Bull. Mater. Sci., Vol. 20, No. 7, October 1997, pp. 1011–1014. © Printed in India.

n–$CuInS_2$/polysulfide photoelectrochemical solar cells prepared by spray pyrolysis

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MS received 26 September 1996

Abstract. *n*–$CuInS_2$ photoanode has been prepared by spray pyrolysis onto SnO_2 deposited glass substrate at 350°C. The conductivity type of the photoanode was tested by hot–probe method and was of *n* type. The conductivity of the photoanode was of the order of $2\text{–}4\,\Omega^{-1}\,cm^{-1}$ and was measured by using four–probe method. The effect of etching ($HCl:HNO_3 = 5:1$ by volume) on photoanode properties has been studied. The best cell had the following parameters: $V_{oc} = 0{\cdot}29$ V, $I_{sc} = 5{\cdot}33$ mA/cm^2, $ff = 0{\cdot}571$ and $\eta = 1{\cdot}275\%$.

Keywords. I–III–VI compounds; $CuInS_2$.

1. Introduction

$CuInS_2$ is a ternary group compound related to that of zinc–blende. $CuInS_2$ possesses several exceptional material properties for photovoltaic specially homojunction. $CuInS_2$ thin films have been grown as *n* type or *p* type majority-carrier concentration (Kazmerski *et al* 1975, 1976; Kazmerski and Shieh 1997) by adjusting the ratio of Cu and In in the films. Masse *et al* (1975) reported the theoretical efficiency of $CuInS_2$ homojunction to be 28%.

The photoelectrochemical cells based on semiconductors form an important class of solar energy conversion system. They have the advantage of being used for both photovoltaic and chemical energy conversion (Gerischer 1977; Kung *et al* 1977; Veh and Hackerman 1977; Shoonman 1982), $CuInS_2$ has a direct band gap of about 1·43 eV (Tembhurkar and Hirde 1992), a value which is close to optimal for terrestrial photovoltaics.

A PEC is a device in which one or both the electrodes is a photoresponsive semiconductor (SC) such that irradiation of the SC with light of $h\nu \geqslant E_g$, the band gap of the semiconductor, which produces a flow of current in the external circuit. The flow of current occurs at the semiconductor/electrotype interface in which light absorption takes place in the semiconductor to produce excess charge carriers (Aruchamy *et al* 1982).

In the present work the characteristics of $CuInS_2$/polysulfide electrochemical solar cell having photoanode were studied in the form of thin films.

2. Preparation of photoanode

$CuInS_2$ photoanode in the form of thin film was deposited on SnO_2 deposited glass substrates so as to cover half the area. The detailed preparation of $CuInS_2$ thin films was discussed elsewhere (Tembhurkar and Hirde 1992). The aqueous solutions of cupric chloride, indium trichloride and thio-urea of 0·02 M were mixed in the proportion of 1:1·2:3·2 by volume for spraying the films on hot glass substrates. The temperature of the substrate was maintained at 350°C and was measured by pre–calibrated copper-constantan thermocouple. The conductivity of the films as tested by hot-probe method was of

n-type. To get a contact lead, a copper wire was placed on the SnO_2 and indium metal was diffused by hot soldering rod on the copper wire and SnO_2. Thus the ohmic contact on the SnO_2 was prepared. The SnO_2 layer works as back contact for $CuInS_2$ thin films. Epoxy (araldite) was used to seal the copper wire contact and all portions of SnO_2 layer on which film was not deposited and to insulate all but the exposed face of the film. The electrode, thus prepared was used as photoanode. The conductivity of the films was measured using four-probe method and was found to be of the order of $2{\cdot}4\,\Omega^{-1}\,cm^{-1}$. Thickness of the photoanode was of the order $2-3\,\mu m$ measured using weighing method by taking density of the film as $4{\cdot}71\,g/cm^2$ (Tembhurkar and Hirde 1992).

3. Study of photoresponse

In order to select the proper light intensity, the photoresponse versus light intensity study was carried out for illumination of photoanodes. When the surface is illuminated by the light of energy greater than the semiconductor band gap, the light is absorbed and excess charge carriers are produced. The photogenerated electron–hole pairs in the space charge region are separated. For *n*-type material the photogenerated electrons move deep into the bulk and the holes move to the surface of the semiconductor which are responsible for the redox reaction (Oshcherin 1976). The electrolytic solution was a mixture of 2 M Na_2S $5H_2O$, 2 M KOH, 3 M S. The electrode was stable in this electrolytic solution. The face of the photoanode was brought to $0{\cdot}5\,cm^2$ of the window to minimize solution light absorption. Platinum electrode of area $1\,cm^2$ was used as a counter electrode. Provision was made for a calomel reference electrode. Short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were measured as a function of light intensity. Potential difference of photoanode was between photoanode and saturated calomel electrode (SCE). V_{oc} is obtained by subtracting 0·244 V (potential of SCE) from the voltage measured between photoanode and calomel electrode. Graph is plotted between short circuit current/open circuit voltage and illumination intensity (figure 1a, b).

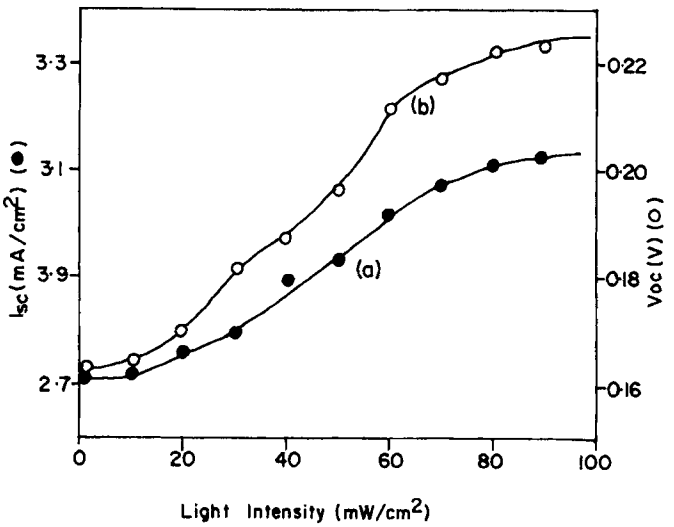

Figure 1. Illumination intensity vs (**a**) short circuit current and (**b**) open circuit voltage of as deposited *n*-$CuInS_2$ in a solution 2 M in Na_2S-5H_2O, 2 M in KOH and 3 M in S.

It was observed that, the open circuit voltage and close circuit current increases with light intensity and approach the saturation value beyond 70 mW/cm^2 light intensity. This behaviour is similar to the case of *p–n* or SC/metal junction is solid-state photoanode (Aruchamy *et al* 1982).

4. *I–V* characteristics

A PEC cell is characterized by its current–voltage output with load resistance. To obtain the conversion efficiency, after 2–3 min of illumination of constant light intensity, the corresponding values of photocurrent (I_{ph}) and photovoltage (V_{ph}) are recorded under variable load resistance.

Figure 2a shows the *I–V* characteristics for constant light intensity at 70 mW/cm^2 of as deposited $CuInS_2$ photoanode. Of special importance in obtaining good photoactive electrodes is their surface preparation. For this the film was etched in 5:1HCl:HNO_3 for 20 sec and rinsed quickly in distilled water. This process was repeated 2–3 times. Figure 2b shows the current voltage characteristics of etched photoanode at light intensity 70 mW/cm^2.

The fill factor (*ff*) can be calculated using the relation,

$$ff = \frac{I_m V_m}{V_{oc} I_{sc}}, \tag{1}$$

V_m and I_m can be determined by computing the product at various points along the curve and selecting the point where the product is maximum. The fill factor indicates the extent of departure from the ideal behaviour of semiconductor electrode (Robbins *et al* 1978). The ideal *I–V* relationship for a PEC cell should yield 'rectangular' shape. Thus the fill factor is a measure of the rectangularity of the output of photovoltage–photocurrent plot. The fill factor value close to unity is desired for a good quality PEC solar cell.

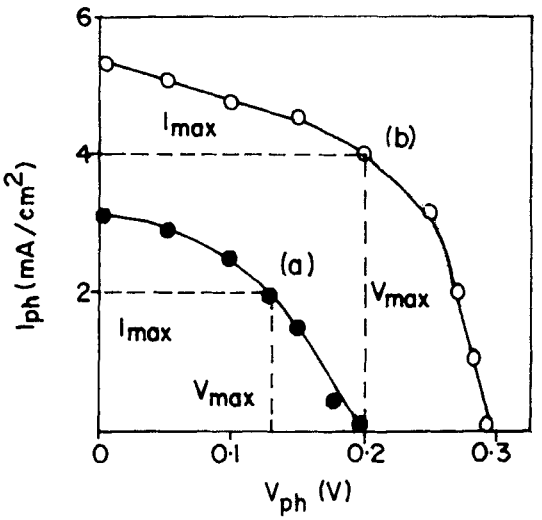

Figure 2. Output power characteristic of *n*-$CuInS_2$ in a solution 2 M in Na_2S-5H_2O, 2 M in KOH and S at room temperature: (**a**) as deposited and (**b**) etched.

Table 1. Parameters of $CuInS_2$ photoanodes.

Thin film	Fill factor *ff*	Efficiency η
$CuInS_2$		
a) as-deposited	0·396	0·385
b) etched	0·571	1·275

The optical to electrical energy conversion efficiency in a semiconductor/liquid junction solar cell given by,

$$\eta = \frac{V_{oc} \cdot I_{sc} \cdot ff}{P_{in}} \times 100, \tag{2}$$

where P_{in} is the light (optical power) input. From the plots (figure 2), the fill factor (ff) and efficiency were calculated using relations (1) and (2) of $CuInS_2$ photoanode. These results are listed in table 1. The similar result was published (Tembhurkar and Hirde 1994) for $CuInSe_2$ photoanode.

5. Results and discussion

It was observed that the short–circuit current, open circuit voltage and fill factor increases after etching the photoanode and thus overall power conversion efficiency. Robbins *et al* (1978) reported the fill factor and efficiency for etched single crystal and pressure sintered polycrystalline electrode of *n*–$CuInS_2$ liquid junction solar cells as 0·23–0·31 and 3·5–4·5% respectively. Our calculated value of fill factor was greater than this while efficiency was less. Our calculated efficiency was less due to the polycrystalline thin films and difference in preparation method.

For good limiting open circuit and short circuit parameters, the fill factor can be increased, the *n*–$CuInS_2$ based cell may be useful in the field of liquid junction solar cell system.

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