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Spray-pyrolytically deposited n-$CuInSe_2$/polysulphide photoelectrochemical solar cells

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Abstract. n-$CuInSe_2$ photoanode has been prepared by spray pyrolysis onto SnO_2-deposited glass substrate. The effect of etching ($HCl:HNO_3 = 5:1$ by volume) on photoanode properties has been studied. The best cell had the following parameters: $V_{oc} = 0.446$ V, $J_{sc} = 18.32$ mA/cm^2, ff = 0.53 and $\eta = 6.22\%$.

Keywords. I–III–VI compounds; $CuInSe_2$.

1. Introduction

I–III–VI_2 compounds are ternary analogues of II–VI compounds. These are closely related to zinc blende. Though a large number of researchers have concentrated on the field of solar energy, there is a need of more attention as solar energy is one of the promising energy sources for the future.

Photoelectrochemical cells based on semiconductors form an important class of solar energy conversion systems. They have the advantage of being used for both photovoltaic and chemical energy conversion (Gerischer 1977; Kung *et al* 1977; Veh and Hackerman 1977; Shoonmann 1982). It is essential to find that the semiconductor electrode will be stable in electrolyte. In view of the Se/S exchange that occurs in CdSe/polysulphide cells, it was interesting to study $CuInSe_2$/polysulphide systems. $CuInSe_2$ has shown considerable promise as a candidate for thin-film solar cells. It has direct band gap of about 0.93 eV (Tembhurkar and Hirde 1992). Films can be made either p or n type easily by varying the proportion of Cu and In in the films.

In this paper we report the characteristics of $CuInSe_2$/polysulphide electrochemical solar cell having photoanode prepared by spray pyrolysis in the form of thin films. The structure of the films was determined on a Philips X-ray diffractometer using CuK_α radiation. Chemical composition analysis was carried out on an inductively coupled plasma atomic emission spectrophotometer (8410 Plasmascan). The intensity of incident light was measured on a SURYAMAPY.

2. Preparation of photoanode

$CuInSe_2$ thin film was deposited on SnO_2-deposited glass substrate so as to cover half the area. Aqueous solutions of cupric chloride, indium trichloride and seleno-urea of 0.02 M were mixed in 1:1.2:3.2 proportion by volume for spraying. Excess selenium is necessary to obtain $CuInSe_2$ films. The films deposited have a selenium deficiency if the ratio of solutions is 1:1:2. The excess selenium is used to remove this deficiency. The temperature of the substrate was maintained at 350°C and was measured by a precalibrated thermocouple. The solution was sprayed at a pressure of 12 kg/cm^2. The glass sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on the hot substrate and to ensure instant evaporation. The rate of flow was maintained at 3·5 ml/min. The conductivity of the film as tested by hot-probe method was of n-type. The conductivity of the films was measured using four-probe method and was found to be of the order of 2–4 $\Omega^{-1}cm^{-1}$. To get a contact lead, 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 layer works as back contact for $CuInSe_2$ films. Epoxy (Araldite) was used to seal the copper wire contact and all portions of SnO_2 layer on which the film was not deposited and to insulate all but exposed face of the film. The electrode thus prepared was used as photoanode. The thickness of the photoanode was of the order of 2 to 3 μm.

Chemical composition of the film was tested by inductively coupled plasma atomic emission spectrophotometer (ICPAES) analysis. The atomic percentages of various elements present in the film were as follows: Cu, 22·346 to 24·926%; In, 25·040 to 26·964%; Se, 49·468 to 50·490%. The structure of the deposited film was confirmed by XRD (Tembhurkar and Hirde 1992).

3. Study of photoresponse

When the surface is illuminated by light of energy greater than the semiconductor band gap, the light energy 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. This is responsible for the redox reaction (Aruchamy *et al* 1982).

In order to select the proper light intensity, variation of photoresponse with light intensity was studied for illumination of photoanodes. The electrolytic solutions were 2 M Na_2S–5 H_2O, 2 M KOH and 3 M S. The electrode was stable in these electrolytic solutions. Short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were measured as a function of light intensity. Potential difference of photoanode was measured 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. Platinum electrode was used as a reference electrode. A graph between short circuit current/open circuit voltage and illumination intensity was plotted (figure 1a, b). It is observed that open circuit voltage and short circuit current increase with light intensity and approach saturation value beyond 70 mW/cm^2 light intensity. This behaviour is similar to the case of p–n or SC/metal junction in solid-state photoanode (Aruchamy *et al* 1982).

A PEC cell is characterized by its current voltage output with load resistance. For this purpose, after 2–3 min of illumination of constant light intensity, the corresponding value of photocurrent (I_{ph}) and photovoltage (V_{ph}) are recorded under variable load resistance to obtain the values of conversion efficiency. Figure 2a shows the I–V characteristics for constant light intensity at 70 mW/cm^2 of as-deposited $CuInSe_2$ photoanode. Of special importance in obtaining good photoactive electrodes is their surface preparation. For this the film was etched in 5:1 HCl:HNO_3 for 20 sec and rinsed quickly in distilled water. This process was repeated three times. Figure 2b shows the current–voltage characteristics of etched photoanodes of $CuInSe_2$ at light intensity 70 mW/cm^2.

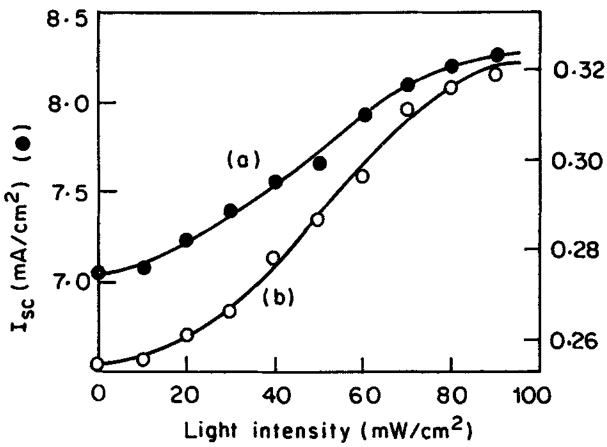

Figure 1. Illumination intensity versus (a) short circuit current and (b) open circuit voltage of as-deposited n-CuInSe$_2$ in a solution 2 M in $Na_2S{\cdot}5H_2O$, 2 M in KOH and 3 M in S.

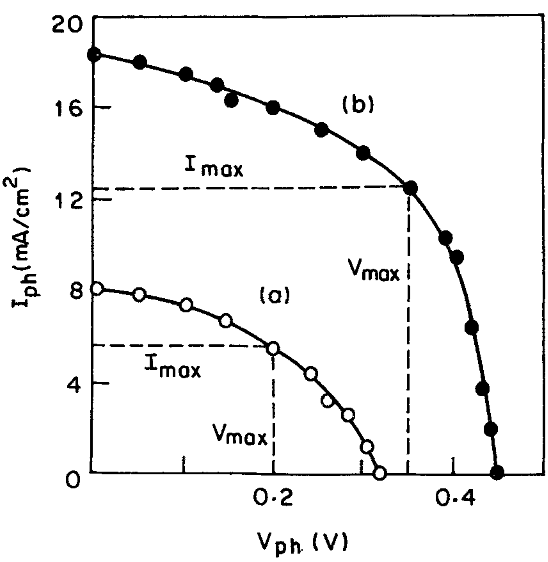

Figure 2. Output power characteristics of n-CuInSe$_2$ in a solution 2 M in $Na_2S{\cdot}5H_2O$, 2 M in KOH and 3 M in S at room temperature: (a) as-deposited, (b) etched.

The fill factor ff $(= I_m \cdot V_m / V_{oc} \cdot I_{sc})$ and efficiency η $(= V_{oc} \cdot I_{sc} \cdot \mathrm{ff}/P_{in} \times 100)$ were calculated for as-deposited and etched photoanode of CuInSe$_2$ thin films. These results are listed in table 1.

4. Results and discussion

It was observed that the short circuit current, open circuit voltage, fill factor and overall power conversion efficiency increase after etching the photoanode. Mirovsky and Cahen (1982) have reported fill factor and efficiency for etched n-CuInSe$_2$/poly-

Table 1. Parameters of $CuInSe_2$ photoanodes.

Thin film	Fill factor (ff)	Efficiency (η)
n-$CuInSe_2$		
(a) As-deposited	0·44	1·62
(b) Etched	0·53	6·22

sulphide PEC cells as 0·38 and 5·6% respectively. These values are less than our calculated values (table 1). The maximum efficiency recorded by Duchemin *et al* (1989) for $CuInSe_2$ sprayed cell was only 4%. In our experiment the efficiency of $CuInSe_2$ PEC cell increased from 1·66% to 6·22% due to etching. This indicates that the spray-pyrolytically deposited thin films with proper etching treatment can be successfully used for preparing photoanode of PEC cell.

Surface and near-surface defects introduce states which act as carrier traps and recombination centres and affect the performance of solar cells. Due to etching, imperfections near or at the surface are removed. As a result trapping and recombination are also reduced. Spectral transitions within band gap are eliminated and short circuit current, fill factor and open circuit voltage increase.

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