap is varied from 2.45 to 3.50 eV. It is observed that the amount of Zn in $Cd_{1-x}Zn_xS$ thin film greatly affects the optical band gap of CdS thin film.
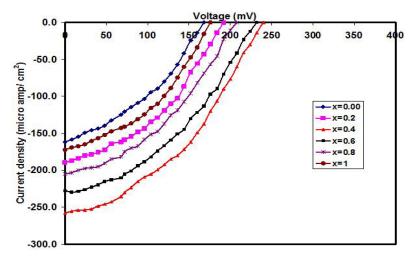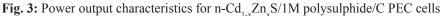
Photovoltaic power output characteristics

When a PEC solar cell is illuminated by means of a light of constant intensity, the current-voltage characteristics shifts in the fourth quadrant, and this behavior is in accordance with the theory of solar cells acting as an electricity generator. A PEC solar cell may operate over a wide range of voltages and currents. By increasing the resistive load on an irradiated cell continuously from zero (a short circuit) to a very high value (an open circuit), it is possible to determine the maximum power point ($P_m = V_m \times I_m$), that is the load for which the cell can deliver maximum electrical power.

Fig. 2: I-V characteristics of n-$CdS_{1-x}Zn_xS$/1M polysulphide/C PEC cells in the illumination

"As shown in Fig. 2", the current-voltage (I–V) curve for PEC cell of configuration n-CdZnS//1 M polysulphide//C under illumination for film deposited on FTO coated glass substrate, respectively. I–V curve characterizes the semiconductor/electrolyte junction which acts like a diode. The interface shows a rectifying behavior with a cathodic current (direct) much greater than the anodic current (reverse), which is typical of a Schottky junction formed between an n-type semiconducting material and a metal or an electrolyte.
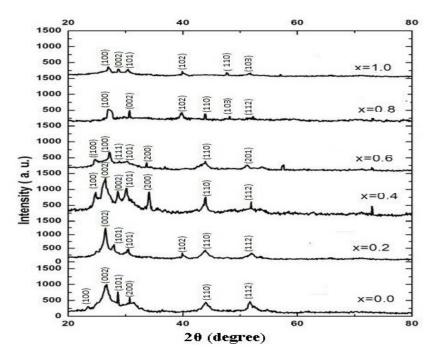

Fig. 3: Power output characteristics for n-Cd$_{1-x}$Zn$_x$S/1M polysulphide/C PEC cells

Fig. 4: XRD Spectra of Cd$_{(1-x)}$Zn$_x$S synthesized for (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)
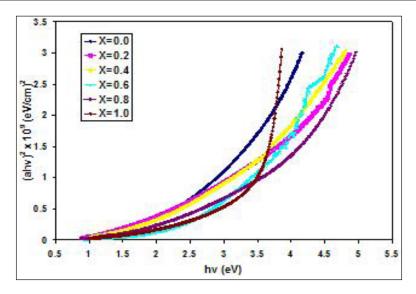
Fig. 5: Shows that graph $(ahv)^2$ versus hv

Photovoltaic output characteristics "As shown in Fig. 3", were studied under the light intensity of 25 mW/cm². Typical photocurrent versus photovoltage characteristics of *n- Cd*$_{1-x}$*Zn*$_x$*S*/ polysulphide under light illumination. It is found that both the I_{sc} and V_{oc} increases with increase in composition parameter '*x*' attain a maximum value at x = 0.4 and then decrease with further increase in '*x*' "As shown in Table 1". We attribute the observed improvement to the increased short circuit current of the cell due to the increased photoelectrode absorption, decreased band gap of *CdS* and decrease in effective series resistance of a cell. These results are analogous to those reported by (Mahapatra P. & Roy C.)[15] and (Deshmukh L.P. *et al.*)[16] for mixed materials. The photovoltaic efficiency (η %), fill factor (ff), Series resistance R_s and the Shunt resistance R_{sh} was calculated from the relation[17-18].

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{input}} \times 100 \qquad \qquad …(2.1)$$

where, *P* input is the power density of incident radiation.

The fill factor (*FF*) was obtained from the formula

$$FF = \frac{V_m \times I_m}{I_{sc} \times V_{oc}} \qquad \qquad …(2.2)$$

where, I_m and V_m are values of maximum current and maximum voltage, which can be extracted from the PEC solar cell.

Series resistance R_s and the shunt resistance R_{sh} were calculated from the slopes of the power output curves using the relations.

$$\left[\frac{di}{dV}\right]_{I=0} \approx \frac{1}{R_s} \qquad \qquad …(2.3)$$

$$\left[\frac{di}{dV}\right]_{V=0} \approx \frac{1}{R_{sh}} \qquad \qquad …(2.4)$$

The variation of power conversion efficiency (η) and fill factor with photoelectrode composition is "As shown in Table 1" and "As shown in Fig. 2". It is observed that both follow similar dependence on 'x'. For higher values of 'x' pinning of Fermi level may decrease V_{oc}. The lower magnitudes of short circuit current for higher values of 'x' may be due to the increased in recombination mechanism not only at the grain boundaries but also at the electrode-electrolyte interface. At higher 'x' values, the role of surface states may also become dominant causing a decrease in both open circuit voltage and short circuit current.

Table 1: Photoelectrochemical performance parameters for $Cd_{1-x}Zn_xS$ thin films PEC cell

Comp. Parameter 'x'	Grain size D (nm)	I_{sc} $(\mu A/cm^2)$	V_{oc} (mV)	$\eta\%$	$FF\%$	R_s (Ω)	R_{sh} $(k\Omega)$	η_d
0.0	20	160	155	0.756	33	360	2.96	2.42
0.2	23	190	180	0.889	36	342	3.21	2.26
0.4	29	260	240	1.124	39.2	310	3.56	1.95
0.6	24	230	224	0.951	37.3	348	3.42	2.28
0.8	21	210	203	0.825	35.2	362	3.36	2.37
1.00	18	172	165	0.706	34	375	3.28	2.48

Table 2: Structural parameter of $Cd_{1-x}Zn_xS$ thin film

Composition 'x'	Material $Cd_{1-x}Zn_xS$	Lattice constant (A^a)		Average grain size (nm) D (mm)	Band gap
		a	C		
$X = 0.0$	CdS	4.17	6.80	20	2.45
$X = 0.2$	$Cd_{0.8}Zn_{0.2}S$	3.99	6.80	23	2.60
$X = 0.4$	$Cd_{0.6}Zn_{0.4}S$	4.11	6.71	29	2.75
$X = 0.6$	$Cd_{0.4}Zn_{0.6}S$	4.10	6.65	24	2.95
$X = 0.8$	$Cd_{0.2}Zn_{0.8}S$	3.80	6.20	21	3.22
$X = 1$	ZnS	3.80	6.20	18	3.50

CONCLUSION

In this work, we prepared Photoelectrochemical (PEC) cell on FTO coated glass substrate the using chemical bath deposition technique. PEC studies show that the I–V curve characterizes the semiconductor/ electrolyte junction which acts like a diode. The interface shows a rectifying behavior with a cathodic current (direct) much greater than the anodic current (reverse), which is typical of a Schottky junction formed between an n-type semiconducting material and a metal or an electrolyte. Power output characteristics were studied under a light intensity of 25 mW/cm². Typical photocurrent versus photovoltage characteristics of n- $Cd_{1-x}Zn_xS$/ polysulphide under light illumination is studied. XRD studies showed that the films are crystalline with cubic and hexagonal structure. It is observed that grain size increasing with increased Zn in (0.0-0.4) further it decreasing with decreasing Cd in (0.6-1). the band gap varied from 2.45 to 3.50 eV. It was observed that changes of small amount of Zn results in marked changes in the optical band gap of CdS. The (002) and (100) diffraction peak was prominent which gives lattice matching to the chalcogenide semiconductor such as $CuIn_xGa_{1-x}Se_2$ and $CuIn(S_{1-x}Se_x)_2$, which are used in photo-voltaic devices.

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