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Effect of zinc composition on properties on PEC cells based on sprayed $Cd_{1-x}Zn_xS$ films

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Abstract. Polycrystalline $Cd_{1-x}Zn_xS$ films were prepared by spray pyrolysis technique, both on conducting and non-conducting glasses. These films were used as photoanodes in photoelectrochemical cells. The optical and electrical properties of these cells are studied and the effect of zinc composition on these properties is revealed.

Keywords. Spray pyrolysis technique; PEC cells; spectral response; photovoltaic characteristics; $Cd_{1-x}Zn_xS$ films.

1. Introduction

Considerable success has been achieved recently in converting visible light energy directly into electrical and/or chemical energy with a semiconductor photoelectrode/electrolyte heterojunction system, as relatively larger amount of incident light reaches the semiconductor space charge region through the transparent electrolyte, than that of the solid junction (Heller and Miller 1980; Tsou and Cleveland 1980; Russak *et al* 1980). The mechanism of the system is that photogenerated electron and hole pairs are separated by electric field in the space charge region resulting in photocurrent and photovoltage. Most of these studies have been done with polycrystalline films of cadmium chalcogenides, such as CdS, CdSe, CdTe, and their alloys ($CdSe_\alpha Te_{1-\alpha}$, $CdS_x Se_{1-x}$) as photoanodes. However, very little data have been published on cells formed with $Cd_{1-x}Zn_xS$ films as photoanodes.

Recently Rajebhonsale and Pawar (1982) developed the chemical bath deposition technique to prepare the $Cd_{1-x}Zn_xS$ alloy films and reported results on PEC cells with these alloy films as photoanodes, with a power efficiency of 0.37% for visible light excitation. However, very little work has been done on semiconductor liquid junction cells formed with sprayed alloy semiconductor films as photoanodes. In the present investigation, the properties of PEC cells formed with sprayed $Cd_{1-x}Zn_xS$ films as photoanodes are studied and the results are reported.

2. Experimental

The polycrystalline $Cd_{1-x}Zn_xS$ films were prepared by chemical spray pyrolysis technique described by Chamberlin and Skarman (1966). The starting solution was made from equimolar solutions of cadmium chloride, zinc chloride and thiourea. By varying the relative proportion of $ZnCl_2$ and $CdCl_2$ in the spraying solution, different cadmium to zinc ion ratios were obtained. The starting solution (300 cc) was sprayed through a specially designed glass nozzle on hot substrate maintained at 400°C. The substrates were pieces of non-conducting and conducting fluorine doped tinoxide [FTO] [20Ω/□] glasses of size 1.2 × 3.7 cm. A spraying rate of 8.5 cc/min was kept constant by controlling the air pressure used to atomise the spray and maintaining the level of the solution at constant height. Fast cooling is used at the termination of spraying as slow cooling produces films with higher resistivity, possibly because of the reaction with oxygen in the air over a longer time used in cooling (Feigelson *et al* 1977). The spray deposited $Cd_{1-x}Zn_xS$ films with different zinc composition in CdS are denoted by Z_0, Z_{10}, Z_{20}, ..., Z_{100} (where subscript denotes percentage of zinc) and PEC cells formed with these films are denoted respectively by Z_0C, $Z_{10}C$, $Z_{20}C$, ..., $Z_{100}C$.

Photoelectrochemical cells were formed in a chamber with a quartz window, using $Cd_{1-x}Zn_xS$ films as photoanodes, graphite rod as counter electrode and an electrolyte solution which was prepared, as an aqueous solution 1 M NaOH - 1M Na_2S - 1 MS. The distance between photoanode and counter electrode was kept constant (0.6 cm) for all cells.

The open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) of the PEC cells were measured directly with a DPM 10 digital voltmeter and Aplab FET input nanoammeter [TFM-13] respectively. A tungsten filament lamp (500 W) was used as light source. The spectral response of these cells was studied using Spekol (Carl Zeiss Jena) as monochromator. In order to understand the nature of the spectral response of the cells, the optical absorption and transmission of the films deposited on glass substrate were studied by Spekol in the wavelength range 350 to 770 nm. Barrier height is determined by measuring the reverse saturation current as a function of temperature.

3. Results and discussion

$Cd_{1-x}Zn_xS$ films prepared by spray pyrolysis technique are found to be uniform and adhere tightly to the substrate. The thickness of these films decreases with increase in zinc composition. This result is similar to the findings reported by others (Rajebhonsale and Pawar 1982) and attributed to smaller density of ZnS than that of CdS.

In the present investigation, the films are deposited on conducting (FTO) glasses and the PEC cells $Cd_{1-x}Zn_xS$/1 M NaOH - 1 M Na_2S - 1 M S/C are formed. The dynamic I-V curves are studied for all the cells, in dark and light. The nature of the I-V curves are similar and a typical I-V plot for cell $Z_{20}C$ is given in figure 1. It is seen that I-V curve in light is shifted in the fourth quadrant which shows that PEC cell is the generator of the electricity.

The short-circuit photocurrent was measured as a function of wavelength for all the cells (figure 2). From figure 2, it is observed that the photocurrent increases with increase in wavelength, attains the maximum value and then decreases sharply.

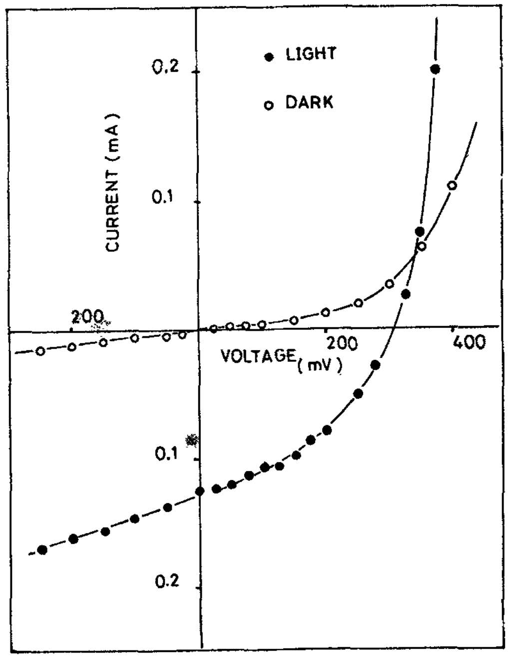

Figure 1. Dynamic current-voltage (I-V) characteristics for a cell $Z_{20}C$ in dark and light. Intensity of illustration 100 mW/cm^2.

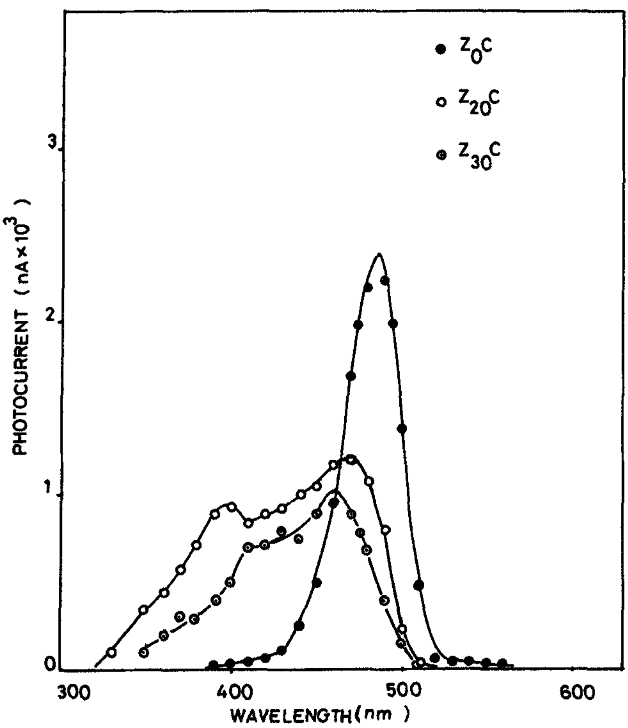

Figure 2. Spectral response curves for Z_0C,$Z_{20}C$ and $Z_{30}C$ cells.

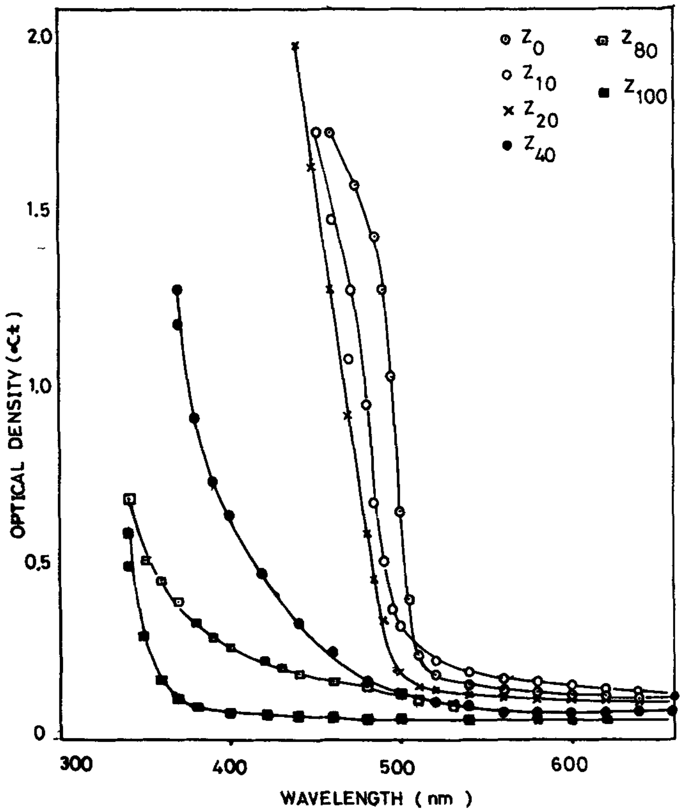

Figure 3. Variation of αt with wavelength (λ) for the films Z_0, Z_{10}, Z_{20}, Z_{40}, Z_{80} and Z_{100}.

The smaller value of photocurrent at shorter wavelength side may be attributed to the large recombination velocity, absorption of light in electrolyte and lower spectral emission of the tungsten lamp. On the other hand sharp decrease in photocurrent at longer wavelength side is attributed to absorption edge of the photoanode. From figure 2 it is further observed that there is a shift in spectral peak and spectral edge towards the shorter wavelength side with increase in zinc compositions in photoanode. This can be understood from the absorption spectrum of the photoanode.

Figure 3 shows the variation of optical density (αt) with wavelength. It is seen that the variation of αt with increasing wavelength is not linear. The steep fall in absorption is attributed to absorption edge. The wavelength corresponding to this absorption edge gives the band gap of a semiconductor. From figure 3 it is observed that absorption edge shifts towards the shorter wavelength side with increasing Zn composition. This reveals that the band gap of photoanode increases with increase in zinc composition. This increase in band gap gives rise to shift in spectral response peak and spectral edge towards the shorter wavelength side.

The variation of short-circuit current (I_{sc}) and open circuit voltage (V_{oc}) with zinc composition given in figure 4, shows that I_{sc} decreases with increase in zinc

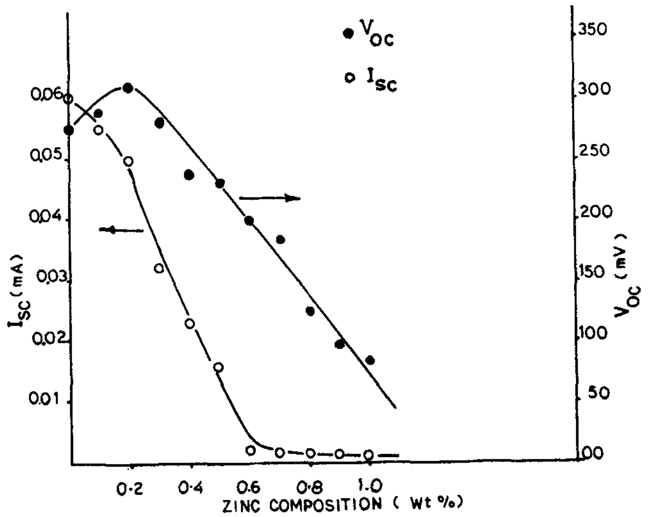

Figure 4. Variation of V_{oc} and I_{sc} of PEC cells with zinc composition in photoanode

Table 1. Parameters of PEC cells formed with $Cd_{1-x}Zn_xS$ sprayed films as photoanodes under intensity of illumination 100 mW/cm^2.

Cell Nos.	Wt. % of Zn in $Cd_{1-x}Zn_xS$ films	Ideality factor (n)	$I_0 \times 10^{-7}$ (amp.)	Barrier height $-\phi_B$ (eV)	$R_s \times 10^3$ (Ω)	$R_{sh} \times 10^3$ (Ω)
Z_0C	0	1.74	8.0	0.278	2.3	22
$Z_{10}C$	10	1.80	7.1	0.305	3.5	25
$Z_{20}C$	20	1.85	5.5	0.378	5.0	25
$Z_{30}C$	30	2.15	13.9	0.332	5.0	16
$Z_{40}C$	40	2.35	15.8	0.313	6.6	20
$Z_{50}C$	50	3.46	17.5	0.283	8.3	10
$Z_{60}C$	60	2.84	17.1	0.233	7.1	62
$Z_{80}C$	80	3.10	22.0	0.213	9.6	60
$Z_{90}C$	90	3.45	23.6		9.8	25
$Z_{100}C$	100	3.82	67.0	0.211	10	10

composition. This is similar to the results earlier reported for solid junctions (Hsu and Burton 1980). The decrease in I_{sc} may be originated due to increase of resistivity in mixed sulphide. The increase in recombination in the depletion region can be understood from the study of junction ideality factor. For ideal junction, the ideality factor (n) is one. Ideality factors for all the cells are measured and tabulated in table 1. It is seen that n varies from 1.74 for the cell Z_0C to 3.82 for the cell $Z_{100}C$.

From figure 4 it is seen that the V_{oc} values change with zinc composition. It increases up to 20% zinc composition and for higher zinc composition it decreases. The variation in V_{oc} can be understood by the relation (Rajeshwar *et al* 1981).

$$V_{oc} = \frac{nKT}{q} \, l_n I_{sc}/I_0$$

where I_0 is the reverse saturation current and all other terms have their usual meanings. The observed variation of V_{oc} with zinc composition is mainly attributed to I_0. The reverse saturation currents are determined from the plots of log I *vs* V for all the cells and are given in table 1. It is found that I_0 decreases up to 20% zinc composition and for further increase in zinc composition, it increases.

The variation of I_0 with temperature is studied for all the cells and the barrier height, Φ_B is estimated using the relation (Rhoderick 1978)

$$I_0 = A^* T^2 \exp(\Phi_B/kT), \tag{2}$$

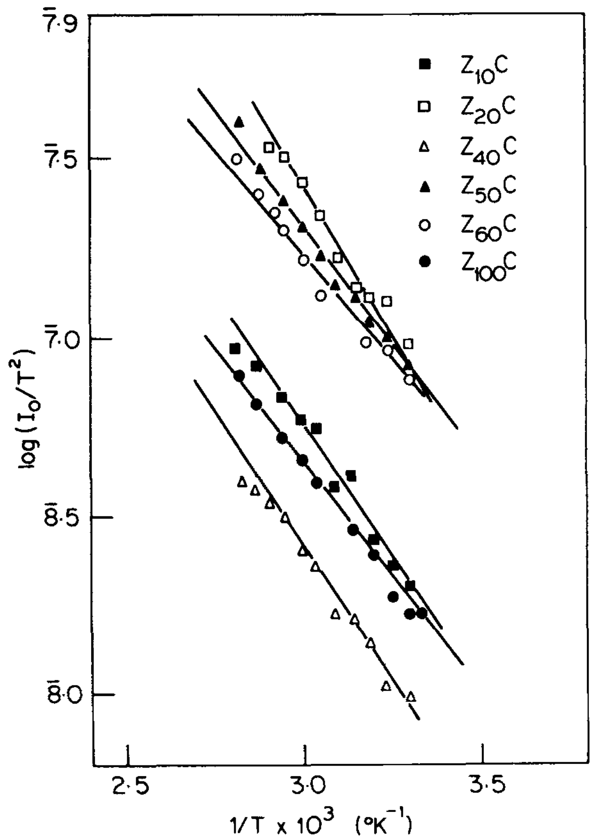

Figure 5. Plots of log I_0/T^2 vs $1/T$ for the typical cells $Z_{10}C$, $Z_{20}C$, $Z_{40}C$, $Z_{50}C$, $Z_{60}C$ and $Z_{100}C$.

where $A^* = (4\pi e_0 m^* K^2)/h^3$ is the Richardson constant and all other terms have their usual meanings. Figure 5 shows the plots of log I_0/T^2 *vs* $1/T$ for typical cells. The slope of this plot gives the barrier height in electron volts (eV). The Φ_B values for all cells are given in table 1. It is observed that Φ_B increases up to 20% zinc composition and for higher compositions it decreases.

The variation of V_{oc} with light level is measured and found to attain a steady-state value at higher level of illumination. This corresponds to the flat band potential. The magnitudes of maximum V_{oc} are measured for all cells and are in fair agreement with those Φ_B values listed in table 1.

The photovoltaic output characteristics for typical cells are shown in figure 6. In the photovoltaic output characteristics, a current is generated internally in the cell giving rise to a voltage across the junction in the forward bias direction and causing current flow through the junction. The maximum power output of the cell is given by the largest rectangle that can be drawn inside the photovoltaic output characteristics. For ideal cell the power output characteristics is rectangular. The series resistance R_s and shunt resistance R_{sh} for ideal cell is zero and infinite respectively. The increase in series resistance causes successively larger rounding of the characteristics. The series and shunt resistances are determined by taking slopes at voltage and current axes respectively. These values are tabulated in table 1.

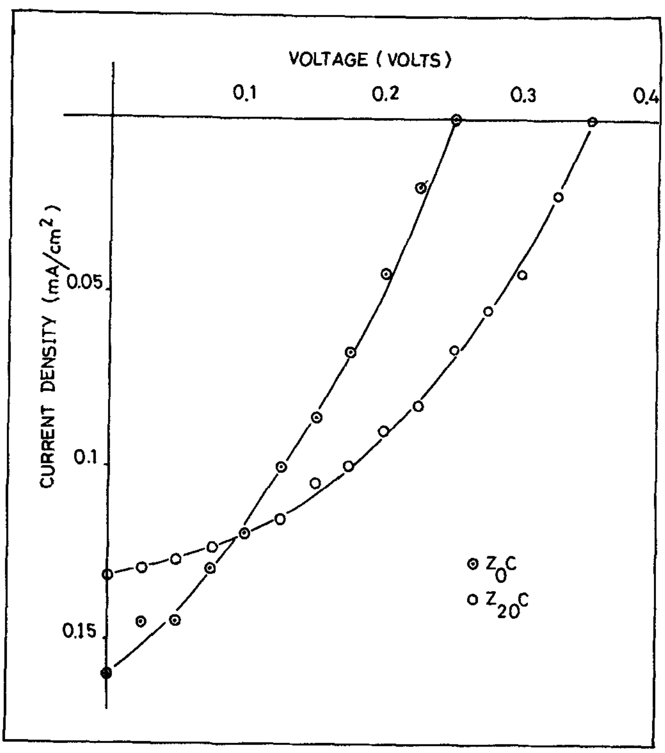

Figure 6. Photovoltaic output characteristics for the cells Z_0C and $Z_{20}C$.

It is found that there is no systematic variation in shunt resistance; however, series resistance increases with increase in zinc composition. This increase in series resistance is originated mainly due to the bulk resistance of photoanode as series resistance of electrolyte and contact resistance are constant. These are similar to the results reported by Devis and Lind (1968). The power output for all the cells is calculated and is higher for the cell $Z_{20}C$.

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