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$CuInS_2$ SEPTUM PHOTOELECTROCHEMICAL CELLS

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The natural photosynthetic systems are the precursors for the septum photoelectrochemical cells, in which much larger outputs are possible than conventional photoelectrochemical cells by a judicious choice of the two electrolytes separated by a partition called spetum. We report, for the first time, the characteristics of septum cells using electrodeposited $CuInS_2$ films. Electrodeposition of Cu-In alloy on Ti substrates followed by sulphurization in flowing H_2S at 823 K for 20 min, yielded polycrystalline $CuInS_2$ films, showing preferred orientation in (112) direction. The films were n type with a band gap of 1.42 eV. The $CuInS_2$ film on the substrate was fitted in a groove and cemented with PVC solution in a PVC cell with a transparent window in such a way that it formed the septum separating the cell into two compartments. 1 *M* polysulphide was used in the photoexposed chamber. The contacting electrodes were graphite in polysulphide solution in the photoexposed side and either graphite, Pt, Cu or Cd in copper or cadmium salt solution in the other compartment. A maximum photovoltage of 608 mV and a current density of 4 $mAcm^{-2}$ were obtained for the configuration Cd/0.5M Cd/Ti/$CuInS_2$/Polysulphide/C with a 0.2 cm^2 area septum under an illumination 60 mW cm^{-2}.

Keywords: **$CuInS_2$, Septum cell and PEC cell.**

INTRODUCTION

The ternary chalcogenides $CuInS_2$ and $CuInSe_2$ are promising candidates for solar energy conversion due to their high absorption coefficient (10^4 cm^{-1}) and optimum band gap (1.1 - 1.6 eV). $CuInS_2$ films have been used in septum photoelectrochemical (PEC) cells for the first time in this laboratory. The previously reported conversion efficiencies for conventional PEC polycrystalline $CuInS_2$ photoelectrodes are 5-6% [1,2] in polysulphide electrolyte and 10% [3] for single crystals in acidic iodine/iodide system.

In septum cells, higher outputs are possible than conventional PEC cells by a judicious choice of the two redox couples separated by a partition called the septum. Investigations on cells with such a configuration were first reported by Tien [4]. Studies on CdSe septum cells [5] and Cd(SeTe) septum cells [6] were reported from this laboratory. In this study, electrodeposition and sulphurization techniques were employed for preparing $CuInS_2$ thin film photoelectrodes. Electrodeposition of Cu-In alloy and subsequent conversion offers an inexpensive means for producing electrodes of almost any size.

EXPERIMENTAL

The electrodeposition was carried out from a bath of indium chloride and copper chloride - triethanolamine complex (0.5 *M* with respect to both indium and copper) adjusted to a *p*H of 2 with HCl on an etched Ti substrate at a constant potential of -1.5 V vs SCE. Cyclic voltammetry was used to fix the deposition potential. After an initial 15 min deposition the electrode was taken out and washed, and the deposition continued for 10 min more. The electrode was again taken out, washed and the deposition continued for another 5 min. If the deposition was carried out continuously for 30 min the film was found to peel off, and the above procedure of interrupted deposition with washing of the deposited substrate appeared to obviate this difficulty, resulting in better adhesion of the deposit. The sulphurization of the

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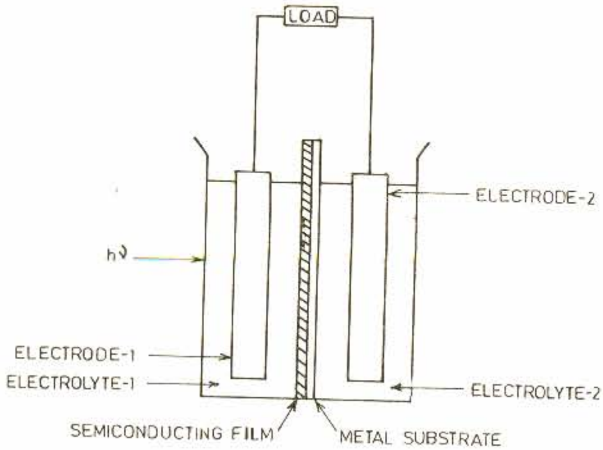

Fig. 1: Schematic of the septum cell

Cu-In alloy was done by heating the alloy 773K in H_2S atmosphere for 30 min. The film was further heat treated at 473 K in argon atmosphere for 30 min, and cooled to laboratory temperature in argon atmosphere.

The diffuse reflectance spectrum was recorded using Hitachi U 3400 UV-VIS-NIR spectrophotometer. X-ray diffraction patterns were taken employing JDX - 8030 X-ray diffraction unit using CuK_α radiation. The electrical resistivity of the films was measured by Agronic microohm meter model 53-C.

The $CuInS_2$ film was fixed in a groove in a PVC compartment with PVC solution. The film on the Ti substrate formed the septum separating the cell into two compartments. 1 *M* polysulphide solution was employed in the photoexposed chamber. Graphite was used as the counter electrode in the photo exposed side and either graphite, Pt, Cu or Cd was the electrode in the dark compartment with $CuSO_4$, $CuCl_2$ or $CdCl_2$ electrolyte depending on the electrode taken. A schematic of the septum cell is shown in Fig. 1.

RESULTS AND DISCUSSION

X-ray diffraction studies (Fig. 2) confirmed the formation of $CuInS_2$ films with additional peaks corresponding to Cu_9In_4 and Cu_4In. By the hot probe method, the film was found to be n-type. The thickness of the films was found to be around 1 μm by the weighing method. The cross-plane resistivity was estimated to be 10^4 ohm cm.

The septum cell of the following configuration C/Polysulphide/$CuInS_2$/Ti/Electrolyte solution/Electrode, was studied under an illumination of 60 mW cm^{-2}. Among all the combinations employed in the present study the highest output was obtained when Cd/$CdCl_2$ was used in the dark compartment.

The power characteristic of the septum cell employing 0.2 cm^2 area $CuInS_2$ film electrode is shown in Fig. 3. A V_α of 608 mV and a J_{sc} of 4 mA cm^{-2} were obtained under an illumination of 60 mW cm^{-2}. The fill factor and power conversion efficiency were 0.27 and 1.1% respectively. The internal resistance of the cells determined from the direct current method employing different load resistance, varied from 500 ohms to 750 ohms.

The septum cell output being higher than that of the PEC cell, for battery (such as Ni-Cd) charging applications, a multiple septum cell configuration will be preferable to a PEC cell array needing a larger number of cells.

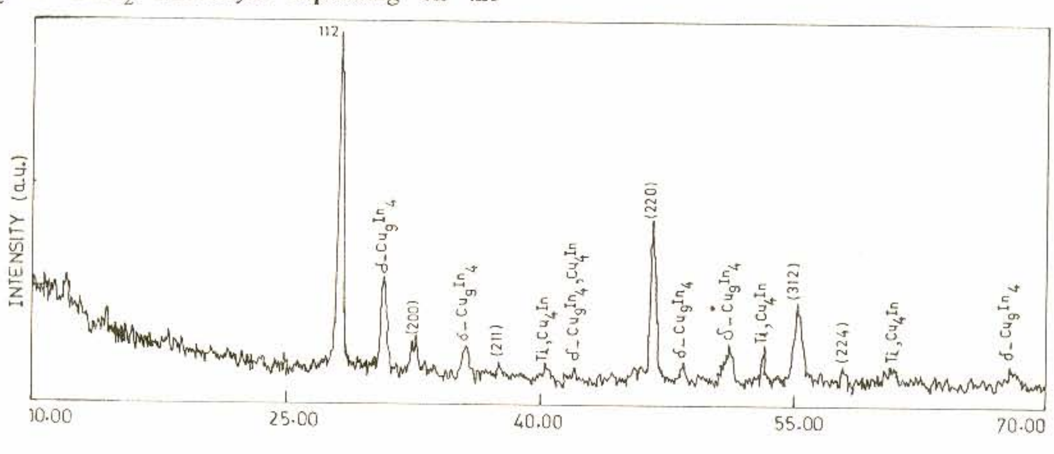

Fig. 2: X-ray diffraction pattern of the $CuInS_2$ film

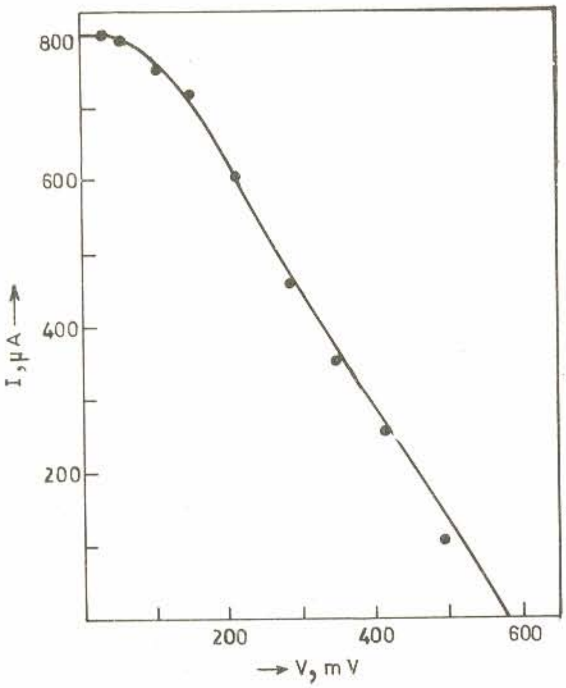

Fig. 3: Power characteristics of the $CuInS_2$ septum cell

CONCLUSION

The films obtained have been found to contain phases of Cu_9In_4 and Cu_4In, though they may be present in small quantities. However, the films show encouraging PEC properties. Efforts are under way to prepare phase pure $CuInS_2$ films with low resistivities and high visible light absorption through optimization of pre and post - deposition procedures.

TABLE I: Comparison of $CuInS_2$ PEC cell and septum cell

Configuration	V_L (mV)	J_{sc} (mA cm^{-2})	FF	η (%)
PEC cell	350	3.2	0.3	0.6
Septum cell	608	4.0	0.3	1.1

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