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Crystal quality studies of $CuInS_2$ films prepared by spray pyrolysis

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Abstract

Raman spectroscopy and XRD methods were applied to determine the phase composition and crystal quality of copper indium sulfide (CIS) films grown by spray pyrolysis. The aim of the study was to develop a low-cost preparation technique for solar cell quality materials. The Cu/In molar ratio in spray solution (0.8–1.1) and post-deposition heat treatment conditions were taken as variables.

According to XRD, KCN-etched films from Cu-rich solutions result in single phase $CuInS_2$. The A_1 phonon modes at 290 and 300 cm^{-1} in Raman spectra show that CIS films deposited at 370 °C consisted of chalcopyrite (CH) and Cu–Au (CA) ordered phases of $CuInS_2$. Both XRD and Raman studies showed the presence of an extra phase in as-deposited films using Cu/In=0.8–1.0, which could belong to $CuIn_5S_8$. Thermal treatments reduced the amount of secondary phase and improved the crystallinity of the films. The heat treatment at 525 °C in H_2S led to an increase in CH content with a decrease in the FWHM of A_1 mode. Furthermore, the rise of the quality factor (I(CH)/I(CH)+I(CA)) up to 62% was observed, indicating the formation of $CuInS_2$ films with better crystal quality.

Keywords: $CuInS_2$; Spray pyrolysis; XRD; Raman spectroscopy

1. Introduction

The properties, such as high optical absorption coefficient and band gap energy of 1.5 eV, have raised researchers' interest in $CuInS_2$ thin films used as an absorber layer in solar cells [1]. In the present work, the spray pyrolysis method was used to produce $CuInS_2$ thin films. Spray pyrolysis is an attractive method for large area thin film production because it is of low-cost and easy to make process. The composition, crystal structure and morphology of the sprayed copper indium sulfide (CIS) films as a function of the substrate temperature and the Cu/In molar ratio in the spray solution have been published earlier [2–5].

Raman spectroscopy has been applied to CIS films obtained from various deposition methods, such as the co-evaporation of Cu, In and S [6], AL-CVD [7] and sulfurization of CuIn alloy [8]. Although Raman spectroscopy has been used to characterize sprayed $CuInSe_2$ films [9], much less attention has been paid to sprayed $CuInS_2$ thin films. Raman spectroscopy is a non-destructive method to analyze the structural quality and to identify the secondary phases in the films [10,11].

Previous Raman investigations have shown that the most intensive Raman mode for the chalcopyrite (CH) structure is the A_1 mode at 290 cm^{-1} [6,11]. An additional mode at 305 cm^{-1} belongs to the Cu–Au ordering (CA), causing the blue shift and broadening of the A_1 mode [6]. The relative intensity of the CA ordering bands at 60 and 305 cm^{-1} (with respect to the CH mode) decrease with an increase in the Cu/In ratio in the films prepared by the co-evaporation process [12]. To enhance the crystal quality of the films, annealing in sulphur containing atmospheres has been performed [7,8,10,13].

To our knowledge, no Raman spectroscopic characterizations of sprayed $CuInS_2$ films have been published. Therefore, the aim of our research is to focus on the crystal quality assessment of spray pyrolysis deposited $CuInS_2$ films as the effect of various Cu/In in solution and different post-deposition heat treatments.

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2. Experimental

Spray pyrolysis deposited $CuInS_2$ thin films were obtained from an aqueous solution containing $CuCl_2$, $InCl_3$ and $SC(NH_2)_2$. The exact preparation of the spray solution is published elsewhere [5]. In the present study, Cu/In molar ratio in the precursor solution was varied in the range of 0.8–1.1. The films were sprayed onto pre-heated glass substrates at the constant substrate temperature of 370 °C. The solution of a total amount of 50 ml was sprayed at the solution feed rate of 5 ml/min with N_2 carrier gas.

As-deposited films were etched in 5% KCN solution for 5 min at room temperature (called as-deposited films) in order to remove the Cu_xS phase from the film surface. The post-deposition heat treatment was performed in various environments, such as H_2 at 450 °C for 1 h, H_2S °C at 450 and 525 °C for 1 and 2 h, respectively. The experiment was performed in half-opened system where the H_2S was produced by leading the hydrogen flow through the melted sulphur at 350 °C.

The crystal structure of the sprayed films was characterized by XRD patterns, recorded by a Bruker AXS D5005 diffractometer. Crystallite size was calculated using the Scherrer formula. Micro-Raman scattering measurements were performed at room temperature with the excitation wavelength of 532 nm and output power of 2 mW by means of the Raman setup with the Spex 340E monochromator. The Raman patterns were taken with the time resolution of 60 s from three different points on the films surface.

3. Results and discussion

3.1. As-sprayed $CuInS_2$ films

Previous studies have shown that the crystalline and structural properties of sprayed CIS films can be controlled by the copper and indium sources molar ratio (Cu/In) in the solution. The most proper growth temperature interval has found to remain between 350 and 380 °C [3,5]. Hence, in the present study, the films were prepared at the substrate temperature of 370 °C using the Cu/In=0.8–1.1 in spray solution.

According to XRD (Figs. 1 and 2), the films prepared from "In-rich" (Cu/In=0.8) as well as from "1:1:3" (Cu/In=1.0) solutions show poor crystallinity. As-deposited films from In-rich solution show only one distinct replica of (220) plane belonging to $CuInS_2$. Similar results were observed for $CuInS_2$ films by the spray chemical vapour deposition [14].

An extra XRD reflection in the low-angle shoulder of the $CuInS_2$ (112) peak at 2θ=26.5° does not belong to the $CuInS_2$ phase (marked by "x" in Figs. 1 and 2). In fact, this reflection was recorded to be present in copper indium sulphide films prepared by spray pyrolysis [2,5], by spray chemical vapour deposition [14,15] and by sulfidization of sputtered Cu–In precursor [16,17]. The secondary phase cannot be identified by the XRD pattern because of the low crystallinity of the film. However, the extra reflection is absent in the case of Cu-rich solutions (Fig. 1).

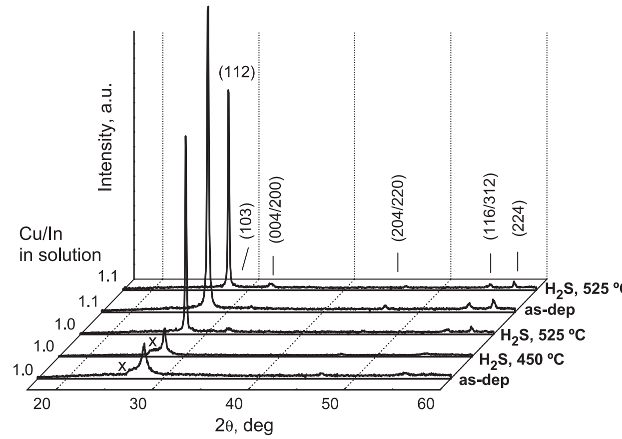

Fig. 1. XRD patterns of as-sprayed and heat treated $CuInS_2$ films at Cu/In=1.0–1.1.

Fig. 3 shows the Raman spectra of the as-deposited CIS films from various Cu/In in solutions. The films deposited from "In-rich" solution exhibit lower scattering intensity, which could be caused by higher density of defects [6]. Lower crystallinity of "In-rich" films is observed from XRD studies (Fig. 2). Raman spectra of the CIS films were fitted with Lorentzians as shown for the films from In-rich solutions (Fig. 3c). In addition to the A_1 modes of the CH and CA structures, several E/B_2 modes of the CH-ordered compound were taken into account in the fitting procedure. The obtained results show that the most intensive Raman band consists of two bands, A_1 band of CH ordered compound at 290 cm^{-1} and A_1* band of CA ordering at 300 cm^{-1}. The intensity of the A_1* mode of Cu–Au ordered phase is higher compared to the A_1 mode of CH ordering, however, the position of these bands was observed to be independent of the Cu/In in spray solution (Fig. 3).

In addition to the Raman bands of the CH and CA ordered $CuInS_2$ at 290 and 300 cm^{-1}, respectively, CIS films grown from In-rich solution contain an intensive Raman band at around 340 cm^{-1} (Fig. 3c). The intensity of the 340 cm^{-1} band is comparable to that of the CA and CH bands of $CuInS_2$. The band can be subtracted into three sub-bands, as shown in Fig. 3c. The low frequency modes at 321 and 338 cm^{-1} could belong to the B_2^1 and E_{LO}^1 modes of the chalcopyrite structure, respectively [13]. The mode at 348 cm^{-1} could belong to the $CuIn_5S_8$ phase [13,18]. The observation that the Raman peak at 348 cm^{-1} vanishes together with the extra reflection at 2θ=26.5° in the XRD pattern (Fig. 1) by increasing the Cu/In in solution supports the assumption of the CIS phase formation. Furthermore, the formation of $CuIn_5S_8$ spinel phase is also reported in CIS films prepared by ALD under Cu-poor conditions [7], in $(Ag,Cu)InS_2$ thin films prepared by the diffusion of Cu, Ag and S into In_xS precursor layer [19] as well in the films