Bull. Mater. Sci., Vol. 7, No. 2, July 1985, pp. 101–104. © Printed in India.

Studies on dynamic *I-V* curves of semiconductor-liquid junction cells formed with $Cd_{0.8}Zn_{0.2}S$ films prepared at various spray rates

M D UPLANE and S H PAWAR

Department of Physics, Shivaji University, Kolhapur 416004, India.

MS received 27 February 1984; revised 8 March 1985

Abstract. $Cd_{0.8}Zn_{0.2}S$ films were prepared by the spray pyrolysis technique on glass and conducting glass (fluorine doped tin oxide) substrates, by spraying aqueous solutions of cadmium chloride, zinc chloride and thiourea. The spray rate was varied from 4 cc/min to 16 cc/min. It is found that film thickness increases with increase in spray rate. The electrical and optical properties of the films namely dark conductivity, thermoelectric power and optical absorption were studied; conductivity and thermoelectric power are higher for the films prepared at lower spray rate (4·3 cc/min).

Keywords. Sprayed $Cd_{0.8}Zn_{0.2}S$ films; spray rate; photoelectrochemical cell; dynamic *I-V* characteristics.

1. Introduction

A solar cell converts light energy directly into electrical energy by means of the photovoltaic effect. The photovoltaic effect can occur in many systems such as: the semiconductor-electrolyte (Heller and Vadimsky 1981; Lokhande and Pawar 1984; Gerischer and Ekardt 1983), the metal-semiconductor, semiconductor-semiconductor junctions etc. Photons with energy larger than the band-gap of the semiconductor can generate electron and hole pairs. If these excess electron and hole pairs are separated by an energy barrier system, an electromotive force is generated and when an external circuit is provided a photocurrent flows. The semiconductor-electrolyte interface has been studied earlier to understand the surface electronic properties of semiconductors (Morrison 1972; Many *et al* 1965). Recently, semiconductor electrolyte systems have been used to derive important information like the mobility gap and the density of localized states in semiconductors (Chan and Jayadeviah 1973). In the present investigation current-voltage (*I-V*) curves were studied in the dark to understand the charge transfer across the junction. *I-V* curves were analysed by using the Butler-Volmer equation. The effect of spray rate on the equilibrium current density I_0, and the symmetry factor β, is described.

2. Experimental

$Cd_{0.8}Zn_{0.2}S$ films were prepared by spraying equimolar (0·2 M) solutions of $CdCl_2$, $ZnCl_2$ and thiourea in appropriate volume ratio to obtain the Cd:Zn ion ratio 4:1, and the CdZn:S ratio 1:1. The substrate temperature was maintained at 400°C. The substrates used were ultrasonically cleaned microslides and fluorine-doped tin oxide coated glass [FTO 16·2Ω/□]. The films were prepared with five different spray rates varying from 4·2 cm^3/min to 16 cm^3/min. An air compressor was used to atomise the spray and the films were allowed to cool rapidly after spraying to avoid oxidation during cooling.

The photoelectrochemical cells $Cd_{0\cdot8}Zn_{0\cdot2}S$/1 M NaOH-1 M Na_2S-1 M S/C were formed by using films prepared at different spray rates and denoted by $P_{4\cdot3}$, $P_{7\cdot2}$, P_{11}, $P_{13\cdot5}$ and P_{16}, where the subscript denotes the spray rate. Dark *I-V* curves were used to determine the equilibrium current density I_0 and symmetry factor β.

3. Results and discussion

The films though prepared at different spray rates are uniform and adhere to the substrate. However, film thickness increases with increase in spray rate (figure 1). The variation of film thickness at high spray rate is attributed to (i) the short spray-time and (ii) the relatively low evaporation at higher spray rates.

The dark conductivity (σ) was measured as a function of spray rate. It is found that σ decreases with increase in spray rate. The decrease in dark conductivity is attributed to the poor crystallinity of the films at higher spray rates. Thermoelectric power measurement data were used to determine carrier concentration as described by Uplane and Pawar (1983). Mobility was determined by using the relation

$$\mu = \sigma / n_e, \qquad (1)$$

where n is the carrier concentration, μ the mobility and the other terms have their usual meaning. It is found that mobility decreases with increase in spray rate and is attributed to the decrease in the intergranular barrier height. Optical absorption of the films was studied within the wavelength range between 700 nm and 400 nm. Optical bandgaps were determined from the $(\alpha h\nu)^2$ versus $h\nu$ plots and no change was observed in the bandgap with spray rate.

Photoelectrochemical cells were formed by using the films prepared at different spray rates. The dynamic *I-V* characteristics in the dark were studied for all the cells. Figure 2 shows dynamic *I-V* curves for typical cells. The dynamic *I-V* curves are

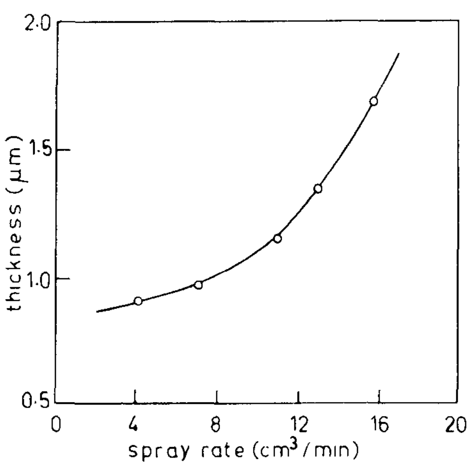

Figure 1. Variation of film thickness with spray rate.

analysed by using the Butler-Volmer equation (Bockris and Reddy 1977)

$$I = I_0\{\exp[(1-\beta)VF/RT] - \exp[(-\beta VF)/(RT)]\} \quad (2)$$

where I_0 is the equilibrium exchange current density, β the symmetry factor, V the over voltage, R the universal gas constant and F the Faraday's constant. If $\beta = 0{\cdot}5$, the I

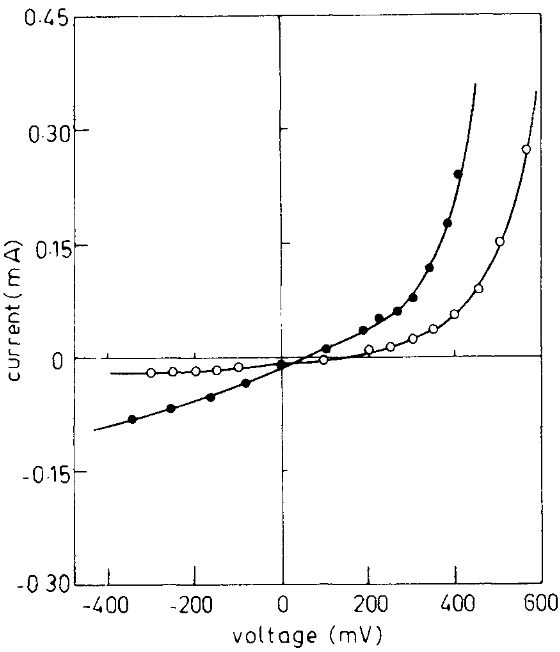

Figure 2. Dynamic I-V characteristics in the dark for typical cells $S_{4\cdot3}$ and S_{16}.

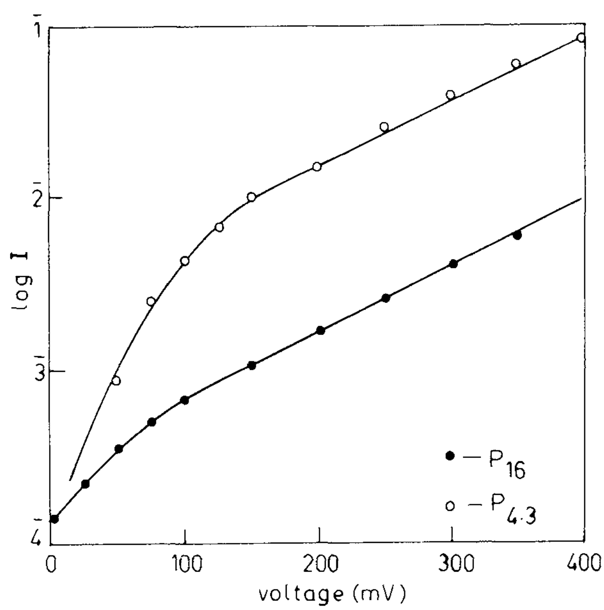

Figure 3. Plot of log I versus V for typical cells $S_{4.3}$ and S_{16}.

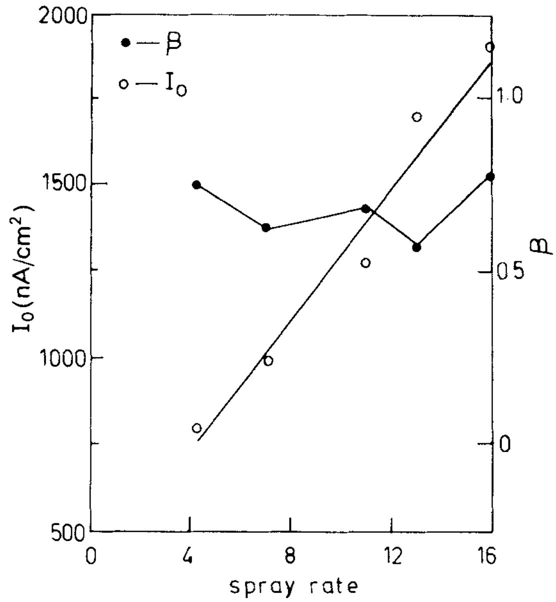

Figure 4. Variation of equilibrium current density, I_0, and symmetry factor, β as a function of spray rate.

versus V curve becomes symmetric suggesting that the interface does not rectify the current. However, if $\beta \neq 0{\cdot}5$ the I-V curves are non-symmetrical and the interface shows rectification properties. The I-V curves in figure 2 are not symmetrical and thus the interfaces have rectifying properties.

The symmetry factor, β, and the equilibrium current density, I_0, were determined by applying the high field ($V > 100$ mV) approximation to (2) and it can be written as:

$$I = I_0 \exp[(1-\beta)FV/RT]. \tag{3}$$

The symmetry factors β are determined from the plots of $\log I$ versus V (shown in figure 3) and the values of I_0 are obtained by extrapolation of the plots of $\log I$ against V to the $\log I$ axes. The values of I_0 and β are plotted as a function of spray rate in figure 4. It is observed that the equilibrium current density increases with increase in spray rates and this may be attributed to the poor crystallinity of the film and the presence of pin holes at higher spray rates. No systematic variation in β was observed with spray rate.

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