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Synthesis and characterization of $CuInS_2$ thin films grown by spray pyrolysis

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$CuInS_2$ (CIS), a potential candidate for absorber layer in thin film heterojunction solar cell, has been successfully deposited by spray pyrolysis technique on heated glass substrates at various temperatures. We have investigated the synthesis conditions and some properties of sprayed $CuInS_2$ thin films in order to determine the best preparation conditions for the realization of CIS based photovoltaic solar cells. In order to optimize the synthesis conditions of the CIS films, two series of experiments have been performed. In the first series the substrate temperature was changed from T=598K to 673K by step of 25K, and the spray duration was fixed at 60 min. In the second series the spray duration was varied between 15 min and 60 min and the substrate temperature was fixed at 648K. The structural, morphological, compositional and optical properties of the CIS thin films have been studied using X-ray diffraction (XRD), Raman scattering measurements, scanning electron microscopy (SEM), EDAX, and optical absorption techniques respectively. X-ray diffraction studies reveal that polycrystalline CIS films with chalcopyrite crystal structure and better crystallinity could be obtained for substrate temperatures in the range 648–673K. The optical band gap of films deposited at the substrate temperature 648 K and sprayed during 60 min is close to the ideal band gap for highest theoretical conversion efficiency, with an optical absorption coefficient of 10^5 cm^{-1}.

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Keywords: Spray technique, Thin films, Chalcopyrite, Solar cell, Raman

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1. Introduction

The development of clean energy resources as an alternative to the fossil fuel has become one of the most important tasks assigned to the researchers of modern science and technology in the 21st century. Among a wide variety of renewable energy sources, solar energy is the best alternative, which is suitable to satisfy the energy demands of the modern society. The ternary $CuInS_2$ (CIS) thin film is a promising candidate for low cost absorber layer in thin film solar cell due to its excellent materials properties for obtaining high efficiency such as suitable band-gap energy of 1.4–1.55 eV, and large absorption coefficient over 10^5 cm^{-1} [1, 2]. In addition to that, this compound semiconductor does not contain toxic element such as Se or Cd, resulting in realizing a solar cell with a lower environmental foot print. A various physical and chemical techniques such a three sources molecular beam epitaxy [3], sulphurization of metallic precursor [4], co-evaporation from elemental sources [5] reactive sputtering [6-7], electrodeposition [8-9-10], chemical bath deposition [11-12], spray pyrolysis [13-14-15], etc, have been used for the synthesis of CIS thin films for solar cell applications. In this work, CIS were deposited by spray pyrolysis in ambient atmosphere onto substrates maintained at temperatures between 598 and 673K. The pulverization technique presents several advantages due to its simplicity, low cost, low energy requirements furthermore it is ideally suited for large scale production.

We have investigated the growth and properties of spray-deposited CIS thin films at various substrate temperatures in the range 598-673K and the different spray duration between 15 min and 60 min in order to optimize the substrate temperature and spray duration to obtain single-phase CIS films. The results of these investigations are presented in this paper.

2. Experimental

$CuInS_2$ (CIS) thin films were deposited by the pulverization technique (Spray pyrolysis) starting with aqueous solution containing cupric chloride CuCl (0,01M), indium chloride $InCl_3$ (0,01M) and thiourea $SC(NH_2)_2$, the excess of thiourea was taken to account to composite the loss of sulphur during pyrolysis, the solution was sprayed using compressed air as the carrier gas and the spray rate was 1.5ml/min. The $CuInS_2$ films are formed on heated glass substrates (25×25×2 mm^3) by the following reaction:

$$CuCl + InCl_3 + 2SC(NH_2)_2 + 4H_2O \rightarrow CuInS_2 + 2CO_2 + 4NH_4Cl$$

To optimize the $CuInS_2$ films two series of experiments were carried out, in the first series the substrate temperature was change from T=598, to 673K by step of 25K and the spray duration was fixed at 60 min and in the second series the spray duration was varied between 15 min and 60 min and the substrate temperature was fixed at 648K, the substrate temperature could be maintained to an accuracy of ± 5K using a digital temperature controller.

Films were analyzed by studying their composition, structural, and optical properties. The elemental composition of $CuInS_2$ thin films was determined from using an energy dispersive spectrometer (EDS) attached to JEOL SEM. X-ray diffractometer (XPERT-PR) was used in Bragg-Brentano to record X-ray diffraction (XRD) pattern. The Cu-K_α radiation of a copper anticathode (0,154 nm) and the generator settings were 40 mA, 45 Kv, was used to record X-ray the spectra in the 2θ range 20-60° with a step size of 0,067. The microstructure and the surface morphology were obtained on a JEOL-JSM 6300 scanning electron microscope (SEM). For Raman spectroscopy, the LASER line used was 514,5 nm and the device a Jobin-Yvon T64000. The optical set of the Raman spectrometer was an Olympus microscope equipped with a 100x magnification lens, it focused the LASER beam down to a spot of spot of 1 µm in diameter, the LASER penetration depth is estimated to be close to 500 nm. Optical properties were monitored by absorbance using a Deuterium-Halogen lamp (DT–MINI–2–GS Micropark) in association with a 500 mm Yvon–Jobin HR460 spectrophotometer using a back-thinned Si-CCD detector (Hammamatsu) optimized for the UV–VIS range. The Spectral transmittance and reflectance were recorded in the wavelength range 300-2000 nm.

3. Results and discussion

3.1. Composition

The elemental composition of $CuInS_2$ thin films determined from EDS analysis for films deposited at various substrate temperatures and at different spray duration is shown in Table 1 and Table 2 respectively. No traces of carbon were detected and chlorine appears in very little amounts, generally less than 1% the detection limit of EDS. There is a considerable deviation from stoichiometry for films prepared at higher temperature (673K; 698K), these films are mostly copper rich, but sulphur deficient. Sulphur deficiency is significantly higher at higher substrate temperatures since sulphur is more volatile.EDS data of sprayed CIS films deposited at different spray duration show that Cu/In ratio is always higher than that in the solution, indicating the excess of copper during the film growth, this effect indicates that possible formation of the Cu_xS [16-17] segregated phase at the surface was caused by the higher Cu content and its mobility. The films deposited in 45 and 60 min show the Cu/In≈1 ratio in the film.

Table 1. Composition analysis of CIS precursor thin film prepared at various substrate temperatures: 598K, 623K, 648K, and 673K for 60 min spray duration.

Spray duration (min)	Composition of elements in atomic (at. %)			Composition ratio	
	Cu	In	S	Cu/In	S/(Cu+In)
15	28, 57	23,47	47,96	1,22	0,92
30	26,35	25,20	48,45	1,04	0,94
45	26,04	24,76	49,20	1,05	0,97
60	25,94	24,23	49,83	1,04	0,99

Table 2. Composition analysis of CIS precursor thin film prepared for different spray duration: 15 min, 30 min, 45 min, and 60 min at 648K substrate temperature.

Temperatures Substrat (K)	Composition of elements in atomic (at. %)			Composition ratio	
	Cu	In	S	Cu/In	S/(Cu+In)
598	24,63	25, 39	49,98	0,97	0,99
623	24,15	25,40	50,45	0,95	1,02
648	26,35	26,06	47,59	1,01	0,91
673	29,44	26,76	43,80	1,09	0,78

3.2. Structural characterization

3.2.1. X-ray diffraction studies

The X-ray diffraction patterns of the CIS films synthesized during 60 min at various substrate temperatures (598K, 623K, 648K, 673K) are shown in Fig. 1. For all of the as-deposited films are polycrystalline structure, we can see some peaks corresponding to the (112), (200), (220) and (312) planes of CIS, which are characteristic of the chalcopyrite structure (JCPD File N° .047- 1372). A preferential (112) orientation was observed for all deposits. The comparison of the XRD spectrum of CIS thin film grown by different growth temperatures reveals that the 112 diffraction peak increased with increasing growth temperature, indicating that the crystallinity of the CIS films becomes better with increasing substrate temperature.

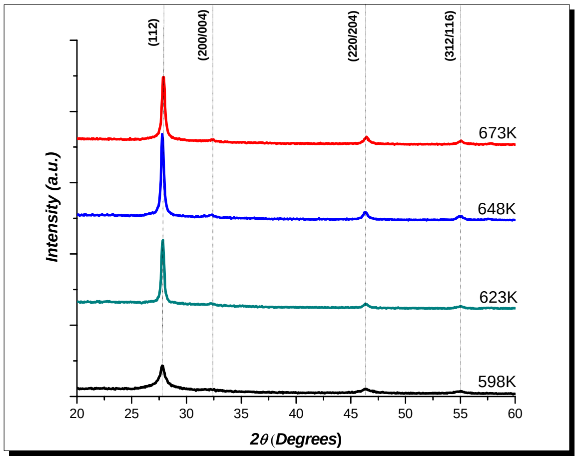

Fig. 1. X-ray diffraction patterns of CIS precursor thin film prepared at various substrate temperatures: 598K, 623K, 648K, and 673K for 60 min spray duration.

Fig. 2 shows the X-ray diffraction curve of the films obtained for substrate temperatures of 375°C at various spray duration. A sharp peak from (112) planes of the CIS type crystal increases with increasing the spray duration. However, as mentioned previously for the spray duration of 15 min and 30 min, some peaks corresponding to secondary phase of Cu_xS [16-17] compound can be observed and the (004) or (200) diffraction peak relatively disappeared. This indicates that the polycrystalline growth was suppressed and the orientation growths were induced in a film grown at low sprays duration.

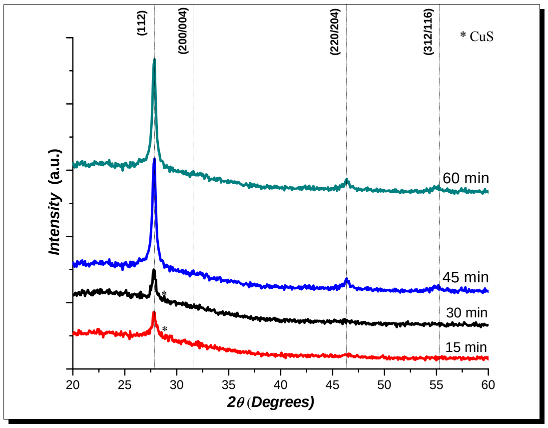

Fig. 2. X-ray diffraction patterns of CIS precursor thin film prepared for different spray duration: 15 min, 30 min, 45 min, and 60 min at 648K substrate temperature. The peak marked as (*) is from Cu_xS phase.

3.2.2. Microstructure

Fig. 3 shows SEM micrographs of CIS films deposited at different substrate temperatures. As soon as the substrate temperature increases, there is an improvement in grain morphology and size. The grain size of films deposited for substrate temperature in the range 623–648K is found to be between 250 and 500 nm. Thus, we can remark that the average roughness value increases when the substrate temperature increases. This result could be explained by the agglomeration at higher temperatures 648K and 673K, consequently this agglomeration is the formation of clusters with a dimension varies in general between 1 and 3 µm. On the other hand, it allows us to suggest that, during deposition; small droplets vaporize above the substrate and condense as micro-crystallites with various dimensions onto the surface of the films.

From Fig. 4 we can see that the grain size increases when the spray duration increases. Moreover, films prepared at spray durations of 45 min and 60 min appear quite smooth compared to those prepared at lower spray durations. The grain size varies between 40 and 600 nm for films prepared in 15 min and 60 min respectively. Concerning the morphological study, it is concluded that the surface morphology of CIS thin film is strongly dependent on the substrate temperature and spray duration.

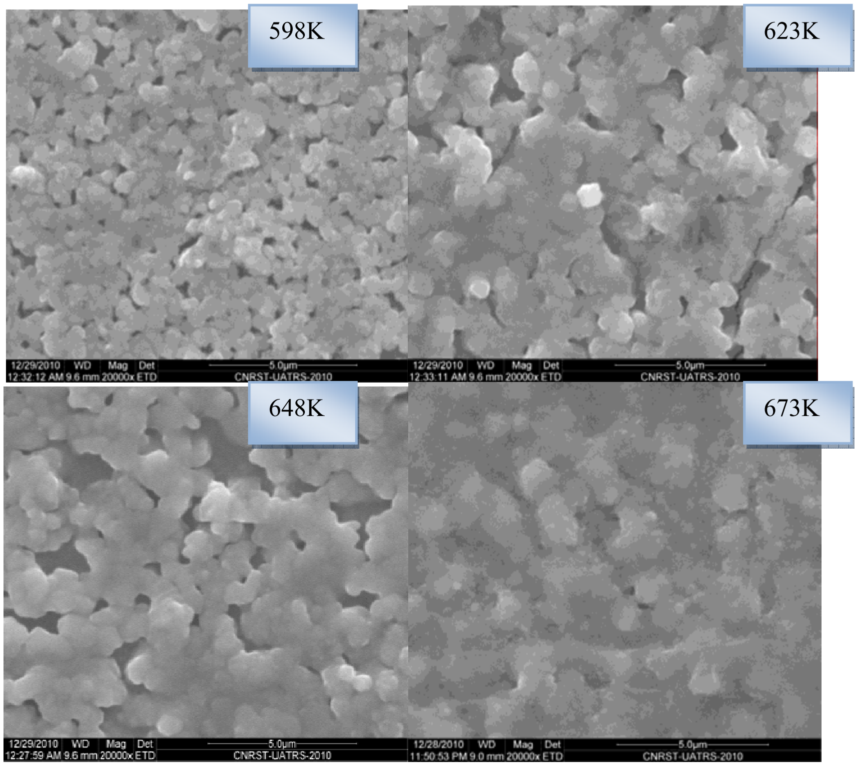

Fig. 3. SEM images of CIS precursor thin film prepared for at various substrate temperatures: 598K, 623K, 648K, and 673K for 60 min spray duration.

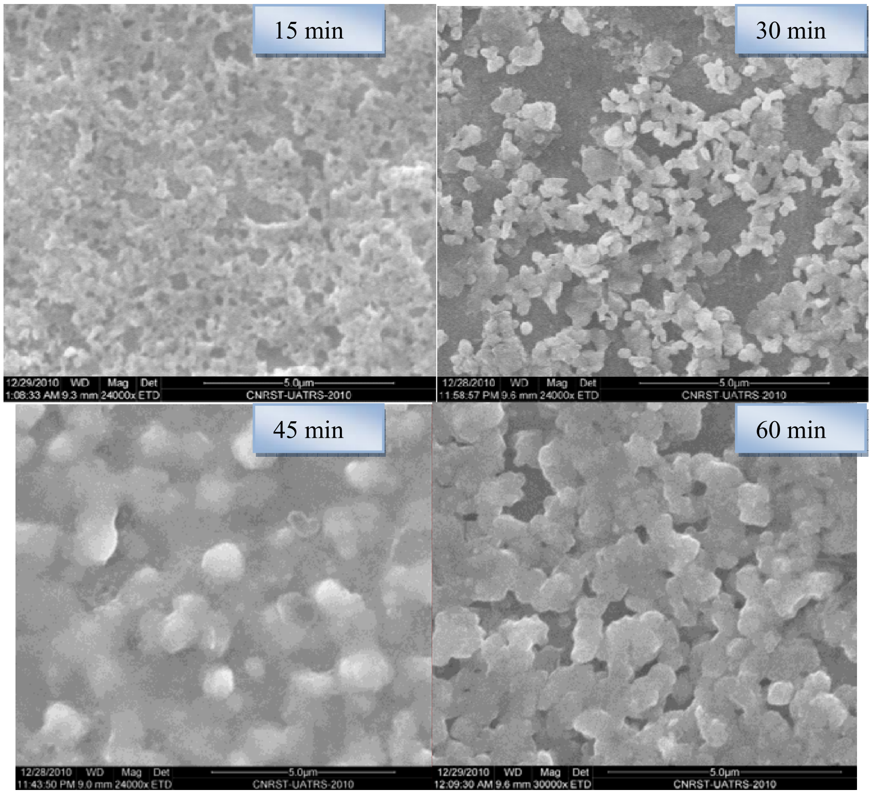

Fig. 4. SEM images of CIS precursor thin film prepared for different spray duration: 15 min, 30 min, 45 min, and 60 min at 648K min spray duration.

3.2.3. Raman spectroscopy

Fig. 5 shows Raman spectroscopy analysis of CIS precursors thin film prepared for different substrate temperatures 598K, 623K, 648K, and 673K during 60 min of spray. As previously mentioned, all CIS films are observed to be grown with two different structures, Cu-Au (CA)-ordered phase and chalcopyrite (CH). A_1 modes for CH and CA-ordering are reported to be observed as the biggest peaks, which appear at 295 cm^{-1} and 304 cm^{-1}, respectively [18-19-20-21]. The broad peaks at 280-310 cm^{-1} indicate that sprayed-films are grown with CH ordering and CA-ordering mixed. Especially, for film fabricated at 648K, A_1 mode of CA-ordering is pronounced, and this feature corresponds to the appearance of (100) peak in XRD result. On the other hand the intensity of A1 mode for CH ordering is seen larger and higher than that for CA-ordering. Also we can observe other peaks at 240 cm^{-1} and 340 cm^{-1} represent Raman modes for CH ordering [18-19-20-21]. Fig. 8 Shows Raman scattering results of same films of Fig. 2. The broad peak at 280–310 cm^{-1} is split into two peaks for all films, which are A1 modes of CH- and CA-ordering. In addition, the peak intensity at 295 cm^{-1} increases in accordance with the spray duration is increased. From the results of Raman scattering measurements, it can be concluded that Raman spectroscopy detects possible structural disorder in CIS film with higher sensitivity.

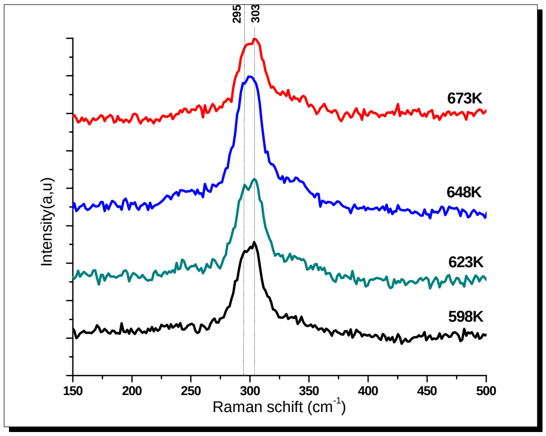

Fig. 5. Raman analysis of CIS precursor thin film prepared at various substrate temperatures: 598K, 623K, 648K, and 673K for 60 min spray duration.

3.3. Optical properties

The optical absorption coefficient (α) was determined from the measured spectral transmittance (T_λ) and reflectance (R_λ) using the following relationship: [22-23]

$$\alpha(hv) = \frac{1}{t} ln \left\{ \frac{(1-R)^2}{2T} + \left| R^2 + \left[\frac{(1-R)^2}{2T} \right] \right|^{1/2} \right\} \qquad (1)$$

Where t is the film thickness. The nature of the optical transition, whether direct or indirect and the optical band gap (E_g) of each film, is obtained from the classical relation [23-24]:

$$\alpha hv - A\left(hv - E_g\right)^n \qquad (2)$$

Where A is a constant. The exponent ‘n’ can take values 1/2, 3/2, 2 and 3 based on whether the optical transition is direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. Thus, if the plot of $(\alpha h\nu)^2$ vs. (hν) is linear, the transition is directly allowed. Also the value of absorption coefficient in the present case is the order of 10^5 cm^{-1}, which supports direct band gap nature of the deposited CIS material. This relatively high absorption coefficient is very important because the spectral dependence of absorption coefficient drastically affects the solar conversion efficiency. Extrapolation, of the straight line to zero absorption coefficients, leads to estimation of band gap energy (E_g) values.

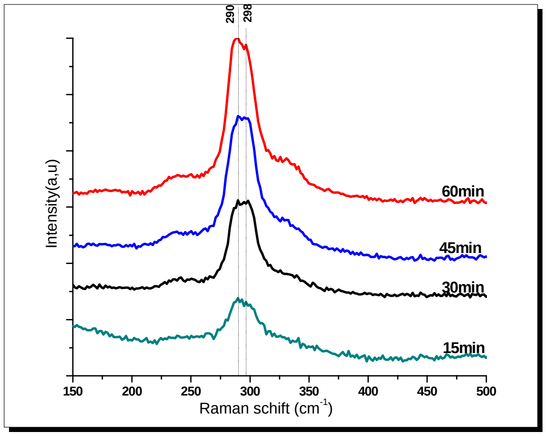

Fig. 6. Raman analysis of CIS precursor thin film prepared for different spray duration: 15 min, 30 min, 45 min, and 60 min at 648K substrate temperature.

Fig. 7 shows variation of $(\alpha h\nu)^2$ as a function of photon energy (hν) for as-deposited precursor film prepared at different substrate temperatures. The decrement in the band gap energies from 1.18 to 1.58 eV with increase in increasing temperature has been observed which is in agreement with the earlier reported E_g values for CIS thin films [24-25-26-27].

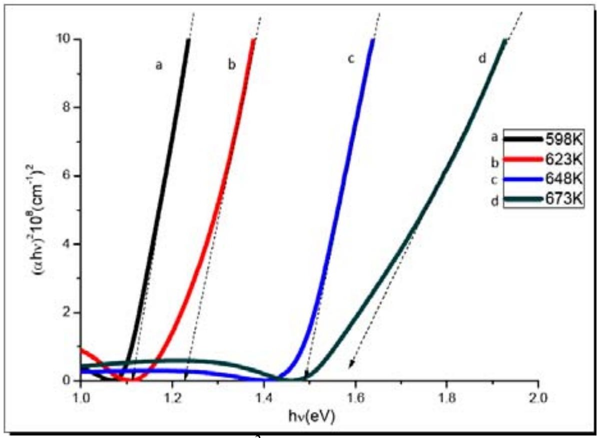

Fig. 7. Variation $(\alpha h\nu)^2$ as a function of photon energy (hν) of CIS precursor thin film prepared for at various substrate temperatures: 598K, 623K, 648K, and 673K for 60 min spray duration.

On the other hand, it can be seen Fig. 8 that Eg decreases from 1.45 to 1.30 eV with increasing of the spray duration from 15 to 60 min. The optical band gap of CIS films prepared by spray pyrolysis at 648 K and 60 min was determined as 1.49 and 1.51 eV respectively. This band-gap energy is quite close to the optimum value for a solar cell. These optical properties show that CIS is suitable for solar cells.

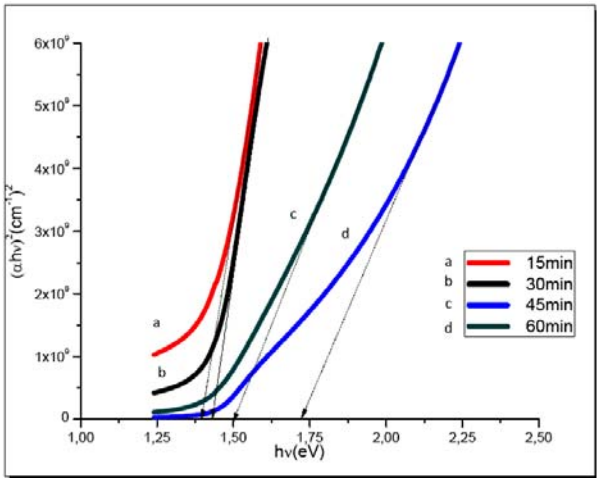

Fig. 8. Variation $(\alpha h\nu)^2$ as a function of photon energy (hν) of CIS precursor thin film prepared for different spray duration: 15 min, 30 min, 45 min, and 60 min at 648K min spray duration.

4. Conclusion

$CuInS_2$ thin films were deposited using pulverization technique (Spray pyrolysis). Among a variety of process parameters in the spray pyrolysis system, the deposition temperature and spray duration ranged from 598K to 673K and 15 min to 60 min respectively. All deposited films were characterized by XRD, Raman scattering, SEM, EDS measurements and absorption technique. The XRD measurements showed that all the films were grown with (112)-oriented texture dominant in the chalcopyrite phase. The intensity of the (112) diffraction peak decreases when the substrate temperature and spray durations rise from 598K to 673K and 15 min to 60 min respectively, indicating that the crystallite size is bigger for films sprayed at 673K and for films prepared at sprayed duration for 60 min. Raman scattering measurement showed that sprayed films were grown with mixture of CH- and CA-ordering. The CA ordering was found to correspond to the sulfur deficiency. SEM observation of the $CuInS_2$ thin films showed that the roughness of films increases with the increase of the growth temperature and spray duration, and consequently the uniformity, growth rate and adhesion of the films depend strongly on the substrate temperature and spray duration. EDS showed that the [Cu]/[In] ratios increased with increasing deposition temperature, this effect indicates that possible formation of the CuS segregated phase at the surface was caused by the higher Cu content and its mobility. The optic band gap of CIS films prepared by spray pyrolysis at 648 K and 60 min was determined as 1.49 and 1.51 eV respectively. These values are smaller than the reported values of 1.50 eV for single crystals of CIS.

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