

Short Communication

On Electrochemical Photovoltaic Cells Formed With CuInS_2 Films

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A single crystal n- CuInS_2 -polysulfide system with 6.4% power conversion efficiency has been reported [1]. The system is stable (10 kC cm^{-2}) and shows no Se/S exchange at the interface; instead, some structural rearrangement takes place in polysulfide electrolyte: heterogeneous patches of Cu-deficient In-O were formed on a surface. A stable (42 kC cm^{-2}) single crystal CuInSe_2 -polysulfide system with 7.5% power conversion efficiency has also been reported [2]. The use of a polyiodide solution as an electrolyte is reported to improve the conversion efficiencies up to 12% for single crystal and polycrystalline CuInS_2 [3, 4] and to 9.7% for melt grown polycrystalline CuInS_2 [5]. The improved efficiency and stability are attributed to the surface modifications during use.

Results on the performance and stability of polycrystalline CuInS_2 in polysulfide and polyiodide electrolytes are reported. The CuInS_2 films were prepared by chalcogenization of Cu-In alloy films in an H_2S atmosphere [6]. The Cu-In alloy films were prepared by electrodeposition from 100 mM $\text{In}_2(\text{SO}_4)_3$ -75 mM CuSO_4 solutions. The potential applied was -1.2 V (SCE) and the current density was $\sim 9 \text{ mA cm}^{-2}$. The films were deposited in unstirred conditions at room temperature. As-deposited films were annealed in an $\text{H}_2\text{S} + \text{Ar}$ (50:50%) atmosphere for 30 min at $480 \pm 10 \text{ }^\circ\text{C}$, followed by dipping in hot ($50 \text{ }^\circ\text{C}$) KCN for 10 min and photoetching in dilute (10%) HCl for a few seconds.

The formation of Cu-In alloy and of CuInS_2 was confirmed by X-ray diffraction (XRD) patterns. In the case of Cu-In alloys the XRD peaks correspond to Cu-In, Cu_4In and Cu_7In . The single phase chalcopyrite structure was observed in the case of CuInS_2 films. Semiquantitative analyses showed that the composition of the CuInS_2 films is in stoichiometric ratio and uniform over the area. Figure 1 shows a scanning electron micrograph of a CuInS_2 covered surface.

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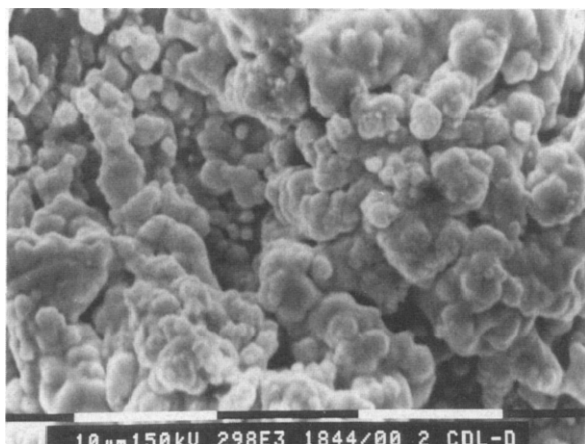


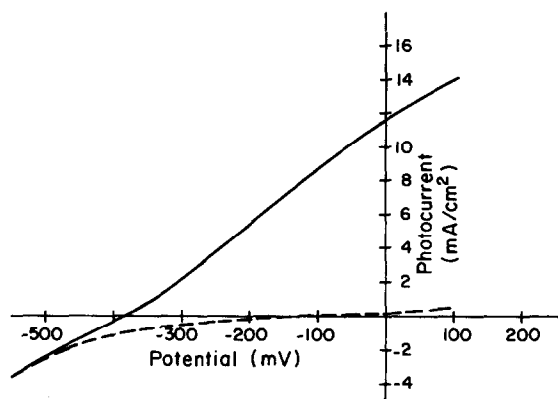
Fig. 1. Scanning electron micrograph of CuInS_2 film ($\times 2980$).

The photovoltaic activities of CuInS_2 films were tested in polysulfide (3 M NaOH-3 M Na_2S -4 M S) and polyiodide (2 M KI-0.02 M I-0.05 M CuI) solutions. The current-voltage characteristics were recorded with a Wenking-83 programmer and Omnigraph recorder-100. The light source was a 500 W tungsten-halogen lamp.

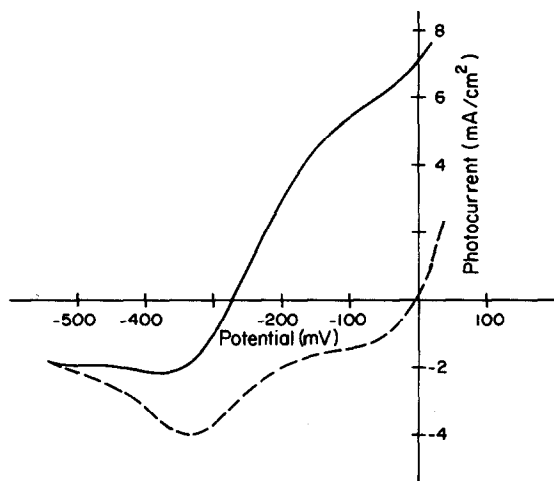
Figure 2 (a) and (b) shows the current-voltage characteristics of CuInS_2 in polysulfide and polyiodide electrolytes, respectively. A steep rise in the dark anodic current under reverse bias for the polysulfide electrolyte is due to the presence of In_2O_3 on the film surface [6]. In polyiodide, a large dark current is observed, which may be responsible for the low photovoltages. Table 1 compares the performance of CuInS_2 in both electrolytes. The photocurrent gradually increases and becomes steady after 3 - 4 min in both electrolytes. Similar behaviour in the case of a slurry painted CuInS_2 -polysulfide system is reported by Hodes *et al.* [7] which could be due to some changes in the electrolytes. The low fill factor obtained in polysulfide is a typical characteristic of the system. A somewhat larger fill factor was obtained in the polyiodide compared with the polysulfide electrolyte. The flat band potential, V_{fb} , in both cases was of nearly the same magnitude.

TABLE 1

Electrolyte	Short circuit photocurrent (mA cm^{-2})	Open circuit photovoltage (mV)	Fill factor (ff)	Power conversion efficiency (n%)	V_{fb} (SCE) (V)
Polysulfide	11.75	375	0.32	0.90	-0.550
Polyiodide	7.50	275	0.42	0.75	-0.540



(a)



(b).

Fig. 2. Current-voltage characteristics of CuInS_2 film electrode in: (a) polysulfide (3 M NaOH -3 M Na_2S -4 M S); (b) polyiodide (2 M KI -0.02 M I -0.05 M CuI) in the dark (---) and under illumination (—) of 100 mW cm^{-2} light intensity.

Figure 3 shows the stability of CuInS_2 electrodes in polysulfide and polyiodide electrolytes under a short circuit condition at 100 mW cm^{-2} light intensity. In the case of slurry painted and electroplated CuInS_2 layers, the stability tests under a short circuit condition showed a decay in photocurrent, while these systems were stable when operated under load or at maximum power output conditions [6, 7]. In our case, polysulfide first showed a rise and then a continuous decay in short-circuit photocurrent with time, while in the polyiodide electrolyte a relatively stable photo-

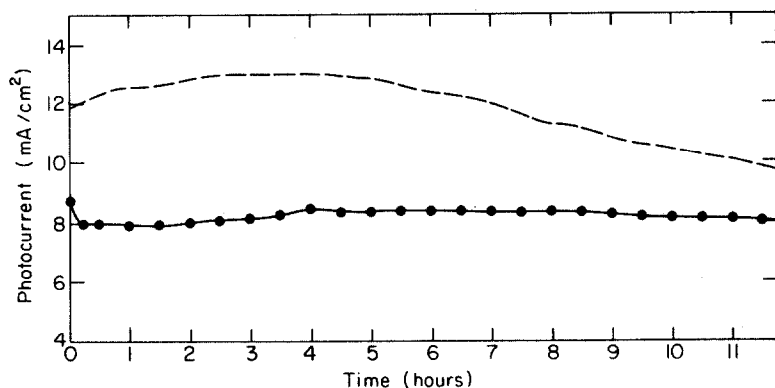


Fig. 3. Stability of CuInS_2 in (a) polysulfide (---); (b) polyiodide (—) electrolytes. Illumination intensity was 100 mW cm^{-2} (area 1 cm^2).

current was observed. The scanning electron micrographs showed no change in the microstructure after the stability test. However, definite conclusions about long term stability should not drawn from the above tests.

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