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# Electrodeposition of Copper Indium Sulfide Films From Organic Solutions

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## Abstract

We report on organic solutions of  $\text{CuCl}_2$ ,  $\text{InCl}_3$ , and elemental sulfur for electrodepositing  $\text{CuIn}_x\text{S}_y$  films.  $\text{CuInS}_2$  and  $\text{CuInSe}_2$  are promising solar cell materials; our work on  $\text{CuInS}_2$  prefaces planned work on plating  $\text{CuInSe}_2$  from nonaqueous solvents. Two promising solvent systems are (1) mixed propylene carbonate and water and (2) mixed ethylene glycol, propionic acid, and water (Engelken et al., 1988). Gray-brown films of  $\text{CuIn}_x\text{S}_y$  (nominally  $\text{CuInS}_2$ ) have been plated from both baths. Major problems include (1) reduction of  $\text{Cu}^{+2}$  to Cu and  $\text{Cu}_x\text{S}$  by the solvent at high temperatures ( $T > 100^\circ\text{C}$ ), hence depleting  $\text{Cu}^{+2}$ , (2) poor adherence/uniformity, (3) controlling stoichiometry, and (4) sluggish indium deposition. The paper will discuss our routes to solving these problems and present film data.

## Introduction

$\text{CuInS}_2$  is a ternary III-VI<sub>2</sub> compound semiconductor with a direct energy gap (bandgap) of 1.5 eV. It has potential as a low-cost photovoltaic material for the fabrication of solar cells, although it has yet to demonstrate the device effectiveness of its sister compound  $\text{CuInSe}_2$ . Electrodeposition of  $\text{CuInS}_2$  is preferred over some other deposition techniques because it is cost effective (requiring very simple and inexpensive materials and equipment) and is easy to monitor and control.

A significant amount of research has been performed over the last decade on the electrodeposition and characterization of  $\text{CuInSe}_2$ , (Pern et al., 1988; Guillen and Herrero, 1994; Fritz and Chatziagorastou, 1994; Molin et al., 1994a; Molin et al., 1994b), but there has been little work and very few publications (Fearheiley et al., 1993; Cattarin, Dietz and Lawerenz, 1994; Cattarin, Guerriero et al., 1994;) on the photoelectrochemistry of  $\text{CuInS}_2$ .

The work reported herein focused on the electrodeposition of polycrystalline  $\text{CuIn}_x\text{S}_y$  films at temperatures near  $100^\circ\text{C}$ . Several organic solvents were investigated. The best results were obtained with mixed propylene carbonate and water baths and mixed ethylene glycol, propionic acid, and water baths pre-saturated with elemental sulfur and containing  $\text{CuCl}_2$ ,  $\text{InCl}_3$ , and KCl. A discussion of these results obtained is presented below.

## Materials and Methods

The apparatus used in the experiments consisted of

an EG&G Princeton Applied Research Model 362 scanning potentiostat, a Hewlett Packard 7046-B x-y-t recorder, Pyrex beakers, and a Teflon beaker cover with appropriate holes for the insertion of electrodes. For voltammetric analysis and actual deposition, the classical three electrode approach was used. A 15 cm x 1.0 cm Poco graphite strip was used as anode and a 5.0 cm x 3.0 cm piece of Donnelly ITO (indium tin oxide-coated glass) as cathode. A saturated Ag/AgCl reference electrode (Fisher Scientific) was also used. Approximately half of the electrode area ( $\approx 7\text{ cm}^2$ ) was immersed in the solution. Other supplies and reagents used included Aldrich propionic acid (PA), Fluka propylene carbonate (PC), Fisher sodium citrate, and Alfa/Johnson Matthey sulfur, ethylene glycol (EG), triethylene glycol (Tri-EG),  $\text{CuCl}_2$ ,  $\text{CuNa}_2\text{EDTA}$ ,  $\text{InCl}_3$ , and KCl.

A Rigaku D-MAX x-ray diffractometer was used to obtain a plot of intensity vs. goniometer angle ( $2\theta$ ). The process gives an indication of the relative crystallinity of the film samples. A Perkin-Elmer Lambda 19 UV/VIS/NIR spectrophotometer was used for optical absorbance vs. wavelength spectroscopy.

Several different deposition voltages were investigated in order to find the value at which the most photoactive and probably most stoichiometric films were obtained. The deposition range was between -0.6 V and -1.4V, and the deposition time ranged from 10 to 40 min. (depending upon the temperature). The voltage was swept from +0.6 V to -1.4 V (Ag/AgCl) during the cyclic (photo) voltammograms. The deposition temperature (T) ranged from  $80^\circ\text{C}$  to  $120^\circ\text{C}$  ( $113\text{-}120^\circ\text{C}$  being the melting point of sulfur). The films were rinsed either in iso-

propanol or water and allowed to dry at room temperature.

Two different solvent mixtures (with several combinations within each) were used as the electrolyte. The different mixtures used were (a) propylene carbonate and water, and (b) propionic acid, ethylene glycol or triethylene glycol, and water. Elemental sulfur was saturated in the organic solvents at  $T > 113^\circ\text{C}$  prior to the addition of water. The bath was cooled and 0.01M  $\text{InCl}_3$ , 0.001 M  $\text{CuCl}_2$ , and 0.05 M KCl (already dissolved in the required water) were added to it. The propylene carbonate and the propionic acid/triethylene glycol-based baths contained 0.015 M sodium citrate, which acted as a metal ion complexing agent. The propionic acid/ethylene glycol-based baths did not contain complexing agents; the pH of the baths ranged between 2.0 and 2.7. The amount of water in the propylene carbonate baths was varied from 5% to 33% by volume, while 15 ml  $\text{H}_2\text{O}$  was always used in the propionic acid/glycol baths. Water was added to the baths to increase the indium salt solubility, indium ion concentration and, thus, the electrical current level. Although the addition of water decreases the elemental sulfur solubility, it aids not only in the dissociation of the ionic salts but also the kinetics of electron transfer.

### Results and Discussion

The propylene carbonate (PC)/water mixture that produced the best results (most uniform and photoactive films) was composed of 100 ml PC, 0.2 M S, 0.01 M  $\text{InCl}_3$ , 0.001 M  $\text{CuCl}_2$ , 0.05 M KCl, 0.015 M sodium citrate, and 10 ml  $\text{H}_2\text{O}$ . The solution was pale yellow in appearance. Thin gray-brown films of  $\text{CuIn}_x\text{S}_y$  were deposited on ITO between -1.0 V and -1.5 V. The films were greenish in tint at less negative potentials, indicating the presence of CuS. Some mixed green-brown films were also deposited. If the films were allowed to deposit for too long of a time, they would become too thick and flake off within the solution. The time it took for the films to grow "too thick" was a function of the temperature of the bath, concentrations of the ions/electrolytes (especially water), and hence the electrical current level(s).

Figure 1 exhibits an x-ray diffraction (XRD) plot for a thin brown film deposited from a propylene carbonate/water bath a -1.4 V for 10 min at  $100^\circ\text{C}$ . The film exhibits both  $\text{CuInS}_2$  (Fig. 1a) and CuS (Fig. 1b) XRD structures. Figure 2 presents a cyclic voltammogram that was run on a comparable solution containing only  $\text{InCl}_3$ . No distinct deposition structures are seen. A sharp rise near -1.0 V corresponding to metallic indium plating is observed and a very small corresponding stripping peak is observed at -0.8 V (Fig. 2a). With the addition of 0.001 M  $\text{CuCl}_2$  and 5 ml  $\text{H}_2\text{O}$  to the solution, a large

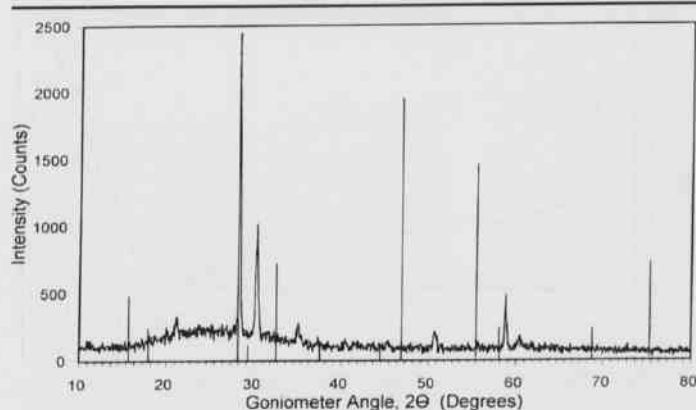


Fig. 1a. X-ray diffraction (XRD) data for a  $\text{CuIn}_x\text{S}_y$  film electrodeposited onto an ITO-coated glass from a mixed propylene carbonate and water bath. Vertical lines denote standard powder diffraction file card peaks for  $\text{CuInS}_2$  (38-777).

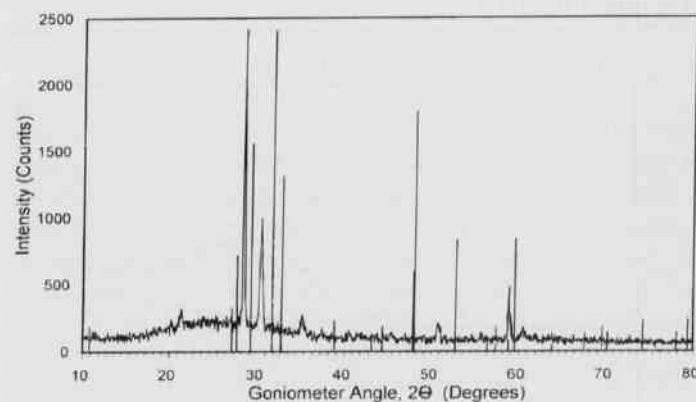


Fig. 1b. XRD data for the same film as in Fig. 1a, with the vertical lines denoting standard powder diffraction file card peaks for CuS (6-464). The result indicates the presence of both  $\text{CuInS}_2$  and CuS phases in the film.

metallic Cu deposition peak and smaller stripping peaks appear (Fig. 2b).

The major problems faced were (a) poor adherence/uniformity of the film, (b) controlling stoichiometry (green CuS, brown  $\text{Cu}_{2-x}\text{S}$ , and golden  $\text{In}_2\text{S}_3$  patches were sometimes present), (c) sluggish indium deposition (as evidenced by the presence of a greenish CuS color in/on the film even at highly negative deposition potentials), and (d) browning of the solution at higher temperatures due to the reducing properties of the solvent and spontaneous formation of Cu-S and/or Cu-In-S precipitates which depleted the copper ions.

The results obtained with propionic acid (PA), triethylene glycol (Tri-EG), and water mixtures were not very encouraging. Tri-EG, a very strong reducing agent at high temperatures, reduced  $\text{Cu}^{2+}$  to Cu and  $\text{Cu}_x\text{S}$ , hence

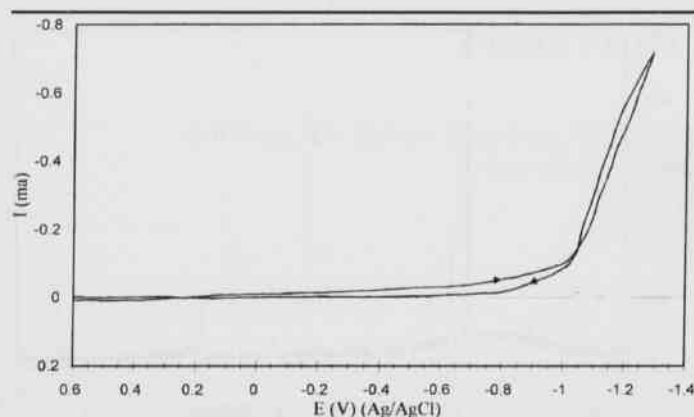


Fig. 2a. Cyclic voltammogram (I-V plot) showing In plating and stripping from a mixed propylene carbonate and water bath (presaturated with elemental S) on an ITO-coated glass.

Scale: X axis: 0.2 V/in                      Y axis: 0.2 mA/in  
 Scan rate: 5 mV/s                          Range: +0.6 V to -1.3 V  
 Temperature: 95°C

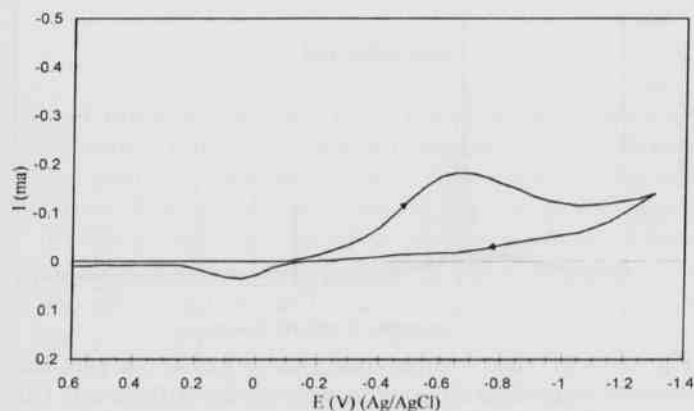


Fig. 2b. Cyclic voltammogram (I-V plot) showing primarily the Cu waves from a mixed propylene carbonate and water bath (presaturated with elemental S) on an ITO-coated glass substrate.

Scale: X axis: 0.2 V/in                      Y axis: 0.2 mA/in  
 Scan rate: 5 mV/s                          Range: +0.6 V to -1.3 V  
 Temperature: 95°C

depleting  $\text{Cu}^{2+}$ . Even though the ratio of Cu:In was 1:10, the films deposited were Cu-rich, as will be evident from the x-ray diffractometry plots presented later. The absence of peaks during XRD in most of the films indicated their amorphous nature. Often, a white, foamy, polymer-like film was observed on the film/substrate; this was probably an organic product.

A mixture of PA, ethylene glycol (EG), and  $\text{H}_2\text{O}$  in the ratio 8:1:1 by volume has produced the best results to date. Gray-brown films were electrodeposited from the above mixture in the voltage range of -0.5 V to -0.8 V.

XRD of a uniform brown film electrodeposited at -0.8 V for 30 min. at 90°C produced matches with the standard powder diffraction file lines for two different phases of  $\text{CuIn}_x\text{S}_y$  ( $\text{CuInS}_2$  and  $\text{CuIn}_{11}\text{S}_{17}$  (Fig. 3)).  $\text{CuS}$  was not indicated at all in this film. An optical spectrophotometer plot of absorbance vs. wavelength for another film deposited at -0.7 V for 30 min. at 100°C shows a sharp rise near 800 nm, which correlates with the wavelength associated with  $\text{CuInS}_2$ 's bandgap of 1.5 eV (Fig. 4). Voltammetry of the bath exhibits three cathodic deposition structures at -0.15 V ( $\text{Cu}_x\text{S}$ ), -0.55 V ( $\text{CuInS}_2$ ), and -1.0 V (beginning of metallic indium plating). Indium and copper stripping peaks are also observed (Fig. 5a). *In-situ* photocurrents were observed when photovoltammetry was performed at room temperature. Their magnitude was the largest from -0.6 V to -0.8 V, which corresponds to the  $\text{CuInS}_2$  plating region (Fig. 5b). At high temperatures the magnitude of the background currents was so large that the photocurrents could not be discerned.

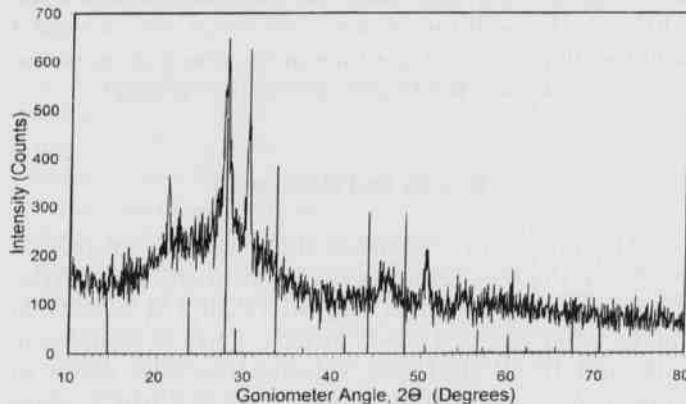


Fig. 3. XRD data for a  $\text{CuIn}_x\text{S}_y$  film electrodeposited from a mixed propionic acid, ethylene glycol, and water bath at -0.8 V. The vertical lines denote standard powder diffraction file card peaks for  $\text{CuIn}_{11}\text{S}_{17}$  (34-797). The result indicates the presence of both  $\text{CuIn}_x\text{S}_y$  and  $\text{CuS}$  phases in the film.

Note that the photocurrents increase substantially at the shoulder of the second cathodic "wave" beginning at -0.55 V. Note that this wave exhibits typical diffusion peaking and limiting behavior, as does the  $\text{Cu}_x\text{S}$  plating wave at -0.15 V. All indications are that this is where the underpotential plating of indium commences positive of the metallic indium plating potential ( $\approx -1.0$  V) due to the activity reduction provided via chemical reaction with the Cu and S to form Cu-In-S, In-S, and Cu-In phases. Since the indium ion concentration is much larger than that of copper, one might expect the indium plating to either "track" the cathode surface sulfur or copper concentrations and diffusion-limited currents or discharge fluxes,

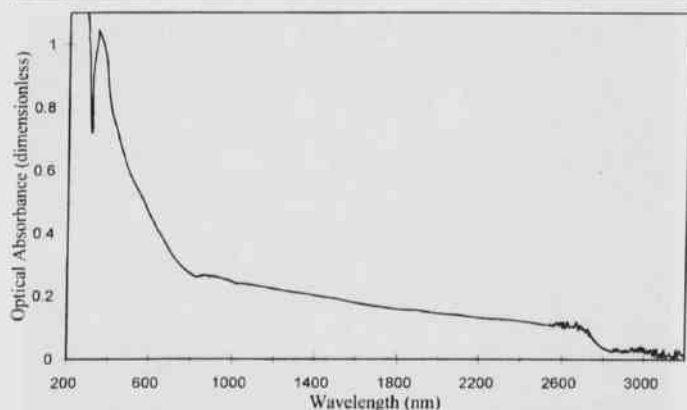


Fig. 4. Plot of optical absorbance vs. wavelength for a film electrodeposited from a mixed propionic acid, ethylene glycol, and water bath at -0.7 V. The absorption edge near 800 nm corresponds to  $\text{CuInS}_2$ 's 1.5 eV bandgap.

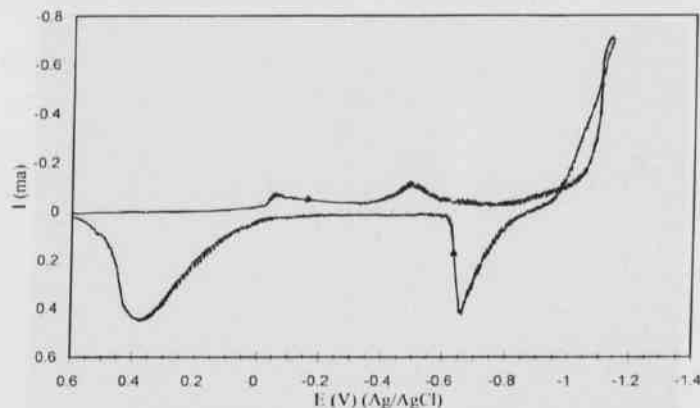


Fig. 5b. Cyclic photovoltammogram (I-V plot) showing the Cu,  $\text{CuInS}_2$ , and In waves for the same bath as in Fig. 5a.

Scale: X axis: 0.2 V/in      Y axis: 0.1 mA/in  
 Scan rate: 2 mV/s      Range: +0.6 V to -1.4 V  
 Temperature: 22°C (room T)

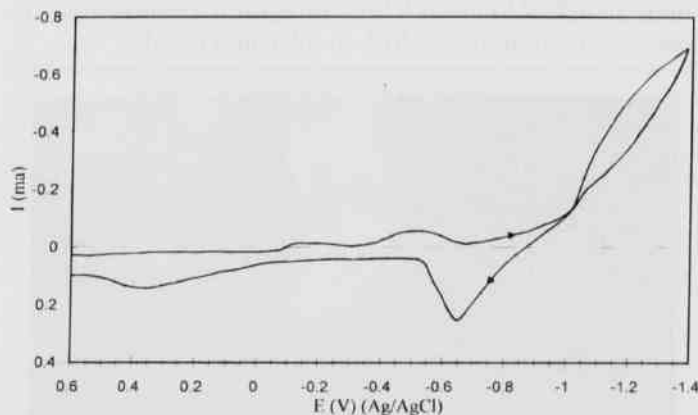


Fig. 5a. Cyclic voltammogram (I-V plot) showing the Cu,  $\text{CuInS}_2$ , and In waves for a solution containing 120 ml ethylene glycol (presaturated with 0.2 M S), 15 ml propionic acid,  $10^{-3}\text{M}$   $\text{CuCl}_2$ ,  $10^{-2}\text{M}$   $\text{InCl}_3$ ,  $5 \times 10^{-2}\text{M}$  KCl, and 15 ml  $\text{H}_2\text{O}$ .

Scale: X axis: 0.2 V/in      Y axis: 0.2 mA/in  
 Scan rate: 2 mV/s      Range: +0.6 V to -1.4 V  
 Temperature: 22°C (room T)

with the smaller set probably the rate/discharge determining factor(s). For example, if the surface sulfur concentration and/or reaction rate (with the metals) were sufficiently low, one might expect the In to plate only in the presence of Cu or S atoms to form  $\text{CuInS}_2$ , with excess Cu existing as a separate phase. The Gibb's free energy associated with Cu-In metallic alloys might support some underpotential plating of In in the presence of Cu but not as facilely as in the presence of both Cu and S. In this case one might obtain a  $\text{CuInS}_2:\text{Cu}_x\text{In}_y$  mixed phase with grains of  $\text{CuInS}_2$  or closely related phases appearing in X-ray diffractometry.

Figures 6a and 6b exhibit scanning electron micrographs of a typical  $\text{CuIn}_x\text{S}_y$  sample at two different magnifications (5 kX and 20 kX, respectively). Note the distinct grains roughly 0.2 to 0.5 microns in breadth. Table 1 exhibits the corresponding energy dispersive X-ray (EDX) analysis after a portion of the film was removed from the ITO-on-glass substrate by the "tape-and-peel" method to avoid interference from the indium and other elements in the ITO. Note that the film is both a bit copper rich and sulfur deficient, as is not surprising because the copper is more facile in plating than the indium, and the copper is able to plate by itself at the -0.6 to -1.0 V range used for deposition (i.e. Cu does not require the presence of In or S to plate in an "underpotential" mode even though In does require at least one of the other two elements to plate at this voltage). Note that the  $\text{Cu}_{0.4163}\text{In}_{0.1979}\text{S}_{0.3859}$  can be expressed as  $\text{Cu}_{0.1930}\text{In}_{0.1930}\text{S}_{0.3859}:\text{Cu}_{0.2233}\text{In}_{0.0049}$ ; that is  $\text{CuInS}_2$  with excess Cu metal since the S atomic percentage is almost twice that of In, as in  $\text{CuInS}_2$ . Similar data for another  $\text{CuIn}_x\text{S}_y$  film is shown in Figures 7a, 7b, and Table 2 with the same trends occurring, and a possible mixture composition of  $\text{Cu}_{0.1366}\text{In}_{0.1366}\text{S}_{0.2732}:\text{Cu}_{0.3404}\text{S}_{0.1132}$  probably indicates a mixture of  $\text{CuInS}_2$ ,  $\text{Cu}_x\text{S}_y$ , and Cu. Cu-rich  $\text{CuIn}_x\text{S}_y$  phases tend to be p-type, which is consistent with the predominantly cathodic photocurrents observed during photovoltammetry.

Note that the photocurrent magnitudes increase again as the currents begin to increase near the metallic In wave near -1.0 V as more indium begins to be discharged due to the increasing electrical energy available. It is likely that additional  $\text{CuInS}_2$  and  $\text{In}_x\text{S}_y$  (versus solely non-photosensitive Cu or  $\text{Cu}_x\text{S}$ ) are being plated in this region; that is, the film is losing its gross Cu-richness and

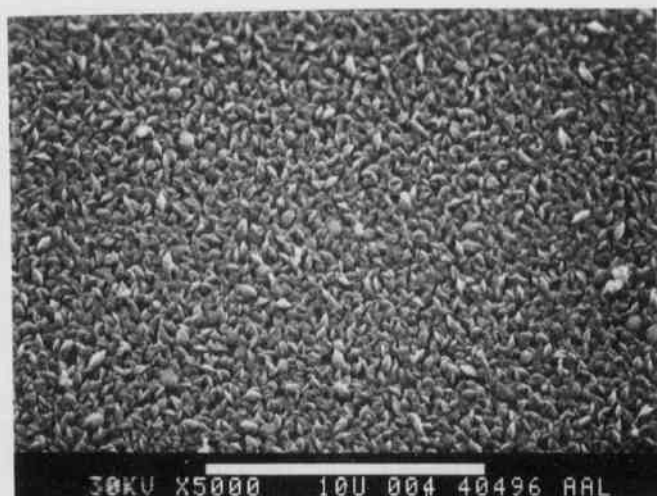


Fig. 6a. Scanning electron microscopy (SEM) data for a CuInS<sub>2</sub> film electrodeposited from a mixed propionic acid, ethylene glycol, and water bath at -0.7 V. The 5kX magnification enables one to observe the uniform nature of the film.

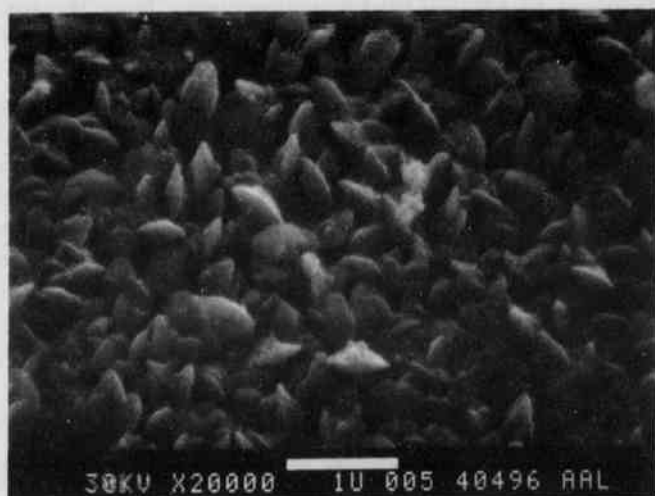


Fig. 6b. SEM data for the same film as in Fig. 6a, with a 20kX magnification factor that clearly shows the polycrystalline nature of the film.

p-type nature and approaching intrinsicity.

The films deposited from this solvent were relatively uniform (as compared to those from propylene carbonate and other baths) and adherent. There was no chemical degradation of the solvent at high temperatures. Effective indium plating was observed and CuCl<sub>2</sub> did not convert to Cu<sub>x</sub>S in solution since EG is not a very strong reducing agent and H<sup>+</sup> ions in the bath tend to redissolve any suspension that is formed. The uniformity of the films might

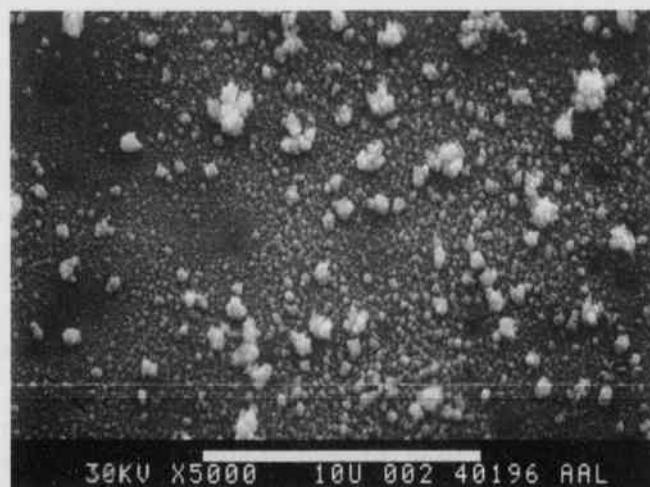


Fig. 7a. SEM data for a CuIn<sub>x</sub>S<sub>y</sub> film electrodeposited from a mixed propionic acid, ethylene glycol, and water bath at -0.6 V. The 5kX magnification enables one to observe the nonuniformities in the film crystals.



Fig. 7b. SEM data for the same film as in Fig. 7a, with a 20kX magnification factor.

be further improved by reducing the reaction rate with the help of complexing agents.

### Conclusions

Gray-brown polycrystalline CuIn<sub>x</sub>S<sub>y</sub> (nominally CuInS<sub>2</sub>) films were successfully electrodeposited from mixed propylene carbonate and water baths and propionic acid, ethylene glycol, and water baths. The films, especially with the latter bath, were uniform and adhered well to the surface of the ITO. *In-situ* photocurrents were

Table 1

Energy dispersive X-ray (EDX) analysis for the film in Figure 6a.

KV = 10.0      TILT = 30.0      TKOFF = 28.4  
BKG PT1 = 4.2      BKG PT2 = 7.0

	CONCENTRATION		
	WT%	AT%	%S.E.
CU L	42.98	41.63	2.24
S K	20.10	38.58	1.35
IN L	35.93	19.79	2.50

Table 2

Energy dispersive X-ray (EDX) analysis for the film in Figure 7a.

KV = 10.0      TILT = 30.0      TKOFF = 28.4  
BKG PT1 = 4.2      BKG PT2 = 7.0

	CONCENTRATION		
	WT%	AT%	%S.E.
CU L	51.91	47.70	2.12
S K	21.22	38.64	1.50
IN L	35.93	13.66	3.50

observed, and the best voltage for the deposition of the films was observed to be between -0.6 V and -0.8 V (Ag/AgCl). Future work will involve further improvement in the uniformity of the films, attempts to obtain perfectly stoichiometric CuInS<sub>2</sub> films, and electrodeposition of CuInSe<sub>2</sub> films for which this process is a precursor. We plan to form n-CdS/p-CuInX<sub>2</sub> (X = S, Se) solar cells completely through high temperature electrodeposition processes as part of our work in the Arkansas Advanced Photovoltaic Materials Research Center under the AR/NASA EPSCoR program.

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