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Photoelectrochemistry of $CuIn_{11}S_{17}$

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Polycrystalline samples of $CuIn_{11}S_{17}$ have been prepared by the homogeneous precipitation technique. The electron probe microanalyses (EPMA) have shown the presence of excess sulphur with as-precipitated samples, which has been considerably reduced by subsequent annealing. From the reflectance measurements, the band gap has been determined to be 1.45 eV. The photoelectrochemical behaviour of n-$CuIn_{11}S_{17}$ has been studied in different redox electrolytes, namely, polysulphide, polyiodide, and ferro/ferricyanide, and the best photoresponse was observed with the polysulphide redox system. Photoetching in a polysulphide electrolyte at a strong anodic bias highly improves the photoresponse of this material. It has also been shown that our n-$CuIn_{11}S_{17}$ photoanode in electrochemical photovoltaic cell has a good stability at working conditions in a polysulphide solution. Finally, the future perspectives of the material have been briefly discussed.

1. Introduction

In recent years, considerable attention has been focused on developing polycrystalline semiconductor materials for their application in electrochemical photovoltaic cells. Of the emerging materials, Cu–In–S is one of the ternary systems which has received the most attention. In particular, the development of a simple and novel procedure to synthesize semiconductor materials is important from the economic point of view. Our group has recently developed a simple and novel homogeneous precipitation technique to prepare chalcopyrite and spinel ternary semiconductors, namely $CuInS_2$, $CuIn_5S_8$ and $CuIn_{11}S_{17}$. The simple preparation technique, as well as the suitable band gap of these semiconductors, make them potential candidates for photoelectrodes in electrochemical photovoltaic cells. The detailed preparation procedure and the preliminary results on photoelectrochemical behaviour have been previously reported. In the present paper, further studies on the photoelectrochemical behaviour of n-$CuIn_{11}S_{17}$ are presented.

2. Experimental details

A precursor powder for $CuIn_{11}S_{17}$ was prepared by taking advantage of homogeneous precipitation reactions which occur in aqueous solutions containing $Na_2S_2O_3$, $CuCl_2$, $InCl_3$ and CH_3COOH at 80° C. The details of this procedure have been reported elsewhere [1–4]. The powder samples were pressed into pellets and annealed in a nitrogen atmosphere. A change in annealing temperature brings about a change in the chemical composition and crystallinity and, in turn, in photoelectrochemical properties. Annealing temperature was fixed at 600° C in the present work. X-ray diffractograms of thus prepared samples showed the existence of a single phase of $CuIn_{11}S_{17}$ material which was identified by referring to the reported value [5]. The disc pellets were polished to 0.5 μm finish with alumina powder. Ohmic contacts were made with indium metal to the back surface of the pellet and a copper wire was attached to it with a silver paint.

The electrodes were chemically etched prior to each use for 60 sec in 1 : 1 : 2 concentrated HCl : concentrated HNO_3 : H_2O and then immediately rinsed with distilled water. Then, the electrodes were photoelectrochemically etched in a polysulphide solution (1 M NaOH, Na_2S and S) at 1.0 V with respect to SCE for 3 to 4 h followed by immersing them in KCN solution to remove any sulphur deposits formed during the photoetching process. All the electrolytes were prepared from analytical grade chemicals with a doubly distilled and deionized water.

A conventional, three-electrode and single-compartment cell was employed for all the electrochemical measurements. A Nikko Keisoku potentiostat with a potential sweeper and an X–Y–t recorder were used to study the current–potential characteristics. The light source was a tungsten–halogen lamp with a light intensity of $100\,mW\,cm^{-2}$. The reference electrode used was a saturated calomel electrode and unless otherwise specified, all the potentials are with respect to SCE.

The reflectance measurements were carried out with a Hitachi 330 spectrophotometer. X-ray diffraction data were obtained using a Rigaku Denki diffractometer with Cu$K\alpha$ radiation. SEM and energy dispersive analysis of X-ray fluorescence were performed on a Hitachi scanning electron microscope (H-8010) and Kevex-microanalyst 8000. Capacitance measurements were made with a frequency response analyser (NF electronic instruments, Model S-5720) coupled with an NEC PC 9801 computer. The copper and indium concentrations in solutions after the stability test were determined by the atomic absorption analyses using a Hitachi instrument. One standard was a

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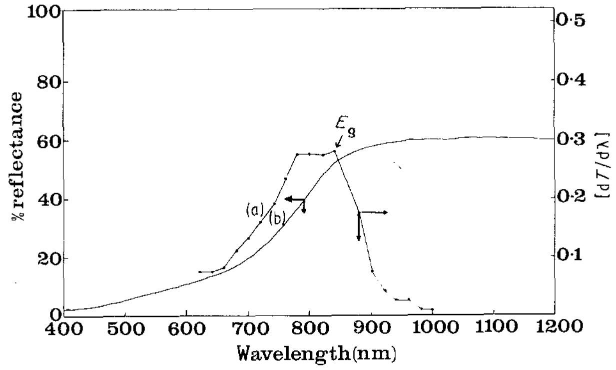

Figure 1 (a) Reflectance spectrum of n-$CuIn_{11}S_{17}$ powder samples. (b) A differential plot ($dT/d\lambda$) of the spectrum.

solution of 1000 μg In/ml (from $InCl_3$) in 0.5 M HNO_3. Standard solutions of indium were prepared from this solution. Similarly, another standard of known concentration of indium in polysulphide solution was also prepared. Atomic absorption analyses in these solutions indicate concentrations of indium less than the actual value compared to the standard solutions in HNO_3. The deviation was 37% (at 100 p.p.m. level) and 17% (at 20 p.p.m. level). Thus the reference standard solutions for calculations of indium concentrations in polysulphide that could result from photocorrosion of $CuIn_{11}S_{17}$ is that determined in polysulphide.

3. Results and discussion

3.1. Structure and composition

$CuIn_{11}S_{17}$ is a semiconductor with the defect spinel structure with $z < 0.75$ (where z is the ratio of cations to anions). The X-ray diffraction patterns of our samples prepared by the homogeneous precipitation technique are in good agreement with those reported by Ohachi and Pamplin on $CuIn_{11}S_{17}$ single crystals [5].

Table I shows the representative compositional data obtained by EPMA for $CuIn_{11}S_{17}$ samples before and after annealing in a nitrogen atmosphere at 600° C. These results indicate the presence of excess sulphur with the as-prepared samples which has been considerably removed by annealing. The excess sulphur present in the as-prepared samples is in accordance with the precipitation reactions as reported previously [1–4].

However, it is noted that the stoichiometry of the annealed samples indicates the presence of excess indium (see Table I). As reported by Hodes and Cahen for $CuInSe_2$ [6], if the ratio of Cu/In is less than unity, then it could correspond to n-type. Hence, we assume that the strong n-type behaviour of our $CuIn_{11}S_{17}$, as will be shown later, could correspond to the excess indium.

TABLE I EPMA data of $CuIn_{11}S_{17}$ (at %)

Element	Observed		Calculated
	As-precipitated	Annealed	
Cu	1.8	3.2	3.44
In	28.0	47.3	37.93
S	70.2	49.6	58.62

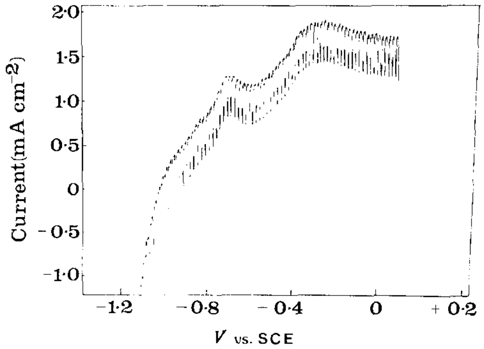

Figure 2 Current-potential characteristic of a chemically etched n-$CuIn_{11}S_{17}$ electrode under chopped light illumination (100 mW cm^{-2}) in 1 M polysulphide solution.

3.2. Reflectance spectrum

Fig. 1 shows the reflectance spectrum of $CuIn_{11}S_{17}$ powder samples taken from 1200 to 400 nm. A sharp absorption is noted in the spectrum in the range 960 to 680 nm. To determine the band gap of the semiconductor, a differential plot ($dT/d\lambda$) was made (Fig. 1), which gives a peak at 1.45 eV, corresponding to the band gap of the semiconductor. The calculated band gap is in good agreement with the value of 1.45 eV reported previously [1–4]. This confirms the existence of single-phase $CuIn_{11}S_{17}$.

3.3. Current–potential characteristics

In our previous paper we have shown that the [Cu]/[In] ratio in the starting solution for preparing $CuIn_{11}S_{17}$ powder is a critical factor in determining photoelectrochemical properties and that photoelectrochemical etching (photoetching) in a polysulphide solution is effective for enhancing the photocurrent [4]. All the results on photoelectrochemical properties given in that paper were those obtained in a polysulphide solution. In the present paper more detailed description of the photoelectrochemical properties will be given.

First, current–potential properties in a polysulphide solution has been examined in connection with the photoetching effect. Fig. 2 shows a typical current–potential curve of a $CuIn_{11}S_{17}$ electrode without the photoetching treatment under chopped illumination. All samples prepared exhibited anodic photoresponse, suggesting n-type behaviour. Photocurrent values as well as anodic dark current values vary considerably

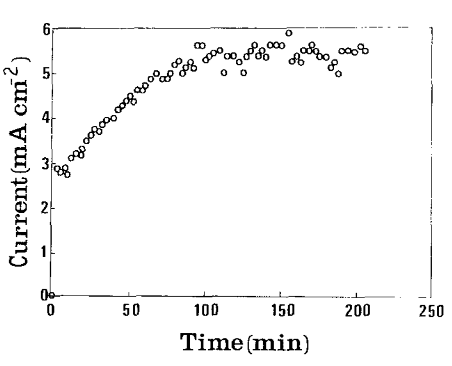

Figure 3 Photocurrent–time characteristics of a $CuIn_{11}S_{17}$ electrode during the photoetching process in polysulphide solution at +1.0 V with respect to SCE.

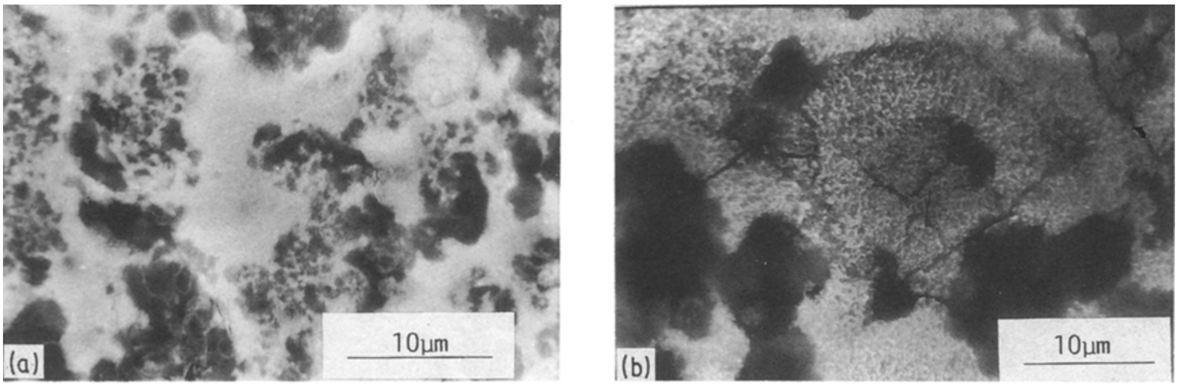

Figure 4 Secondary electron images of (a) chemically etched, (b) photochemically etched $CuIn_{11}S_{17}$ surfaces.

from sample to sample. This may indicate that sample preparation conditions significantly affect the chemical composition of the precipitates, e.g. the existence of an excess sulphur, Cu/In ratio, etc.

Fig. 3 shows the photocurrent–time characteristic of an n-type $CuIn_{11}S_{17}$ electrode at 1.0 V in a polysulphide solution. As seen from this, the photocurrent increases with time and saturates. This process is usually referred to as a photoetching process. Such an increase in anodic photocurrent has been reported with other compound semiconductors (CdSe, $CdIn_2S_4$, etc.) in inert electrolytes [7]. It is interesting to note that a polysulphide solution, which has been reported to stabilize most of the chalcogenide semiconductors against photoanodic dissolution, is an effective photoelectrochemical etchant for n-$CuIn_{11}S_{17}$. Our finding was that such a beneficial process was observed only in a polysulphide solution among all the electrolytes used which includes a few inert electrolytes. This is a unique feature of this electrode and a clear indication of the occurrence of the selective etching process at the n-$CuIn_{11}S_{17}$ electrode surface in a polysulphide solution.

Fig. 4 shows scanning electron micrographs of (a) chemically and (b) photoelectrochemically etched n-$CuIn_{11}S_{17}$ surfaces. A characteristic etch pattern is observed with a photoelectrochemically etched sample.

It is clear from Fig. 3b that the surface area was increased due to the photoetching process. This confirms that the photoetching process in a polysulphide solution brings about the selective photoanodic dissolution of $CuIn_{11}S_{17}$.

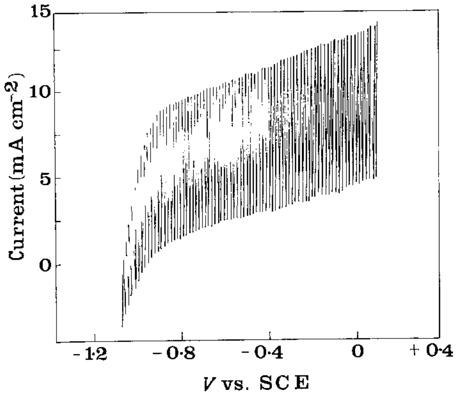

Figure 5 Current–potential characteristics of an n-$CuIn_{11}S_{17}$ electrode under chopped illumination ($100\,mW\,cm^{-2}$) in 1 M polysulphide solution after photoetching.

It is important to note that such a selective photoetching which is responsible for a substantial improvement in anodic photocurrent occurs only when performed at highly anodic potentials such as 1.0 V. This is in accordance with the stability as will be shown later.

As a result of effective photoetching, photoelectrochemical behaviour of an n-$CuIn_{11}S_{17}$ electrode is improved as shown in Fig. 5. No decay of photocurrent with time was observed. Also, the photoetched samples show about a ten-fold increase in photocurrent compared to the unetched samples, which is a substantial effect of photoetching. This observation is unique with this material. However, the electrodes photoetched in polysulphide solution do not show good photoresponse in other redox systems as discussed below.

A current–potential curve of an n-$CuIn_{11}S_{17}$ electrode in 0.5 M KCl solution is shown in Fig. 6. The same curve was obtained in Na_2SO_4 solution. It is interesting to note that photocurrents in these electrolytes are much smaller than those in a polysulphide solution, although photons with wavelengths shorter than 500 nm are absorbed by a coloured polysulphide electrolyte. It is an anomalous behaviour that the saturation photocurrent, which usually is a photon flux-limited process, varies by changing the redox electrolytes used. The photocurrent decays rapidly with time. This may be ascribed to the covering of the electrode surface with sulphur and/or indium hydroxide formed by the photoanodic dissolution.

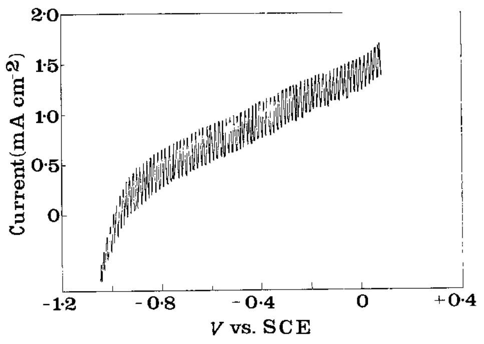

Figure 6 Photoelectrochemical behaviour under chopped white light illumination ($100\,mW\,cm^{-2}$) of an n-$CuIn_{11}S_{17}$ electrode in 0.5 M KCl solution.

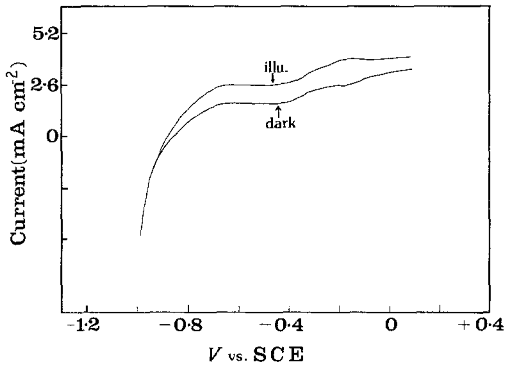

Figure 7 Current–voltage curves of n-$CuIn_{11}S_{17}$ electrode (in the dark and under illumination) in 0.1 M $Fe(CN)_6^{4-/3-}$ redox couple.

Next, the behaviour in two redox electrolytes, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ (Fig. 7) and I^-/I_3^- (Fig. 8), which are known as stabilizing electrolytes for some semiconductor photoelectrodes, was examined. A polyiodide redox system containing Cu^{2+} ions has been reported to be very efficient for an n-$CuInSe_2$-based photoelectrochemical cell [8]. But unexpectedly, the photoelectrochemical behaviour of our n-$CuIn_{11}S_{17}$ electrodes was found to be poor in this redox system, as shown in Fig. 8. The photocurrent values are nearly the same as those in the above-mentioned inert electrolytes. A marked difference is their slow photoresponse. When measured by a lock-in technique by a chopped light with a frequency of 80 Hz, a negligibly small photocurrent was observed. Such a slow photoresponse may be ascribed to an interaction of reducing agents, $Fe(CN)_6^{3-}$, I^-, with surface states, which are assumed to exist at the electrode surface with high densities. Samples annealed at higher temperatures, e.g. at 800° C do not show such a slow photoresponse in these electrolytes, which will be shown in our forthcoming paper.

3.4. Stability studies

The electrode stability against the photocorrosion is the most crucial factor for constructing photoelectrochemical cells for practical use. Our stability test was carried out only in a polysulphide electrolyte, as other electrolytes used in this study were not found to be good candidates for our n-$CuIn_{11}S_{17}$-based cell, as was shown in the previous section. It must also be remembered, however, that even in the polysulphide solution, n-$CuIn_{11}S_{17}$ electrode dissolved anodically under the strong anodic polarization. But as for the stability, the behaviour at more negative electrode potentials is of practical importance because the redox potential of the polysulphide electrolyte is about -0.8 V with respect to SCE. Based on this consideration, we checked the photoelectrochemical stability in the following way.

Initially, the electrode was biased at 0 V for 10 to 11 h under illumination. A total electric charge of 100 C cm^{-2} was passed during this process. The current increased gradually in the first 3 to 4 h and then was stabilized. The electrode potential was changed to -0.8 V in a fresh polysulphide solution, which is near the working potential of a photoelectrochemical cell employing a polysulphide electrolyte, and the above electrolysis experiment was repeated. Finally, the same process was repeated but at 0.2 V. After electrolysis, the indium content in each solution was analysed by atomic absorption spectroscopy. Stability calculated from the indium content obtained by assuming that the photocorrosion reaction is expressed as follows

$$CuIn_{11}S_{17} + 34h^+ \rightarrow Cu^+ + 11In^{3+} + 17S$$

has shown that n-$CuIn_{11}S_{17}$ has 97% stability against the photocorrosion. However, for a blank test (just immersing an electrode in a polysulphide solution for the same duration), an approximately equal concentration of indium was detected, which suggests that the corrosion process observed may be of a chemical nature, not a photoelectrochemical one. It is, therefore, concluded that our n-$CuIn_{11}S_{17}$ photoanode has a good stability at working conditions in a polysulphide solution.

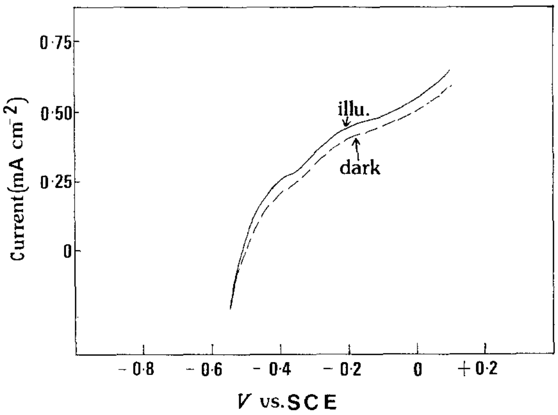

Figure 8 Current–voltage curves of n-$CuIn_{11}S_{17}$ electrode (in the dark and under illumination) in 0.1 M polyiodide electrolyte.

The present results, as well as our previous results, indicate that n-$CuIn_{11}S_{17}$ could be a novel semiconductor for use in photoelectrochemical cells. The unique behaviour of this material opens the way for further research in photoelectrochemistry. The interesting and unique results must be viewed with respect to its crystal structure and other surface properties in detail. The related studies are in progress. In subsequent publications, we will discuss the effect of annealing at different temperatures on its PEC behaviour, and also the photoetching processes of $CuIn_{11}S_{17}$ occurring with different solutions, which can be anticipated from the present results depending on the various experiments.

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