

Ultrasonic spray deposition of CuInS_2 absorber thin films: effect of nozzle frequency

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Copper indium disulphide (CuInS_2) thin films have a huge potential as absorber layer for thin film photovoltaic applications. In this work, a very simple, and therefore, cost-effective technique, ultrasonic spray pyrolysis, have been used to deposit CuInS_2 films on soda lime glass substrates. Two different nozzles, with 48 and 120 kHz frequencies, were used to control the droplet size of the precursor solution. It has been observed that nozzle frequency had a dramatic effect on both solution consumption and the surface morphology of the films. Scanning electron microscopy (SEM) analysis of the films revealed that 48 kHz nozzle resulted very rough surfaces and low adhesion. On the other hand, 120 kHz nozzle resulted lower deposition yield than 48 kHz nozzle due to the smaller droplet size. Energy Dispersive X-Ray Analysis (EDAX) has been used to determine the chemical structure of sprayed CuInS_2 films. Films deposited using 20 ml precursor solution and 120 kHz nozzle had the closest Cu:In:S atomic ratio to the targeted 1:1:2 value. Crystal structure of the spray-deposited films was confirmed using X-ray Diffraction (XRD) analysis. Regardless of the solution amount and the nozzle frequency, polycrystalline CuInS_2 thin films were observed. All sprayed films showed nanocrystalline nature. As a general trend, optical transmission and band gap energy values of the films decreased with increasing the solution amount for both 48 and 120 kHz nozzles. The absorption coefficient of sprayed CuInS_2 films was found to be in the order of 10^5 – 10^3 cm^{-1} in the wavelength range 200–2000 nm. As a result, in terms of solution consumption 48 kHz nozzle was superior to the 120 kHz nozzle. However, 120 kHz nozzle allows us to obtain more homogenous and well crystallized films.

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1. Introduction

Thin film solar cell technology has been gaining more attention due to its unique properties such as less material need and better device performances [1]. Among I-III-VI₂ chalcopyrite-type mixed crystal semiconductors, CuInS_2 is one of the trending materials for thin film solar cell applications. CuInS_2 used as absorber layer has direct band gap energy of 1.53 eV and high absorption coefficient [2]. Efficiency of the CuInS_2 -based solar cells has been reached to 12.5% for Mo/ CuInS_2 /CdS/ZnO cell-structure [3]. It is very critical to increase the efficiency/production cost ratio for thin film solar cell applications [4]. With this motivation numerous methods have been applied to deposit CuInS_2 thin films such as reactive magnetron sputtering [5], a combination of evaporation and sulfurization processes [6], chemical bath deposition [7], flash evaporation [8] and spray pyrolysis [9]. Among these methods spray pyrolysis (SP) technique has been investigated extensively because it is a very simple, and therefore, cost-effective method [10, 11]. It also allows deposition of thin films on very large areas.

SP process includes precursor solution atomization, droplet transport, solvent evaporation, drying and decomposition of the precursor material [12]. Generally, the following atomization techniques are preferred to

generate droplets in this method: i) air blast [13], ii) electrostatic field [14] and iii) ultrasonic vibration [15]. Ultrasonic generators are usually adapted out of the system and generated droplets are transported through the nozzle over the pipes. However, in this study we have used ultrasonic impact nozzles, which generate droplets by using piezoelectric crystals just before directing mist through the preheated substrates. Hence, it is possible to form very homogenous thin films using this technology. Droplet size in the mist changes as a function of oscillation frequency of the impact nozzle. At last but not least, ultrasonic impact nozzles are superior to other technologies in terms of reducing the over spray, which cuts back production cost and minimizing the atmospheric contamination.

Pyrolysis conditions and film properties are directly affected by the droplet size in the mist. Droplet size can be controlled either by changing solvent type or nozzle frequency. Here, ultrasonic impact nozzle with two different oscillation frequencies, 48 and 120 kHz, has been used to change droplet size while spraying CuInS_2 . 48 and 120 kHz nozzle were generating 38 and 18 μm -sized droplets, respectively. Besides, mist generated by 120 kHz nozzle forms larger cones than that of 48 kHz (Fig. 1).

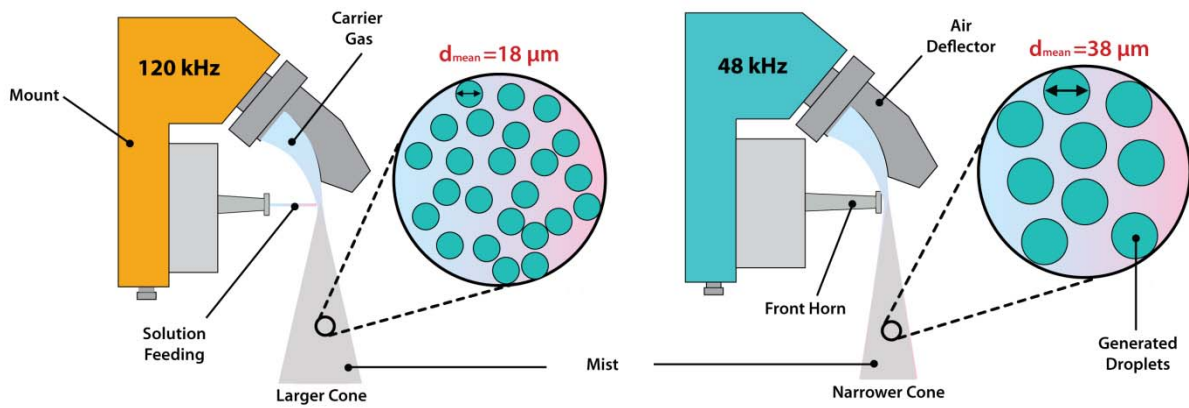


Fig. 1. Structure and comparison of 120 and 48 kHz ultrasonic impact nozzles.

2. Experimental methods

CuCl₂, InCl₃ and NH₂CSNH₂ were dissolved in double distilled water as copper, indium and sulfur sources, respectively. Aqueous precursor solution was sprayed on preheated soda lime glass substrates (26x76x1 mm³) by SonoTek Flexi Coat ultrasonic spray pyrolysis system. The experimental set-up for the deposition has been described in our previous study [16]. Prior to deposition, glass substrates were cleaned with Alconox® solution and acetone. Substrate temperature was kept constant at 350 °C during all experiments. After deposition, samples were allowed to cool at room temperature. The molar ratio of the Cu/In/S in solution and infuse rate were also kept constant for all samples at 1.11/1.00/3.33 and 1.5 ml/min, respectively. Sprayed solution amount has been changed from 5 to 40 ml in order to determine the film formation properties and deposition yield. Nitrogen was used as the carrier gas at 4.0 MPa pressure. Process time was ranging between 25 and 90 min depending on the solution amount. The crystal structure of the films was confirmed using Panalytical, X'pert Pro MPD XRD. The surface morphology of the films was investigated by FEI, Quanta 200 FEG SEM. EDAX microanalysis has been used to evaluate the chemical compositions of the films. Optical transmittance was recorded in wavelength range of 200-2000 nm using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. Electrical measurements were conducted via Keithley 2400 I-V source measure system.

3. Results and discussion

3.1 Structural Properties

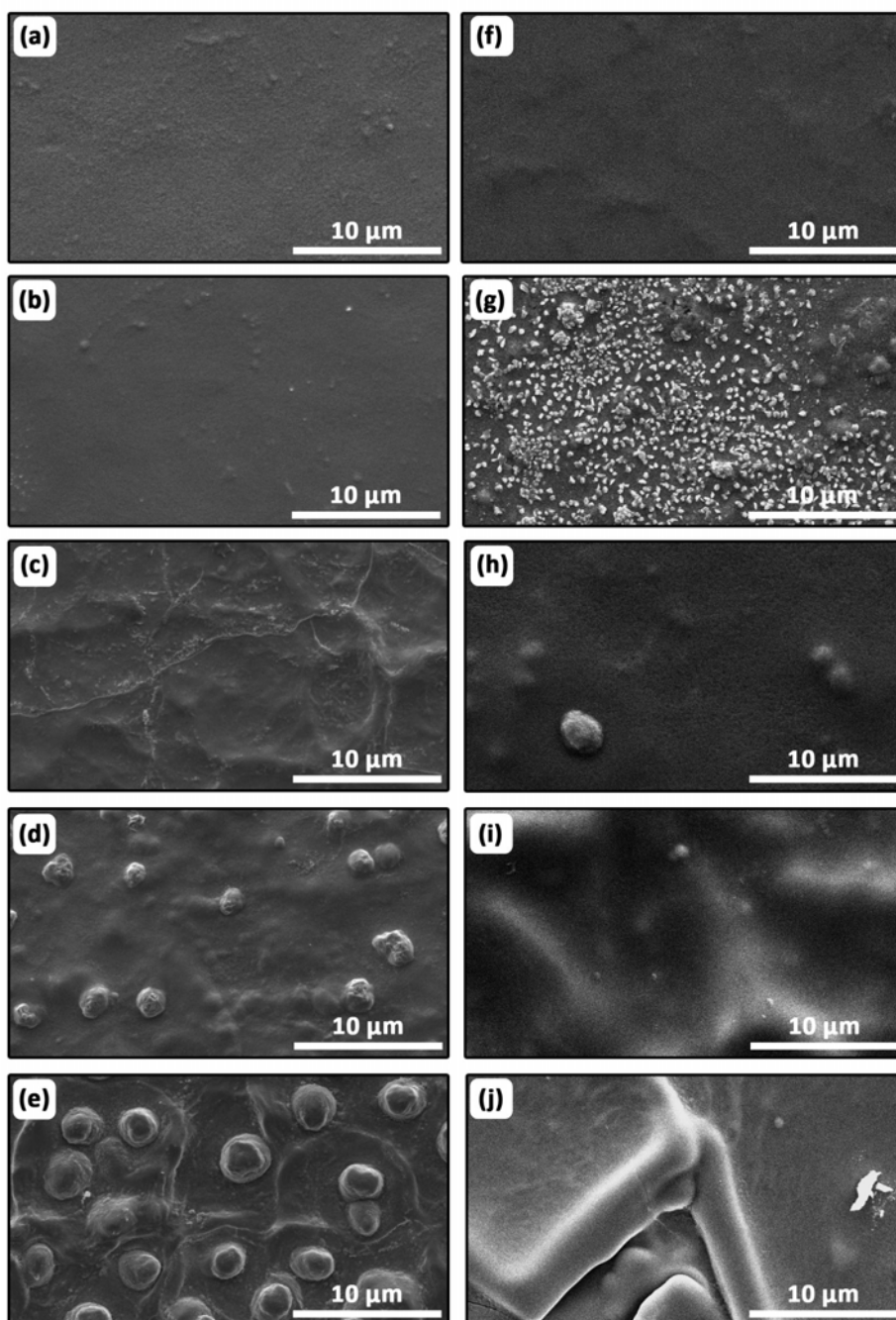
SEM micrographs of the CuInS₂ films prepared with different solution amounts and different nozzle frequencies can be seen in Figure 2. It has been obtained that all CuInS₂ films sprayed with 120 kHz nozzle were pin-hole and crack free. On the other hand, some pin-hole formations have been observed for 48 kHz impact nozzle. Moreover, samples deposited using precursor solution more than 20 ml and 48 kHz nozzle could not retain their uniformity and peeled from the substrate. Surface of 30 ml and 40 ml sprayed films by 120 kHz nozzle contains some agglomerated round shapes. Density of agglomerated areas and surface roughness of the films increased with increasing the solution amount. For the constant substrate temperature and the nozzle-to-substrate distance, smaller droplet size resulted faster solvent evaporation due to the higher surface to volume ratio. Most probably, the larger droplet size of 48 kHz resulted the fast cooling of the substrate, and therefore, defect formation occurred on the surface. Cross sectional SEM studies showed that, thickness of the films for both frequencies increased by increasing the solution amount as expected (Table 1 and Table 2). Also, 120 kHz nozzle resulted thinner films compare to the 48 kHz for the same amount of solution. Hence, it is possible to conclude that 48 kHz nozzle results higher deposition yield due to the more precursor materials transferring to the surface with the help of larger droplets.

Table 1 Some structural, optical and electrical properties of CuInS₂ films deposited via 120 kHz impact nozzle

Solution Amount (ml)	Film Thickness (μm)	E _g (eV)	Mean Crystallite Size (nm)	Max. Peak Intensity at (112) (a.u.)	Bulk Resistivity (Ωm)	PS [(I _L -I _D)/I _D]
5	0.28	2.85	13.63	1208.67	0.52	0.4
10	0.68	2.70	12.70	2430.00	2.96	1.0
20	1.27	1.45	12.37	3195.33	2.80	0.9
30	1.95	1.38	20.77	6555.33	3.47	1.5
40	2.25	1.40	26.72	14508.00	3.42	1.2

Table 2 Some structural, optical and electrical properties of CuInS_2 films deposited via 48 kHz impact nozzle.

Solution Amount (ml)	Film Thickness (μm)	E_g (eV)	Mean Crystallite Size (nm)	Max. Peak Intensity at (112) (a.u.)	Bulk Resistivity (Ωm)	PS $[(I_L - I_D)/I_D]$
5	0.36	2.76	3.53	1078.67	1.55×10^{-1}	0.14
10	0.74	2.42	23.13	4949.33	6.46×10^{-3}	0.05
20	1.15	1.43	17.89	9544.00	6.24×10^{-1}	0.38
30	2.64	1.33	13.40	4976.67	7.39×10^{-2}	0.23
40	3.16	1.30	13.04	3693.33	1.32×10^{-1}	0.35

Fig. 2 SEM micrographs of CuInS_2 thin films deposited with a) 5 ml, b) 10 ml, c) 20 ml, d) 30 ml, e) 40 ml precursor solution by 120 kHz nozzle, f) 5 ml, g) 10 ml, h) 20 ml, i) 30 ml, j) 40 ml precursor solution by 48 kHz nozzle.

Crystal structure of the spray-deposited films was confirmed using XRD analysis. Figure 3 depicts XRD patterns of the films deposited with different solution amounts and nozzle frequencies. All films sprayed over 10 ml solution had intense characteristic chalcopyrite peaks around 27.9° (2θ) and 46.3° (2θ) (JCPDS no. 27-159). No other secondary phases were observed in XRD data. Crystallinity of the films deposited with 120 kHz nozzle increased with increasing solution amount. Both increase in deposition time and thickness of the films with increasing the solution amount could be the reason for this improvement in the crystallinity. Sprayed films with 48 kHz nozzle could not retain its adherence on glass substrates when the solution amount exceeded the 20 ml. This resulted structural changes in the sprayed films so intensity of peaks had a tendency to decrease.

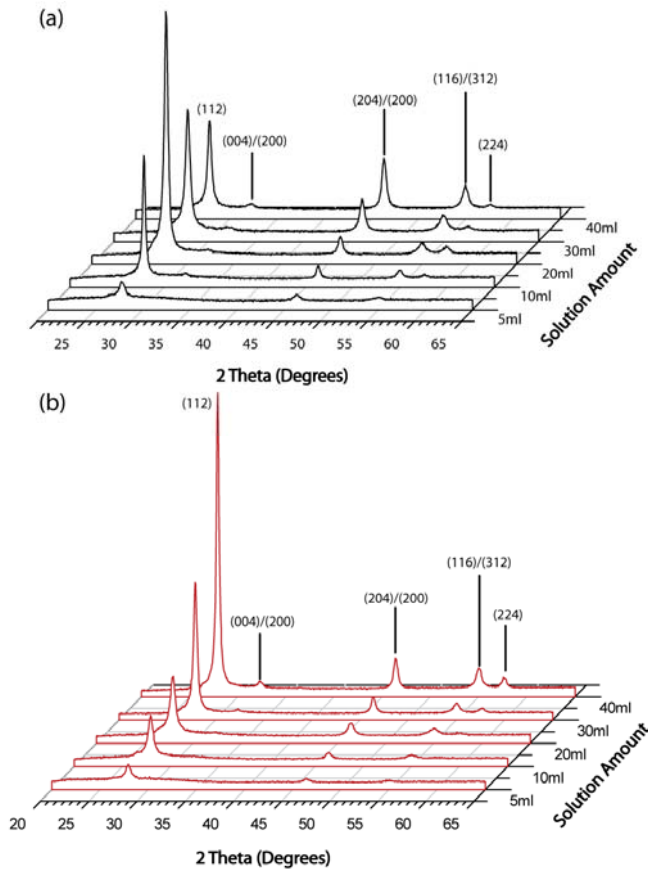


Fig. 3. XRD of ultrasonically sprayed CuInS₂ thin films deposited using a) 48kHz nozzle, b) 120kHz nozzle

The crystallite size of the films were calculated using the most intense diffraction peak observed around $2\theta = 27.9^\circ$ using well known Debye-Scherrer formula;

$$d = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where d is the crystallite size; λ is the X-ray wavelength used; β is the angular line width of half maximum intensity; and θ is the Bragg's angle. As a general trend, mean crystallite size of the films sprayed with 120 kHz nozzle increased with increasing the solution amount (Table 1). The calculated values of crystallite size were ranging between 12.37 nm and 26.72 nm for the films sprayed with 120 kHz nozzle. Similar crystallite sizes have been observed for 48 kHz nozzle. Maximum crystallite size for the CuInS₂ films sprayed with 48 kHz nozzle was 23.13 nm for the 10 ml precursor solution. These values are in good agreement with previously reported data [17, 18].

Atomic concentrations of the sprayed CuInS₂ films have been obtained from EDAX analysis carried out at accelerating voltage of 15 kV and spot size 3 μm. It has been observed that all films were sulphur rich (Figure 4). EDAX analysis also revealed that all sprayed films contained some Cl contamination up to 5.76 % due to the chloride based precursors. On the other hand, we obtained very close Cu, In, S atomic ratios to the targeted 1:1:2 value for the films deposited from 20 ml solution and 48 kHz nozzle. It is also worth to mention here that, In rich structures have been observed from the high acceleration rates most probably due to the Cu diffusion through the surface of the films. Moreover, atomic percent of the copper was higher in the island like structures compare to the flat regions. Therefore, it is possible to conclude that when the solution amount, and the production time increased Cu_xS phases were segregated on the surface of the films without the dependence of solution amounts. Sherer et al. reported the formation of similar island like Cu_xS phases on the surface of co-evaporated CuInS₂ films [19].

As a general trend, Cu/In and S/In ratio in the film increased with increasing solution amount for 48 kHz nozzle (Fig. 5). 20 ml solution sprayed films using 120 kHz nozzle showed the closest values for targeted Cu:In:S=1:1:2 stoichiometry.

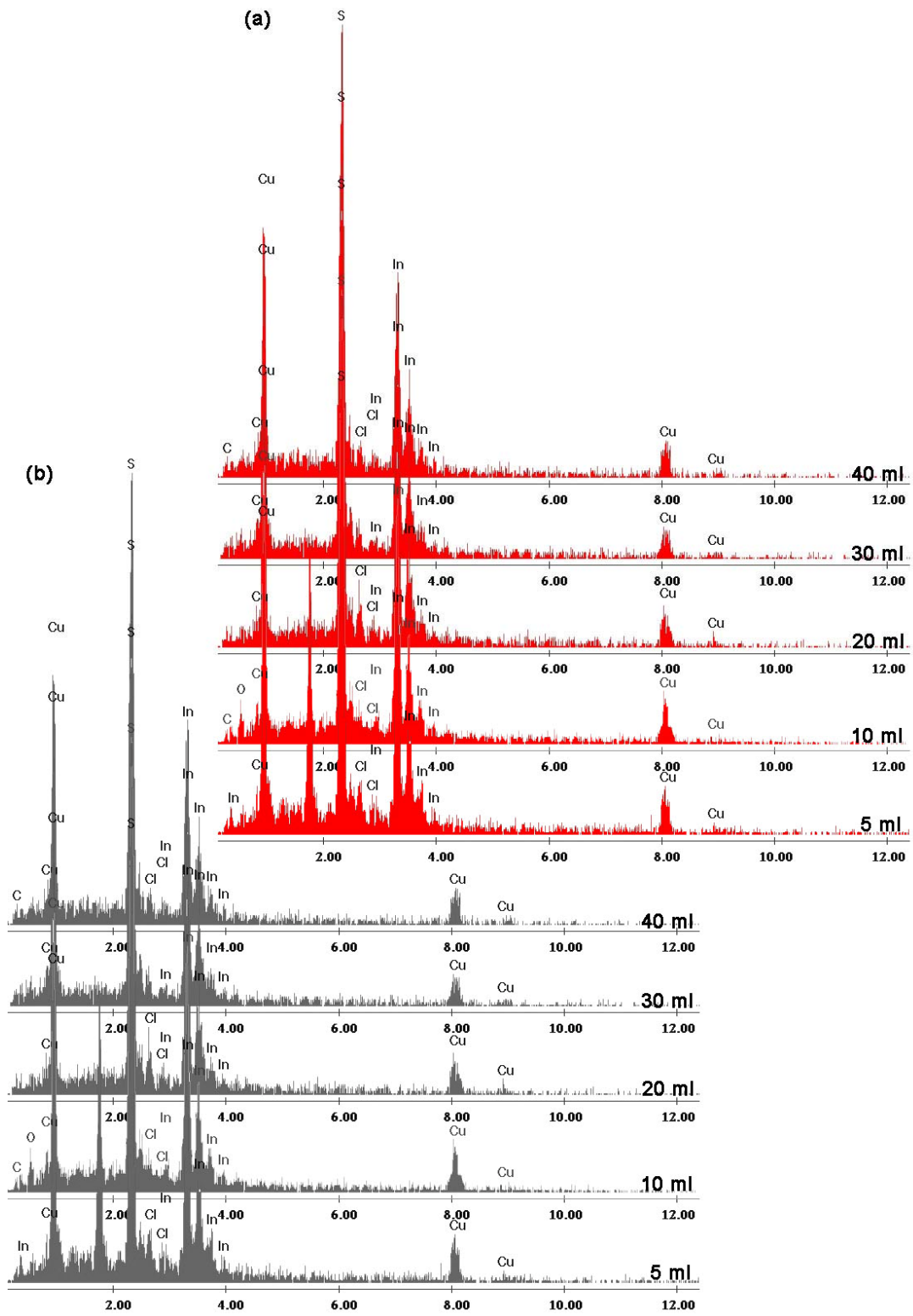


Fig. 4 EDAX spectrum of 20 ml precursor solution sprayed CuInS_2 thin films deposited by a) 48kHz nozzle, b) 120kHz nozzle

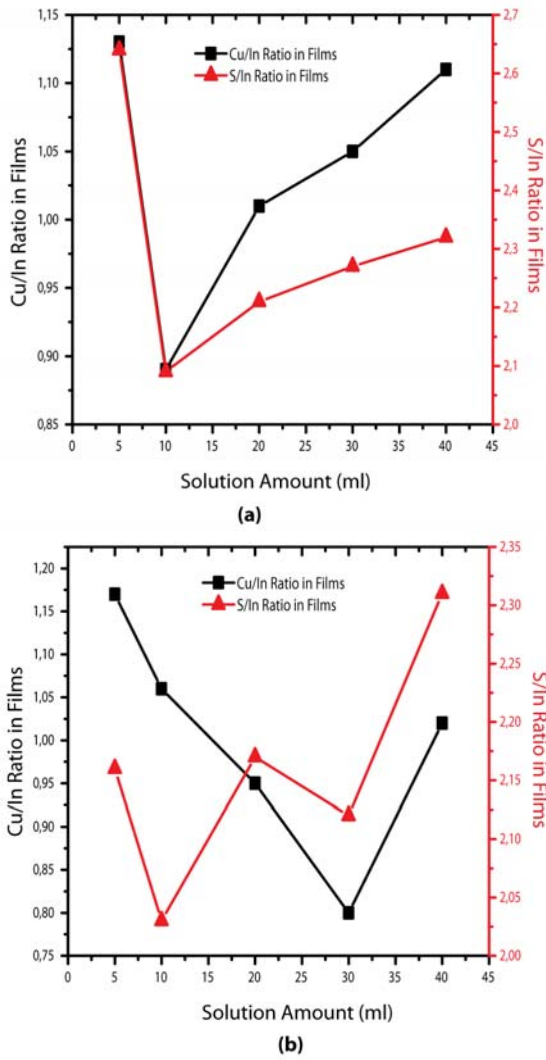


Fig. 5 Variation of stoichiometry in CuInS₂ films deposited by a) 48kHz, b) 120kHz nozzle as a function of solution amount .

3.2 Optical Properties

Fig. 6 shows the optical transmittance versus wavelength plots of the CuInS₂ films deposited using various amounts of precursor solution. Absorption coefficient and band gap values for sprayed CuInS₂ films were determined from the optical transmission data. $(\alpha h\nu)^2$ versus photon energy plots were used to calculate band gap values of sprayed CuInS₂ films. For an allowed direct band gap transition, the absorption coefficient can be related to the photon energy $h\nu$ by;

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (2)$$

where A is a constant, and E_g is the energy gap. It has been observed that band gaps of CuInS₂ films decreased with increasing solution amount as a general trend. As expected, transmittance of sprayed films decreased with increasing the solution amount. Afforementioned, films could not retain their adherence and peeled from the

surface when the sprayed solution amount exceeded 20 ml CuInS₂ for 48 kHz nozzle. This resulted the increase in transmittance of the films deposited using 40 ml solution (Figure 6-b). As a general trend, band gaps of films decreased with increasing the solution amount. Regardless of the nozzle frequency, optimum band gap values were calculated for the 20 ml solution sprayed films. These values were 1.45 and 1.43 eV for the 120 and 48 kHz nozzle, respectively (Table 1 and Table 2). Finally, it can be concluded that nozzle frequency has no pronounced effect on the band gap values of CuInS₂ films.

The absorption coefficient of the samples prepared using both 120 and 48 kHz were increasing with decreasing the precursor solution amount. This was most probably due to the increase in trap levels by increasing the solution amount or the thickness of the films. The highest absorption coefficient obtained in the examined wavelength region was about $\sim 10^5 \text{ cm}^{-1}$. This confirms that sprayed films are suitable candidates as absorber layer for thin film solar cell applications [11].

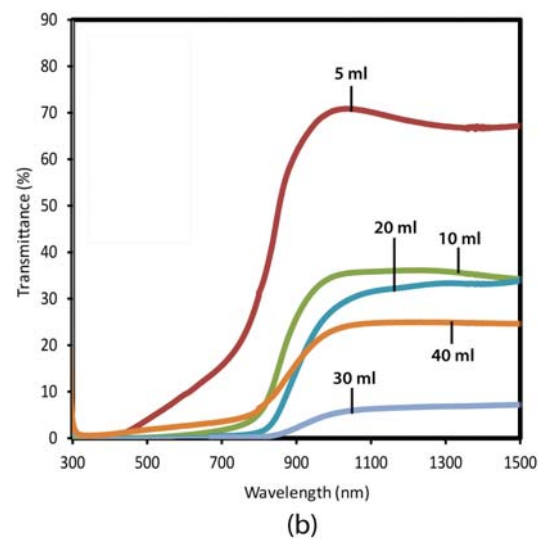
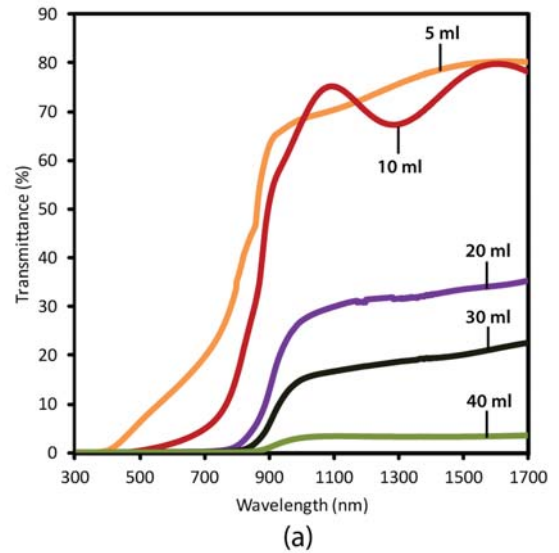


Fig. 6 Transmittance vs wavelength plots of CuInS₂ thin films deposited via a) 120kHz nozzle, b) 48 kHz nozzle.

3.3 Electrical Properties

Bulk resistivity measurements of the films were conducted via 2 point-probe technique. Silver contacts are sputtered on the films with 2.5 mm distance between two strips. Bulk resistivity values were calculated using the following well-known equation;

$$\rho = \frac{R.A}{l} \quad (3)$$

where ρ is the resistivity, R is the resistance of the film, A is the cross sectional area and l is the lateral distance between silver contacts. Although, bulk resistivities of the CuInS_2 did not change much with nozzle frequency, 48 kHz nozzle resulted more conductive films except 20 ml solution (Figure 7-a). Photosensitivity (PS) measurements of the sprayed CuInS_2 films were also performed via 2 point-probe technique. Samples were illuminated using a Xenon short arc lamp, with intensity 150 W/m^2 , on the substrate surface. PS values calculated using the following formula:

$$\text{PS} = (I_L - I_D) / I_D \quad (4)$$

where I_L represents the current under illumination and I_D represents the dark current. Figure 7-b shows the variation in PS with solution amount for 48 and 120 kHz nozzles. All sprayed films showed very low PS values. The maximum PS value, was obtained for the films deposited using 30 ml solution and 120 kHz nozzle. It can be concluded that PS of CuInS_2 was not directly related to the solution amount. However, film obtained by 120 kHz nozzle showed higher PS values than that of 48 kHz. Aforementioned, Cu amount in the films increased with increasing spraying solution volume. Cu rich films showed better crystallinity as shown XRD spectra (Figure 3). Better crystallinity and low resistivity of the Cu rich films could be the reason of low photosensitivity. Hot-probe technique was used to determine the type of conductivity of the films. According to these studies, both CuInS_2 films sprayed using 48 kHz and 120 kHz impact nozzle showed p-type conductivity.

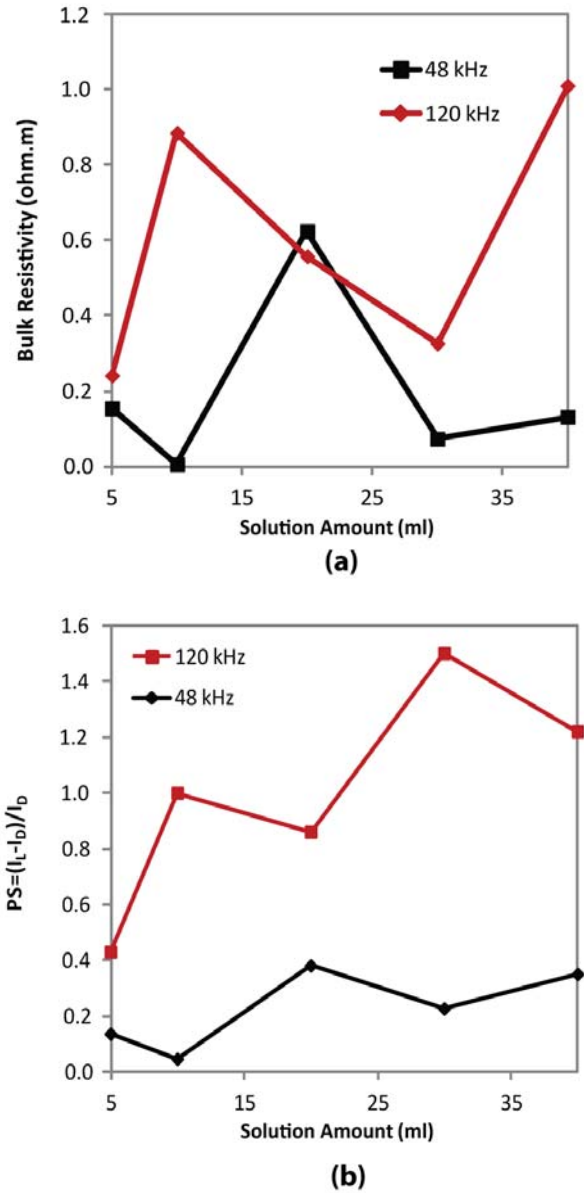


Fig. 7 Variation of a) bulk resistivity, b) PS of the CuInS_2 films with different amount of solutions

4. Conclusions

It has been observed here that uniformity, growth rate and adhesion of the spray pyrolyzed CuInS₂ films strongly depended on the nozzle frequency. In other words, smaller droplet size in the mist resulted more homogenous and adhered films. Although, 48 kHz nozzle were superior to 120 kHz nozzle in terms of solution consumption, some pin-hole and crack formations were obtained on the surface of CuInS₂ films deposited by 48 kHz nozzle. Moreover, 120 kHz nozzle provided better optical and electrical properties. There has been no evidence for Cu-rich secondary phase formation on the surface of CuInS₂ thin films deposited using precursor solution less than 30 ml for 120 kHz nozzle. This helps to avoid highly toxic KCN etching process before fabricating cells. Finally, ultrasonic impact nozzles used in this study lowered dramatically the solution consumption compare to the other solution based manufacturing technologies. This is a key for commercialization and large area application of spray deposited solar cells. According to best of our knowledge both 0.010 ml/mm² (48 kHz nozzle) and 0.015 ml/mm² (120 kHz nozzle) solution consumption obtained here were the highest deposition rate reported in literature.

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