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Effects of the growth temperature on the properties of spray deposited $CuInS_2$ thin films for photovoltaic applications

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Abstract

$CuInS_2$ absorber thin films were prepared by spray pyrolysis deposition at different substrate temperatures (250 °C, 300 °C and 350 °C) using an aqueous solution of $CuCl_2$, $InCl_3$ and $SC(NH_2)_2$ at a precursor molar ratio of Cu:In:S = 1:1.25:4.5. The effect of the substrate's temperature on the structural, morphological, optical and electrical properties of $CuInS_2$ thin films was investigated. The X-ray diffraction patterns showed that $CuInS_2$ has a tetragonal structure. The results show that the films deposited at 300 °C have improved electrical conduction and photocurrent values. When increasing the substrate's temperature the absorbance decreases while the band gap energy increases, as a combined effect of crystallinity, morphology and deviation from stoichiometry.

Keywords: $CuInS_2$; Thin films; Spray pyrolysis; Growth temperature; Absorber materials

1. Introduction

Polycrystalline thin films with semiconductor properties have special importance in the fabrication of low-cost solar cells, despite their lower conversion efficiency, when compared with the mono-crystalline Si solar cells [1–4]. Copper indium disulfide, $CuInS_2$ (CIS) is one of the most promising ternary chalcopyrite materials, used as solar cell absorber [5,6]. It has excellent physical and chemical properties such as an absorption coefficient of almost 10^5 cm^{-1} in the visible spectral range [7], tolerance to defects [8], chemical stability, a direct band gap of 1.5 eV (which is the optimum value for the photovoltaic conversion of solar energy [9]), and has possibility to be developed as n- or p-type semiconductor [10]. This material was successfully used in thin film solar cells with conversion efficiencies up to 11.4% [11]. Many studies focused on developing correlations between the CIS thin films deposition methods and the resulted structure, morphology and electrical conduction. A variety of techniques are reported to obtain $CuInS_2$ thin films, such as reactive radio frequency magnetron sputtering [12], co-evaporation [13], ion layer gas reaction [14], and wet chemical process [15]. However, only a few papers report on sprayed $CuInS_2$ thin films [16]. Considering scaling up, spray pyrolysis is a viable method because large area films with good uniformity can be obtained at low cost. The properties of the films can be effectively controlled by varying the deposition parameters and by changing the precursors' concentration in the sprayed solution [17,18]. The crystalline parameters (cell, size, and shape), and the surface aspect (morphology and roughness) can be modified to control $CuInS_2$ thin film properties for photovoltaic applications [19].

The main purpose of this work is to optimize the $CuInS_2$ opto-electric properties for photovoltaic applications, by tuning the spray pyrolysis deposition parameters. In this work, sprayed $CuInS_2$ absorber layers are analyzed considering the influence of the substrate temperature on the structural, morphological and opto-

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electric properties. It is shown that the properties are significantly affected by rather small temperature variations and the optimum deposition temperature is recommended considering the electric output.

2. Experimental details

2.1. Precursor preparation and deposition parameters

The $CuInS_2$ thin films were deposited by spray pyrolysis on preheated FTO substrates, from aqueous-alcohol solutions containing $CuCl_2$, $InCl_3$ and $SC(NH_2)_2$ with a precursor molar ratio Cu:In:S = 1:1.25:4.5. The solvent was a 4:1 mixture of deionized water and ethanol. The solvent volume was 50 mL with $[Cu^{2+}]$ = 2 mmol L^{-1}. Copper (II) chloride and indium (III) chloride solutions were mixed, then the thiourea was added [20]. Before use, the substrates were successively cleaned in an ultrasonic bath, using ethanol and distilled water and were further dried in air. The substrate temperature was varied from 250 °C to 350 °C. Compressed ambient air was used to atomize the solution at the pressure of 2 bar.

2.2. Thin films characterization

The crystalline structure of the samples was investigated by XRD, using a Bruker D8 Discover Advanced Diffractometer with locked coupled continuous scan with a scintillation counter (12,800 steps, 2 s/step) and a radiation with 1.5406 Å wavelength ($CuK\alpha_1$ at 40 kV, 20 mA); a dedicated software was used to evaluate the crystallinity percentage (EVA Bruker).

The surface morphology was investigated using a Scanning Electron Microscope (SEM, Hitachi model S-3400N type 121 II) and an Atomic Force Microscope (AFM,NT-MDT model BL222RNTE). The images were taken in semi-contact mode with Si-tips (NSG10, force constant 0.15 N/m, tip radius 10 nm). The reproducibility of the average roughness measurements was of 5%. The surface elemental analysis of the films was performed by an energy dispersive X-ray spectrometer Ultra Dry, Noran System 7, NSS Model (2,000,000 counts/s).

Absorption spectra were recorded using a UV–vis spectrophotometer (PerkinElmer Lambda 25 UV/vis), in the 300–1200 nm range, with a scan rate of 60 nm/min (lamp changes at 326 nm).

The *I–V* (current–voltage curves in dark) and the photocurrent measurements used a multichannel potentiostat (PAR Instruments, model HM8143) with frequency analyzer and a light source (Oriel, model 7123). Two graphite contacts were used for applying the voltage (on the substrate) and as receiver (on the CIS thin film), and the current intensity was recorded.

3. Results and discussion

3.1. Structural analysis

The X-ray diffractograms (Fig. 1) of the $CuInS_2$ thin films deposited at different temperatures show that the patterns well matched the JCPDS 65-1572 standard, corresponding to tetragonal $CuInS_2$ (the chalcopyrite phase).

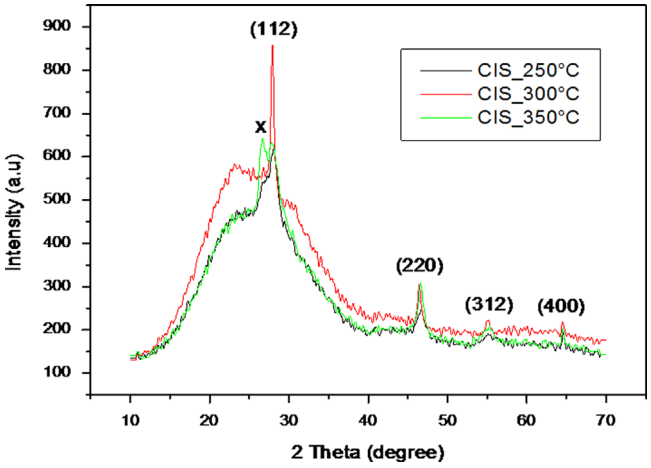

Fig. 1. The XRD patterns of $CuInS_2$ films deposited at different substrate temperatures.

Table 1
Crystallite sizes, percentage of crystalline phase, thickness, roughness and band gap of $CuInS_2$ films deposited at different substrate temperatures.

Sample code	Percentage of crystalline phase (%)	Crystallite sizes (nm)	Thickness (nm)	Roughness (nm)	Band gap (eV)
CIS 250	84	5.9	552	107.7	1.50
CIS 300	86	26.7	517	205.7	1.59
CIS 350	90	21.8	526	134.8	1.70

Extended crystalline phases represent a prerequisite in photovoltaic applications, therefore the crystallinity percentage was evaluated (Table 1) and indicates that the content of amorphous phases is decreasing (as expected), when increasing the deposition temperature. The highest crystallinity degree corresponds to the sample obtained at 350 °C; however, this sample has not the largest crystallites, supporting the conclusion of a process mostly governed by nucleation [21].

The average crystallite sizes (Table 1) corresponding to the predominant peak (112) were calculated using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where β is the observed angular width at half maximum intensity (FWHM) of the peak, λ is the X-ray wavelength (1.5406 Å for $CuK\alpha_1$) and θ is Bragg's angle.

The crystallites' size increases with temperature up to 300 °C (reaching a maximum of 26.7 nm), followed by a slight decrease, when further increasing the deposition temperature. However, higher temperatures may yield lattice stress, defects formation and increases non-stoichiometry [22,23]. That is the case of the $CuInS_2$ film obtained at 350 °C which shows a new (and undesired) peak at 2θ=26.9°. A similar peak, at 2θ=26.4°, is reported in the literature for CIS films deposited by SPD [24], and was assigned to In_xS_y or to $CuIn_5S_8$ phases. Additionally, the use of compressed air (21 vol% of oxygen) as carrier gas and the rather high deposition temperatures can support secondary oxidation