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Characterization of sprayed $CuInS_2$ films annealed in hydrogen sulfide atmosphere

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Abstract

The effect of post-deposition annealing in flowing H_2S atmosphere at 530 °C on the properties of sprayed $CuInS_2$ (CIS) thin films was studied. The structure and composition were characterized by XRD, SEM and EDX. The density of carriers was obtained from $C-V$ measurements of CIS/Al Schottky barriers at room temperature (RT), the resistivity was measured at RT and as a function of temperature. H_2S annealing eliminates the deficiency of sulfur and results in closely stoichiometric, well-crystallized films of $CuInS_2$. Annealed films are consisting of grains with a size up to 300 nm. By treatment, the optical band gap increases from 1.44 to 1.49 eV as determined from absorbance spectra. The electrical properties are depending on the cooling rates. The specific resistivity of 10^7 and 10^5 Ω cm and carrier concentrations in the order of 10^{14} and 10^{17} cm^{-3} are characteristics of rapidly and slowly cooled films, respectively. Pronounced parabolic behaviour of the $\ln\sigma$ vs. $1/T$ plot of rapidly cooled samples shows that grain boundaries effect should be considered in the conductivity mechanism. Slow cooling favours the removal of a resistive phase from the grain boundaries and the film conductivity increases. The different predominating defects are assumed to be present in the rapidly and slowly cooled films. The conductivity thermal activation energies of 80 and 160 meV are characteristic of slowly cooled samples deposited from "stoichiometric" or "Cu-rich" solutions, respectively. It shows that not only the treatment conditions but also the film deposition parameters are highly important in the development of the material properties.

Keywords: $CuInS_2$; Spray pyrolysis; Post-deposition treatment; Electrical properties; Structure

1. Introduction

Large-scale introduction of solar energy requires a drastic price reduction. This is why the efforts in the field of thin films cost-effective deposition techniques and new design of solar cells are continuously in progress.

Spray pyrolysis is an inexpensive technique which proved its convenience to deposit homogeneous films over a large area [1]. In the present study the method has been used to prepare thin films of $CuInS_2$. Copper indium disulfide is a potential absorber material for high efficiency solar cells due to its direct band gap of 1.5 eV, although actually the output parameters are low compared to selenide based devices [2].

It has been shown that well-adherent (112) orientated $CuInS_2$ films could be deposited by spray technique [3,4]. As-deposited films grown at temperatures below 400 °C in air contain residues originating from both the precursors and the ambient [5,6]. Post-deposition treatments in reducing and sulfur containing atmospheres were found to be effective to remove undesired residues and improve the structural properties [6,7]. Still, very little attention is paid to the carriers transport properties in the films prepared by chemical methods. The electrical properties of the sprayed $CuInS_2$ films have been studied in few works only [7–9].

In our recent study we showed by Raman spectroscopy that treatment at temperatures around 500 °C in flowing H_2S atmosphere is effective to improve the crystal quality of sprayed $CuInS_2$ films [10]. In the present work we introduce the effect of annealing in H_2S atmosphere at different cooling rates on the crystallinity, stoichiometry, optical and electrical properties of sprayed $CuInS_2$ films.

2. Experimental

$CuInS_2$ (CIS) thin films were obtained by spraying the solution containing $CuCl_2$, $InCl_3$ and $SC(NH_2)_2$ onto pre-

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heated ITO covered glass substrates at 370 °C. The exact description of the deposition procedure is published elsewhere [9,10]. In the present work, molar ratios of precursors Cu/In/S of 1:1:3 and 1.1:1:3.15 were used and the spray solutions were called "stoichiometric" and "Cu-rich", respectively. As-deposited films were etched in KCN solution for 5 min (called as-deposited films) in order to remove the Cu_xS phase at the film surface. Post-deposition heat treatments were performed in flowing H_2S atmosphere at 530 °C for 1 and 2 h, followed by rapid or slow cooling with cooling rates about 25 °C/min and 2 °C/min, respectively.

The crystal structure of the films was characterized by the XRD patterns recorded by a Bruker AXS D5005 diffractometer. The average crystallite size was calculated from the FWHM of the (112) diffraction peak of $CuInS_2$ (PDF 27-0159) using the Scherrer formula. The elemental composition of the films was studied by the X-ray microanalysis (EDX) on a Link Analytical AN 10000 spectrometer using an accelerating voltage of 7 kV and a beam current of 3 nA. EDX measurements were made from the surface area of 2×2 μm^2 at four different characteristic points. The film cross-section micrographs were made on Leo Supra 35. The optical band gap was determined from the absorbance measurements using a Varian Techtron model 635 UV–VIS spectrometer.

To perform the conductivity measurements, the Pt–Au contacts with area of 1.83 mm^2 were made by sputtering on the top of the film. The ITO was used as a back contact. A Keithley-616 electrometer was used to measure the film's resistance. The temperature dependent conductivity was measured in the temperature interval 200–400 K using a vacuum cryostat to set the temperature. The concentration of carriers was determined from the capacitance–voltage (C–V) measurements of CIS–Al Schottky barriers prepared by evaporation of Al contacts with area of the 1.83 mm^2 on the top of the CIS layer. C–V measurements were performed at room temperature (RT) using an Autolab PGSTAT 30 set-up.

3. Results and discussion

3.1. Structural and compositional properties

The crystallinity of sprayed CIS films could be significantly improved by post-deposition treatments [6,7,10]. The effect of annealing in flowing H_2S atmosphere at 525 °C with rapid cooling on the structure of sprayed CIS films is reported elsewhere [10]. It has been shown that the annealing for 2 h significantly increases the film crystallinity and relative importance of the chalcopyrite ordered $CuInS_2$. Furthermore, it was established that the treatment was effective to remove the second ternary compound $CuIn_5S_8$, which was present in as-deposited films prepared from Cu-poor solutions.

The use of an annealing time of 60 min and a slow cooling results in well-crystallized $CuInS_2$ films independent of the spray solution composition according to XRD (Fig. 1). XRD patterns of slowly cooled samples are similar to those presented for rapidly cooled ones in [10]. The average crystallite size is 98 nm as calculated from the FWHM of the (112) replica of $CuInS_2$ (Fig. 1). For comparison, the treatment for 120 min at 525 °C with rapid cooling results in mean crystallite size of about 90 nm [10].

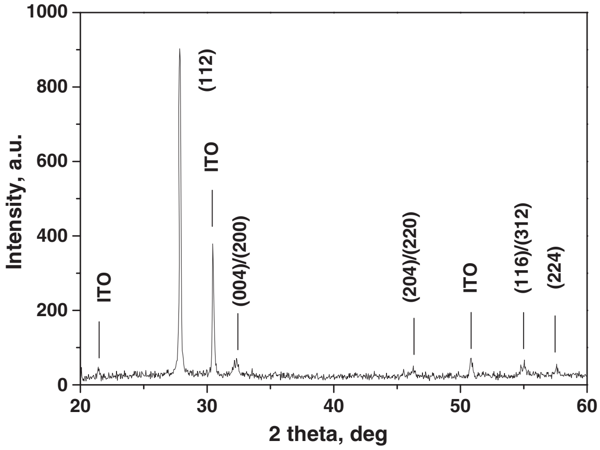

Fig. 1. XRD pattern of the film deposited from the "stoichiometric" (Cu/In = 1.0) solution and annealed for 60 min at 530 °C in flowing H_2S atmosphere and subjected to slow cooling.

The development of grains by H_2S annealing is characterized by the SEM cross-sectional micrographs (Fig. 2). It could be seen that as-deposited film, consisting of grains with size less than 20 nm (Fig. 2a), is turned into a film which comprises grains with sizes up to 300 nm on preserved ITO electrode (Fig. 2b). By annealing, significant changes could be observed in the film elemental composition. The deficiency in sulfur (Table 1) and contamination with chlorine with an amount of about 1.5 mass% are characteristic of as-deposited films. The results are in accordance with the literature data [6,7,11]. Upon H_2S treatment, the content of sulfur is significantly increased and the chlorine is not detectable by EDX. The films on glass substrate exhibit nearly stoichiometric composition whereas on ITO covered glass a slightly In-rich composition has been observed (Table 1). In the latter case the impact of indium from ITO electrode is not excluded. The elemental composition of the films from "Cu-rich" solutions is not affected by the treatment time and cooling rates. The case of the films deposited from "stoichiometric" solutions will be discussed in Section 3.3.

3.2. Optical properties

The optical band gap of as-sprayed and H_2S annealed films was deduced from the absorption spectra measured at RT. The absorption coefficient α was calculated using the expression $I = I_0 e^{-\alpha t}$, where t is the thickness of the film. Following the conventional analysis, the energy dependent absorption coefficient can be expressed by the relation for the allowed direct transition as $\alpha h\nu = A(h\nu - E_G)^{1/2}$, where A is a parameter depending on the transition probability and E_G is the direct band gap. Thus, E_G is found from the plot $(\alpha h\nu)^2$ vs. the photon energy $h\nu$ by extrapolating the linear portion of the plot up to $\alpha = 0$.

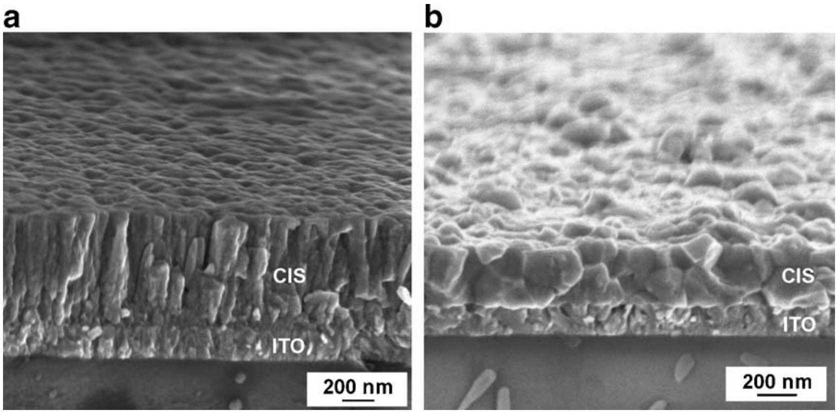

Fig. 2. SEM cross-sectional micrographs of CIS films deposited from “stoichiometric” (Cu/In = 1.0) solutions: (a) as-deposited; (b) annealed for 60 min at 530 °C in flowing H_2S atmosphere and subjected to slow cooling.

As-sprayed films show the optical energy gap of 1.44 eV, corresponding to the literature data for spray-deposited $CuInS_2$ films [4,5], as well as for those prepared by reactive annealing [12] or sulfurization of Cu–In alloys [13]. The treatment was found to increase the band gap energy (Fig. 3). It appears that H_2S treatment followed by rapid cooling results in E_G approximately 1.46 and 1.48 eV using the treatment duration of 1 or 2 h, respectively. Using the treatment time of 1 h followed by slow cooling, the band gap reaches a value close to 1.49 eV. The increase in energy gap is reported for $CuInS_2$ films subjected to annealing in sulfur atmosphere [14]. Observed widening of optical band gap could be explained by the improved crystallinity, nearly stoichiometric composition and higher purity of annealed films as shown above and in [10].

3.3. Electrical properties

The films were characterized by specific resistivity, carrier type, concentration, and temperature dependent conductivity measurements. Hot probe measurements confirm the p-type conductivity of all our films. Mott-Schottky model has been used to determine the concentration of carriers. The results are presented in Table 2.

As-deposited samples show a resistivity of about 10^4 Ω cm. Similar resistivity values are reported for $CuInS_2$ films prepared by spray [8] and reactive sputtering [12]. H_2S treatment, which was found to improve the film’s structural and optical properties, significantly decreases the conductivity and concentration of carriers (Table 2). The influence of different cooling rates is distinctly expressed whereas the deposition parameter (Cu/In in the solution) has minor effect (Table 2). Specific resistivity of 10^7 Ω cm and concentration of carriers in the order of 10^{14} cm^{-3} is characteristic of rapidly cooled films (Table 2). Such low carrier concentration is reported for $CuInS_2$ films prepared by sulfurization of stacked Cu–In layers [15] and reactive sputtering in H_2S [12] as well for as-grown single crystals [16]. It is believed that such low carrier density is a sign of heavy compensation since the concentration of intrinsic defects in this material is reported to be much higher [16]. Applying slow cooling after the treatment for 1 h, an increase in conductivity and carriers’ density has been observed (Table 2). This observed behaviour is similar to that described for polycrystalline $CuInS_2$ films grown by coevaporation and subjected to annealing in sulfur atmosphere [17], where the higher conductivity of slowly cooled films was explained by the saturation of sulfur vacancies during the cool-down period.

The results of temperature dependent conductivity measurements are presented as a plot of lnσ vs. $1000/T$ in Fig. 4. We have assumed that the mobility of holes does not significantly vary within the temperature region used. It could be seen that as-sprayed samples follow the thermally activated electrical conductivity according to the Arrhenius

Table 1
Elemental composition by EDX of CIS films as-sprayed and annealed at 530 °C in H_2S atmosphere, as a function of the treatment time and cooling conditions

Substrate	Cu/In/S in solution	Annealing time (min)	Cooling rate	Cu (at.%)	In (at.%)	S (at.%)	Cu/In	S/(Cu+In)
Glass	1.1:1:3.15	–	–	26.40	26.64	44.36	0.99	0.83
	1:1:3	120	Rapid	25.79	24.51	49.70	1.05	0.99
			Rapid*	0.45	35.25	64.48	0.01	1.83
	1.1:1:3.15	120	Rapid	24.67	25.28	50.05	0.98	1.00
ITO	1.1:1:3.15	120	Slow	24.30	26.40	49.20	0.92	0.97
	1.1:1:3.15	60	Rapid	24.76	26.04	49.07	0.95	0.97
	1.1:1:3.15	60	Slow	24.34	26.08	49.48	0.93	0.98
	1:1:3	60	Slow	24.14	25.72	48.41	0.94	0.97

*From the flake-like crystallites on the surface.

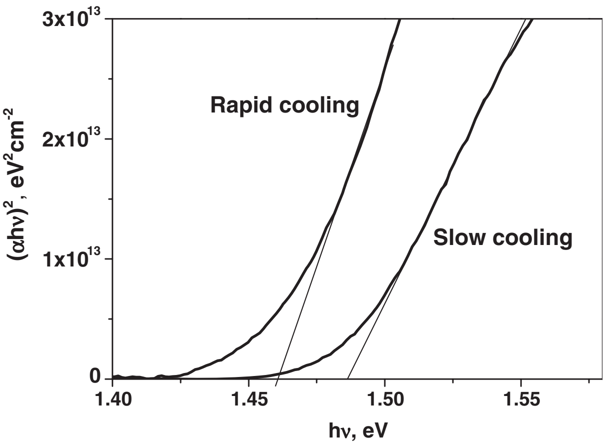

Fig. 3. The plot of $(\alpha h\nu)^2$ vs. energy for $CuInS_2$ films deposited from “Cu-rich” solution (Cu/In = 1.1) and treated for 60 min at 530 °C in flowing H_2S atmosphere and subjected to rapid or slow cooling.

relation $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ_0 is a pre-exponential factor, E_a is the activation energy and k is the Boltzmann’s constant. The thermal activation energies of 114 meV and 170 meV were obtained for as-sprayed films deposited from “Cu-rich” and “stoichiometric” solutions, respectively.

The plots of lnσ vs. 1000/T of H_2S treated films show parabolic behaviour (Fig. 4) and thus the mixed conductivity activation mechanisms due to the defect levels and grain boundary effects could be proposed [7,18,19]. Parabolic behaviour is highly pronounced for the films subjected to rapid cooling. By allowing the samples to cool down slowly, an increase in conductivity with less pronounced curvature of lnσ vs. 1000/T plot could be observed.

In high temperature region (T > 320 K) the plot of lnσ vs. 1000/T of H_2S treated films follows the Arrhenius dependence for both rapidly and slowly cooled samples. Infinitely high activation energies of 340 and 520 meV were found for rapidly cooled samples prepared from “Cu-rich” and “stoichiometric” solutions, respectively (Table 2). We believe that these activation energies indicate that there are residues of some unknown phase between the grains in rapidly cooled samples and are not caused by some very deep acceptor level in $CuInS_2$. An indium and sulfur containing phase was detected on the surface of the film from “stoichiometric” solution after rapid cooling (Table 1, marked by asterisk). Similar phase could be present at grain boundaries as well. The existence of an indium sulfide phase has been observed at grain boundaries of sprayed CIS films annealed in sulfur atmosphere [7].

Table 2
Specific resistivity (ρ), carrier concentration (N_p) at room temperature and conductivity thermal activation energy (E_a) for CIS films as-deposited and annealed at 530 °C in H_2S atmosphere

Cu/In/S in solution	Treatment time (min)	Cooling	ρ (Ω cm)	N_p (cm^{-3})	E_a (meV)
1:1:3	–	–	$4.6 \cdot 10^4$	$4.0 \cdot 10^{16}$	170
	120	Rapid	$1.0 \cdot 10^7$	$2.2 \cdot 10^{14}$	520
	60	Slow	$6.9 \cdot 10^5$	$1.5 \cdot 10^{17}$	83
1.1:1:3.15	–	–	$2.5 \cdot 10^4$	$1.9 \cdot 10^{17}$	114
	120	Rapid	$4.0 \cdot 10^7$	$3.2 \cdot 10^{14}$	347
	60	Slow	$2.5 \cdot 10^5$	$2.3 \cdot 10^{17}$	160

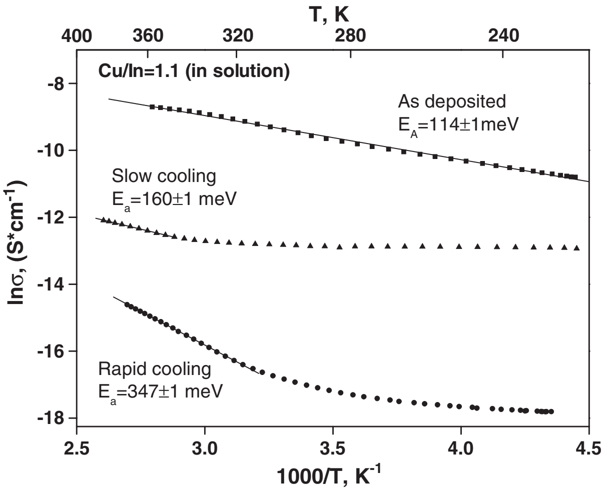

Fig. 4. The plot of lnσ vs. 1000/T for as-deposited from “Cu-rich” solution (Cu/In = 1.1) and annealed for 60 min at 530 °C in flowing H_2S atmosphere $CuInS_2$ films subjected to rapid or slow cooling.

By slow cooling, this highly resistive phase disappears and the conductivity of samples increases. Thus, the slow cooling results in the conductivity thermal activation energies of 80 and 160 meV (for the samples grown from “stoichiometric” and “Cu-rich” solutions, respectively), which could be assigned to the acceptor levels in $CuInS_2$.

4. Conclusions

The post-deposition annealing of sprayed CIS films in flowing H_2S atmosphere significantly improves the film’s crystallinity and stoichiometry by increasing the sulfur content. The mean crystallite size in H_2S annealed films is close to 100 nm as determined from the XRD pattern. Annealed films are consisting of grains with size up to 300 nm according to SEM. The optical band gap could be increased up to 1.49 eV, which is the highest value reported for the $CuInS_2$ films initially prepared by spray technique.

H_2S treatment, which was a right action to improve the films structural and optical properties has an adverse effect on the electrical properties, particularly when cooled rapidly. The specific resistivity of 10^7 Ω cm and carrier concentrations in order of 10^{14} cm^{-3} are characteristic of rapidly cooled films. Such low carrier density indicates that the material could be highly compensated. The temperature dependent conductivity measurements show that the grain boundaries effect should be considered in the conductivity mechanism. We believe that there are residues of some unknown phase between the grains in these samples.

The film conductivity could be increased using slow cooling which favours the removal of highly resistive phase from the grain boundaries. The increased carrier density refers to the changes in the predominating defects compared to the rapidly cooled films. The conductivity thermal activation energies of 80 and 160 meV, which could be assigned to acceptor levels in

$CuInS_2$, are dependent on the Cu/In molar ratio in the spray solution. Thus, not only the treatment conditions but also the film deposition parameters are highly important in the development of the material properties.

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