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Characterization of cadmium-doped copper indium sulphide films prepared by a two-step technique

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Abstract

Cadmium-doped $CuInS_2$ films were prepared from electroless-deposited cadmium-doped films of CuIn alloy in H_2S gas at 550 °C. The compositional, morphological, and photoelectrochemical properties of both doped and undoped films were examined and compared.

Introduction

The ternary semiconductors $CuInSe_2$ and $CuInS_2$ have been considered to be promising photoanodes for photoelectrochemical (PEC) cells due to their high absorption coefficients and direct band-gaps lying in the optimum range for solar energy conversion. While the reported [1] efficiency for a single-crystal-based n-$CuInS_2$ PEC cell is about 6.4%, the polycrystalline-based cells have been found to be comparatively efficient, one of them having an exceptional efficiency of 9.7% [2]. Thin-film-based PEC cells are not so efficient, however, having a maximum reported efficiency of ~2% [1].

One of the recommended methods for the preparation of $CuInS_2$ and $CuInSe_2$ thin films is a two-step procedure involving, first, preparation of CuIn alloy and, second, conversion to the corresponding chalcogenide. Methods of producing CuIn alloy have included: vacuum evaporation [3]; molecular beam deposition [4]; sputtering [5]; electrodeposition [6–11]; electroless deposition [12, 13].

Doping n-$CuInS_2$ with cadmium or indium has been found [14] to improve the PEC characteristics of the material. While cadmium doping has been carried out for a single crystal [15], films have only been prepared by introducing excess indium, i.e., In/Cu > 1 [7, 16]. It was therefore, considered interesting to prepare and study $CuInS_2$ films doped with cadmium.

The formation of n-$CuInS_2$ thin films by sulphurization of an electroless-deposited CuIn alloy film has been discussed previously [13]. In this paper, we report the preparation of a cadmium-doped CuIn alloy film by an electroless technique and the conversion of this film to n-$CuInS_2$ by sulphurization. The

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resulting film is characterized by X-ray diffraction (XRD) and Auger electron spectroscopic (AES) methods. The PEC characteristics of the film are also discussed.

Experimental

For the electroless deposition of cadmium-doped and undoped CuIn alloy films, smooth titanium sheets (substrate) were etched in 10% HF, cleaned with detergent, and thoroughly rinsed in de-ionized water. The titanium electrode was connected to aluminium to form a short-circuited local cell, and the assembly was immersed in a solution containing 25 mM $CuCl_2$, 32.5 mM $InCl_3$, 1% (v/v) triethanolamine, 0.75% (v/v) ammonia. For doping experiments, the solution contained 7.5 mM $CdCl_2$. The pH of the solution was adjusted to 1.3 by adding dilute HCl dropwise. All the depositions were carried out at 40 °C in an unstirred bath.

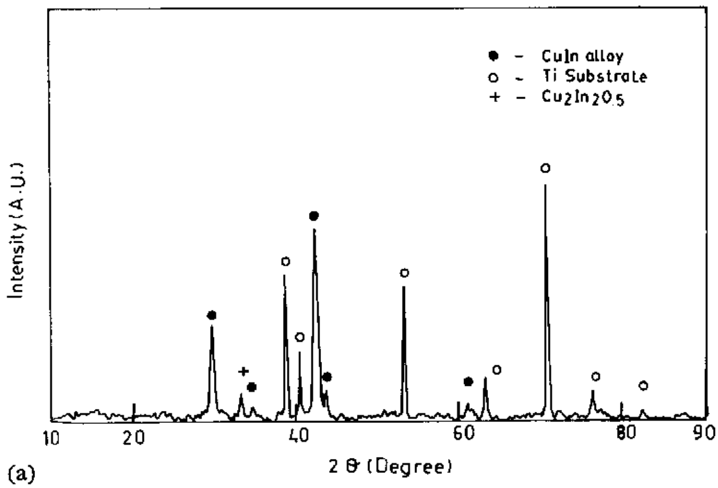
The sulphurization of alloy films was carried out in flowing H_2S gas at 550 °C for 30 min. The XRD patterns for the films were obtained on a Rigaku diffractometer with Cu Kα radiation of 1.5 Å wavelength. The elemental composition of the films was determined with a scanning Auger Microprobe (PHI model 5 AM, 590 A), and depth profile analysis was obtained by sputtering with an argon ion beam. Morphological studies were carried out on a Cambridge S-4 scanning electron microscope. Photoelectrochemical (PEC) investigations were conducted with a conventional three-electrode electrochemical cell using a PAR model 173 potentiostat in conjunction with a universal programmer, model 175, and a digital coulometer, model 179. An alkaline solution of polysulphide (3 M NaOH, 3 M Na_2S, 4 M S) was used as the electrolyte in these experiments. The cell was illuminated with a 650 W tungsten lamp (150 mW cm^{-2}).

Results and discussion

Cadmium doped and undoped CuIn alloy films

The physicochemical characteristics of cadmium-doped CuIn alloy films were compared with those of undoped films prepared from a solution of the same Cu/In composition by using XRD, SEM, and AES techniques. Before characterization, all the films were annealed in N_2 at 200 °C for 15 min. Such treatment is necessary to ensure a uniform composition of copper, indium, and sulphur in the bulk of the $CuInS_2$ prepared subsequently by sulphurization of CuIn alloy [13].

The XRD pattern for the doped film (Fig. 1(a)) is very similar to that for the undoped film [13]. This may be due to a low concentration of cadmium in the film. A perceptible difference exists, however, in the morphologies of the two films (Fig. 2): films of cadmium-doped CuIn alloy contain larger grains but these grains are not uniformly distributed. AES depth-profile



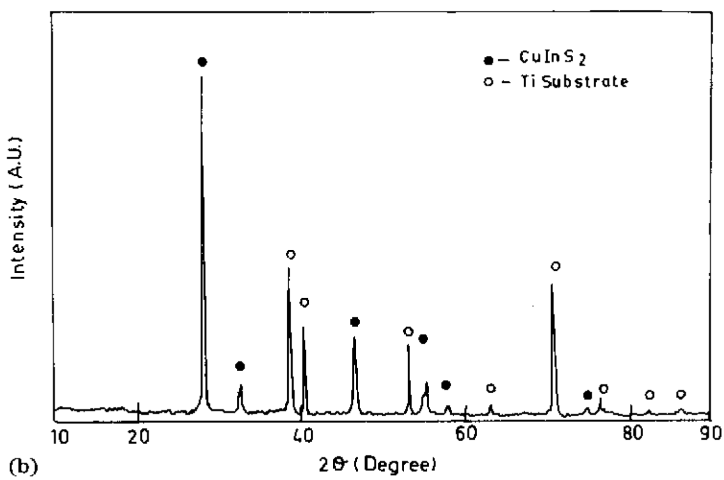
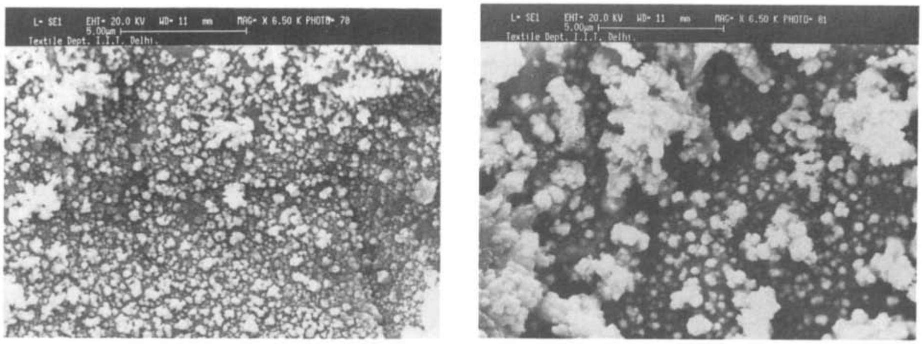


Fig. 1. XRD patterns of: (a) cadmium-doped CuIn alloy film; (b) cadmium-doped $CuInS_2$ film.

analysis of the doped film shows, Fig. 3, that cadmium, copper, and indium are uniformly distributed in the bulk. The amount of copper is more than that of indium; this is possibly due to the more noble nature of copper. A preferential deposition of copper has been noticed under stirred conditions. As soon as stirring is stopped, the deposition of cadmium and indium commences and is visible to the naked eye. All the depositions have therefore been carried out in unstirred baths. Oxygen is also present in these films and is evenly distributed in bulk. It should be noted that oxygen is also present in undoped films [13].

The compositional analysis (Table 1) for both films, determined by AES, shows that films obtained from solutions containing cadmium in place of copper, i.e., when $(Cu+Cd)/In=1$, do not correspond to the expected



(a) (b)

Fig. 2. Electron micrographs of: (a) CuIn alloy film; (b) cadmium-doped CuIn alloy film.

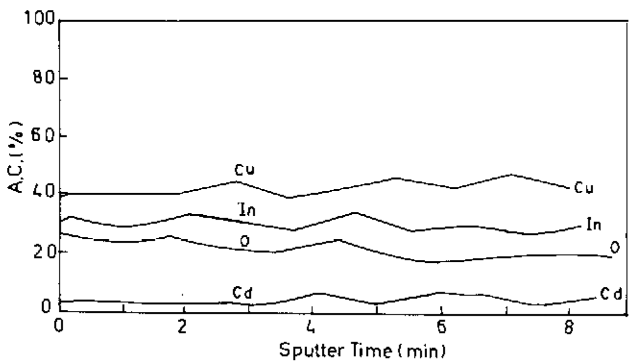


Fig. 3. Auger depth-profile analysis of cadmium-doped CuIn alloy film.

TABLE 1

AES data for alloy films

Sample	Cd:Cu:In (in solution)	Film composition (at.%)					
		Cd	Cu	In	O	Cu/In	Cu/(Cd + In)
Undoped alloy	0:1:1.3		37.0	35.0	28.0	1.06	
Doped alloy	1:4:5	4.0	37.7	31.2	27.1	1.21	1.07

composition, but to a Cu/In ratio of 1.21, which is unexpectedly high. The Cu/(In + Cd) ratio is close to the Cu/In ratio (1.06) of an undoped film. This indicates that cadmium replaces indium rather than copper in the film. This is possibly due to the fact that the reduction potential of cadmium (−0.40 V) is closer to that of indium (−0.34 V) than to that of copper (0.34 V).

$CuInS_2$ films

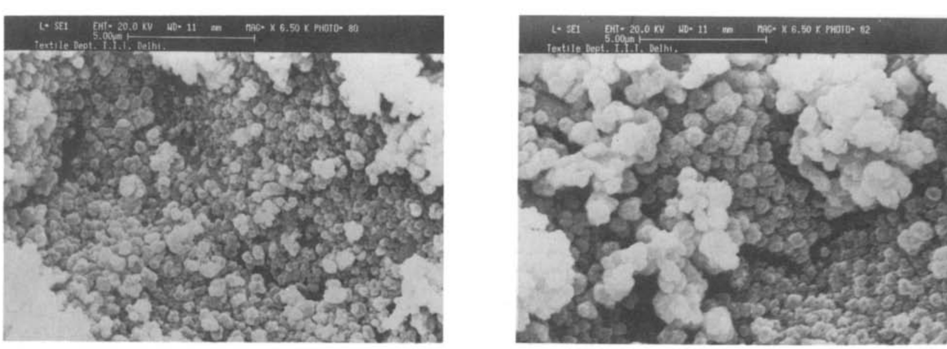
$CuInS_2$ films, with and without doping, were obtained by annealing the alloys at 550 °C for 30 min in H_2S. The XRD pattern of the doped film (Fig. 1(b)) exhibits the same number of peaks as an undoped film [13], but with minor shifts in the positions of the major peaks. The latter may result from the presence of a cadmium impurity. The XRD pattern also indicates that cadmium-doped $CuInS_2$ has a sphalerite structure with (112) preferred orientation. Such a structure has been reported [4, 5] for $CuInS_2$ prepared by a two-step technique. On the other hand, Hodes *et al.* [7] concluded that $CuInS_2$ films have a chalcopyrite structure and suggested that a high conversion temperature (e.g., 550 °C) is responsible for the development of this structure. Nevertheless, films prepared in the present study and converted at the same temperature for the same time exhibited only the presence of a sphalerite structure.

A marked difference is observed between the morphology of undoped and doped $CuInS_2$ films, Fig. 4. The doped film grains are spherical and larger than those of the undoped film grains.

Photoelectrochemical characterization

Film conductivities (n- or p-type) were examined by measuring the PEC characteristics in polysulphide solution. Most of the undoped films are of n-type behaviour. The photo- and dark-current/voltage characteristics of a $CuInS_2$ film are shown in Fig. 5(a). The various PEC parameters are given in Table 2. A steep rise in dark anodic current at a reverse bias of ~10 mV is typical for these films.

All the doped $CuInS_2$ films exhibit n-type behaviour which is enhanced by doping. The photo- and dark-current/voltage characteristics of a doped film are given in Fig. 5(b). It is clearly observed that while the current density in both films is about the same, doping increases the open-circuit potential from 315 to 370 mV. The onset potential, which is a measure of the flat-band potential, is also increased by doping. Overall, doping raises the efficiency



(a) (b)

Fig. 4. Electron micrographs of: (a) $CuInS_2$ film; (b) cadmium-doped $CuInS_2$ film.

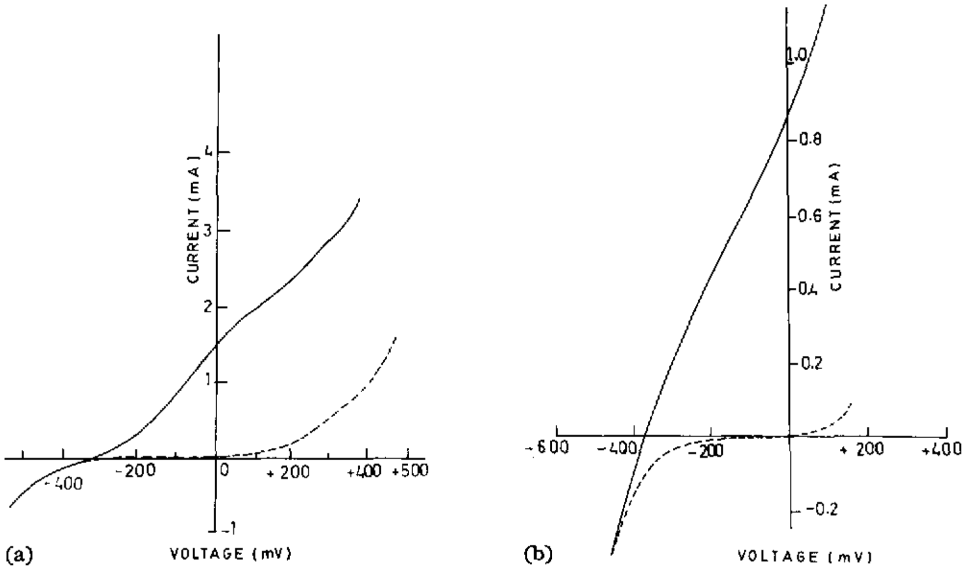


Fig. 5. Current/voltage characteristics of: (a) n-$CuInS_2$ film, area = 1.0 cm^2; (b) cadmium-doped n-$CuInS_2$ film, area = 0.6 cm^2. – – –, In the dark; —— under illumination; 150 mW cm^{-2}. Polysulphide solution.

TABLE 2

PEC data for cadmium-doped and undoped $CuInS_2$ films

Sample	Light intensity (mW cm^{-2})	Current density (mA cm^{-2})	Open circuit voltage (mV)	Fill factor	Efficiency (%)	Flat-band potential (mV vs. SCE)	Band gap (eV)
$CuInS_2$	150	1.45	315	0.19	0.06	−1.08	1.37
Cd–$CuInS_2$	150	1.42	370	0.27	0.10	−1.16	1.36

by 60% (although the actual value is still low) and the fill factor from 0.19 to 0.27.

The spectral response of the PEC cell is shown in Fig. 6(a) for a cadmium-doped film. There is an almost flat response between the short wavelength absorption of the electrolyte and the long wavelength absorption edge of the semiconductor. A certain degree of sub-band-gap response is also observed. The quantum efficiency data are further used to determine the band gap of the material by plotting $(\phi h\nu)^2$ versus $h\nu$ (Fig. 6(b)). Extrapolation of the linear portion of the plot to the horizontal axis yields a 1.38 eV band gap for the material. This value is very close to that for an undoped film [14], lower than that for single-crystalline material [15], and comparable with thin films, namely, 1.38 [17], 1.30 [18], and 1.43 eV [19].

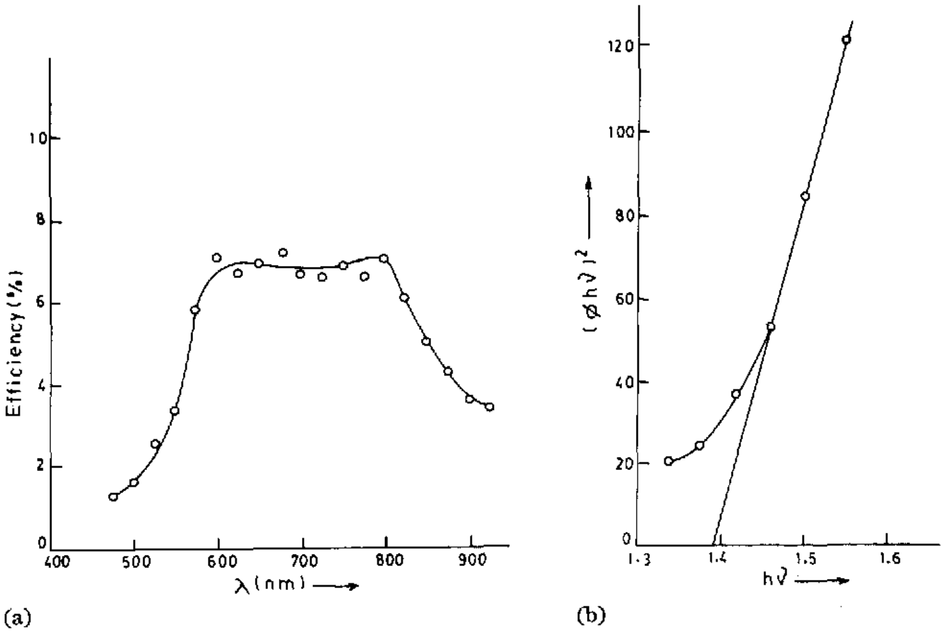


Fig. 6. (a) Spectral response curve for cadmium-doped $CuInS_2$ film in polysulphide solution; (b) band-gap calculation for cadmium-doped $CuInS_2$ films.

It is to be noted that the n-type behaviour of the material increases despite the opposing fact that cadmium rather than copper doping occurs in place of indium. An explanation may be that, during conversion of doped CuIn alloy to $CuInS_2$, cadmium is also converted to CdS which is a well known n-type semiconductor.

Conclusions

Cadmium-doped and undoped films of $CuIns_2$ have been prepared successfully by sulphurization of electroless-deposited, doped and undoped CuIn alloy films. Both types of $CuInS_2$ films have a sphalerite structure. While XRD patterns did not reveal much difference in structure, SEM studies clearly demonstrate that doping produces a marked change in film morphology. Photoelectrochemical studies in polysulphide solution demonstrate that doping causes increases in efficiency, fill factor, and open-circuit voltage.

Acknowledgement

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