

# Characterization of Spray Pyrolysed CuInS<sub>2</sub> Thin Films

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**Abstract:** An indigenously developed chemical spray pyrolysis system was used to deposit polycrystalline CuInS<sub>2</sub> thin films. It was found that smaller spray rate results in films with better crystallinity and lower resistivity. Increase in surface roughness of the films was observed for higher spray rates. Variations in film stoichiometry with composition of spray solution were analyzed along with its opto-electronic and structural properties. Sulfur rich starting solution with equimolar ratio of copper and indium resulted in nearly stoichiometric p-type CuInS<sub>2</sub>. Type conversion, modification of surface morphology and wide range of opto-electronic properties could be achieved by large off-stoichiometric variations. Temperature dependent conductivity study was used for defect analysis and levels at 436 meV, 294 meV, 131 meV, 76 meV and 50 meV were identified.

**Keywords:** Chemical spray pyrolysis, CuInS<sub>2</sub>, defect study.

## 1. INTRODUCTION

The ternary compound CuInS<sub>2</sub>, has attracted attention as a promising material for photovoltaic applications, due to its optimum direct band gap of 1.5 eV, easiness of type conversion and nontoxic constituents [1, 2]. CuInS<sub>2</sub> based solar cells have reached efficiencies of above 10% [3]. Efficiency of 9.5% was achieved by our group, for an all sprayed solar cell, having CuInS<sub>2</sub> as the absorber layer and In<sub>2</sub>S<sub>3</sub> as the buffer layer [4].

Chemical spray pyrolysis (CSP) is an attractive method of thin film deposition, as large-area films can be grown economically. In this method, composition of the film is controlled effectively, by varying concentration of constituents in the spray solution. As a result, films with wide range of compositions could be prepared unlike any other deposition processes. Ease with which doping can be done by incorporating dopants in spray solution and possibility of variation of stoichiometry along depth by multiple spray, are the other advantages of this technique. Versatility of this process makes it suitable for depositing thin films of compound semiconductors. Moreover, CSP is a scalable process and hence can be used for depositing large area films, which is essential for solar cell applications [5].

Already much works on spray pyrolysed CuInS<sub>2</sub> has been reported, where effect of deposition parameters like substrate temperature [6], ratio between Cu/In and S/Cu [7] etc has been studied. But not much works have been done in the optimizing spray rate. Present work specifically deals study of effect of spray rate on the properties of film formed and also effect of Cu/In and S/Cu ratio variations at very small spray rates. Also, since reports on defect studies in sprayed CuInS<sub>2</sub> films are scarce, defect analysis of the samples were also given importance.

In the present work, CuInS<sub>2</sub> thin films were prepared at different spray rates and characterized. Fixing the spray rate at an optimum value, Cu/In and S/Cu ratios were also varied over a wide range so as to study the effect on film properties. With these studies, we aimed at a better understanding of structural, optical and electrical properties as well as defect chemistry of CuInS<sub>2</sub> thin films prepared using CSP technique.

## 2. METHODOLOGY

CuInS<sub>2</sub> thin films were deposited on glass substrates. Cleaned glass slides were placed on a base plate (mild steel) and heater rods embedded in it facilitated heating. The substrate temperature was maintained with the help of a feedback circuit that controlled the current flow to the heater coil. In our indigenously developed automated spray system, temperature of the substrate could be varied from room temperature to 723 K. During spray, substrate temperature was kept constant at 573 K with an accuracy of  $\pm 5$  K. Spray head and heater with substrate were kept inside a chamber with an exhaust fan for removing gaseous byproducts and vapors of solvent. Aqueous solution, containing required quantities of CuCl<sub>2</sub>, InCl<sub>3</sub> and Thiourea (CS (NH<sub>2</sub>)<sub>2</sub>) was sprayed onto the substrate, using compressed air as carrier gas. The carrier gas and the solution were fed into the spray nozzle at a constantly maintained pressure and flow rate. The carrier gas flow rate could be varied in the range 0 to  $2 \times 10^4$  kg/m<sup>2</sup> while the solution flow rate could be varied from 1ml/minute to 8 ml/minute. The spray head can scan an area of 150 mm x 150 mm (X and Y directions). The X movement was at a speed of 100 mm/sec and the movement in Y-direction was in steps of 50 mm/sec. The microcontroller of the device communicates with PC through serial port and the data of each spray can be stored in the PC.

Fixed volume of CuInS<sub>2</sub> solution was sprayed at spray rates of 1ml/min, 2 ml/min and 4 ml/min. Films were not formed at still larger spray rates. These samples were named CIS1, CIS2, and CIS4 respectively and were characterized using X-Ray diffraction (XRD), optical absorption and resistivity studies to find the most optimum spray rate. Fixing the

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spray rate at optimum value, Cu rich, equimolar and In rich samples were prepared, in which Cu/In ratio was 1.5, 1 and 0.5 respectively, keeping S/Cu ratio constant (S/Cu = 5). These samples were named as CIS 0.5-5, CIS 1.0-5 and CIS 1.5-5 respectively. To study the effect of variation of chalcogen concentration in the film, S/Cu ratio was changed, keeping Cu/In = 1. The S/Cu ratios were varied as 2, 5 and 10 and the samples were named as CIS 1.0-2, CIS 1.0-5 and CIS 1.0-10 (the sample C1.0-5 is same as that mentioned above in Cu/In variation studies). In all the cases, the substrate temperature was maintained at 573 K, and volume of the spray solution was 40 ml.

Thickness and roughness of the films were measured using stylus profiler (Dektak 6M). Crystallinity of the films was analyzed using Rigaku (D. Max. C) X-Ray diffractometer employing  $\text{CuK}\alpha$  line ( $\lambda = 1.5405 \text{ \AA}$ ) and Ni filter operated at 30 kV and 20 mA. Chemical composition was determined with the help of energy dispersive X-Ray analysis (EDAX) technique (JEOL JSM-840). Surface morphology of the samples was studied employing scanning electron and atomic force microscopes (AFM-Nanoscope-E, Digital Instruments, USA, in contact mode). A UV-VIS-NIR spectrophotometer (Model Jasco V 750) was used for the studies on optical properties.

Resistivity and photosensitivity were measured employing Keithley 236 source measure unit. Electrical contacts were given through two silver paint patches separated by 5 mm. The sample was illuminated with the help of a tungsten halogen lamp with intensity  $100 \text{ mW/cm}^2$  through an IR filter and water column, kept in between the sample and the light to prevent heating of the sample. Temperature dependent conductivity study was performed using IMS 2000, Lab Equip setup.

### 3. RESULTS AND DISCUSSIONS

#### a) Effect of Variation of Spray Rate

It was observed that spray rate played a decisive role in controlling the uniformity and adhesion of the films. Smaller spray rates favoured formation of uniform films devoid of pinholes or cracks. Increasing the spray rate beyond 4ml/min resulted in powdery discontinuous deposits. All the films deposited had thickness of  $\sim 0.25 \mu\text{m}$ , but the rms roughness increased with increase in spray rate from 28 nm for CIS1 to 40nm for CIS4.

XRD pattern of films deposited at different flow rates are given in Fig. (1). The d values coincided with that of  $\text{CuInS}_2$  (JCPDS data card 270159) with preferential orientation along (112) plane. The grain size was calculated using Debye Scherrer formula [8],  $D = 0.9\lambda/\beta \cos\theta$ , where D is the diameter of the crystallites forming the film,  $\lambda$  is the wavelength of  $\text{CuK}\alpha$  line,  $\beta$  is the FWHM in radians and  $\theta$  is the Bragg angle. Increase in spray rate resulted in formation of smaller crystallites as observed from the broadening of XRD peak. The calculated value of grain size decreased from 25.3 nm for CIS1 to 8.4 nm for CIS4.

From the plot of  $(\alpha h\nu)^2$  vs  $h\nu$ , it was found that band gap increased from 1.3 eV to 1.4 eV as flow rate varies from 1 ml/min to 4 ml/min (Fig. 2). Here  $h\nu$  is energy in eV and  $\alpha$  is the absorbance. Consequently, resistivity of the samples also increased from 0.023 ohm-cm to 0.420 ohm-cm, which

can be explained in terms of smaller grain size and higher band gap. For further studies the spray rate was fixed at 1ml/min as lower spray rate favoured formation of films with superior surface morphology, opto-electronic and structural properties.

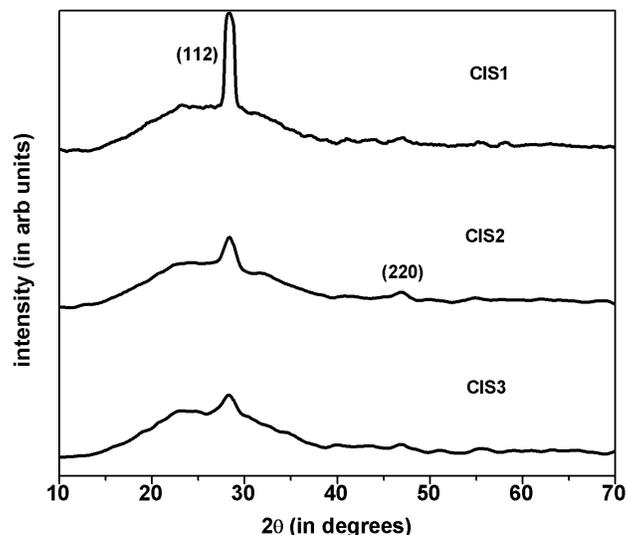


Fig. (1). XRD pattern of samples prepared at different spray rates.

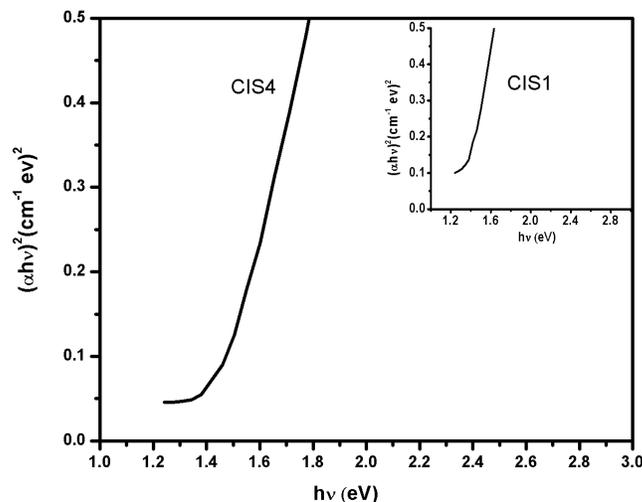


Fig. (2).  $(\alpha h\nu)^2$  vs  $h\nu$  graph of samples prepared at different spray rates.

#### b) Effect of Variation of Cu/In and S/Cu Ratios

Systematic study was conducted on samples deposited by varying the molarities of precursor solutions. Atomic concentrations of Cu, In and S in the films were obtained through EDAX analysis and the results are given in the Table 1 and 2. EDAX measurements were taken from different points of each sample and average value was tabulated. It was observed that variation of Cu/In ratio in the spray solution resulted in corresponding change in the composition of the films, as expected. But the Cu/In ratios from EDAX were

not exactly same as the ratios taken in the solution. However it was difficult to control Sulfur concentration.

**Table 1. Atomic Concentration from EDAX of Samples Prepared with Different Cu/In Ratio Keeping S/Cu=5 in Solution**

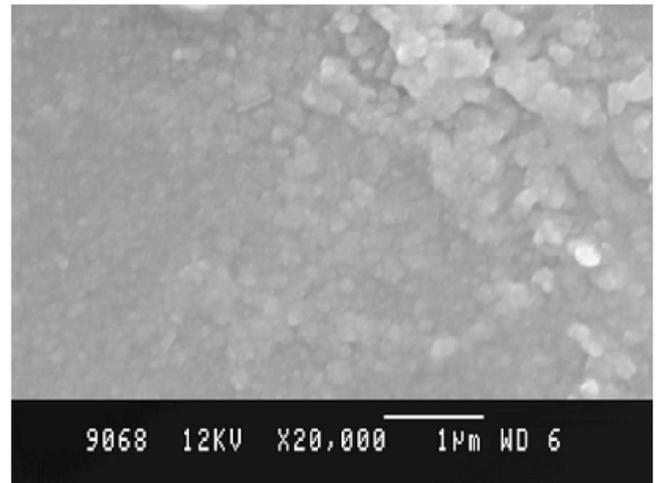
Sample Name	Cu/In Ratio in Solution	Cu%	In%	S%	Cl%
CIS 0.5-5	0.5	14.8	30.25	47.8	7.15
CIS 1.0-5	1	22.37	24.26	46.58	6.78
CIS 1.5-5	1.5	28.3	22.85	48.8	0.05

**Table 2. Atomic Concentration from EDAX of Samples Prepared with Different S/Cu Ratio Keeping Cu/In=1 in Solution**

Sample Name	S/Cu Ratio in Solution	Cu%	In%	S%	Cl%
CIS 1.0-2	2	35.98	16.47	37.49	10.06
CIS 1.0-5	5	22.37	24.26	46.58	6.78
CIS 1.0-10	10	25.66	23.21	46.45	4.68

Percentage of Cu increased from 14.8 to 28.3 in the sample, as Cu/In ratio was changed from 0.5 to 1.5 in the solution. In these films, S concentration remained more or less constant. In CIS 1.5-5, the composition varied largely from point to point due to the formation of agglomerated Cu rich areas, as seen in SEM micrograph (Fig. 3). EDAX taken specifically from the agglomerated area showed copper concentration as 36.01% and Cu/In ratio in this region as 2.01. AFM studies revealed significant variations in the surface morphology of the samples (Fig. 4). Films formed from Cu rich solutions showed formation of sharp edged crystallites as observed from increase in surface roughness, while indium rich samples promoted formation of smoother film

surface. Krunks *et al.* have observed similar results on spray pyrolysed CuInS<sub>2</sub> thin films [6].

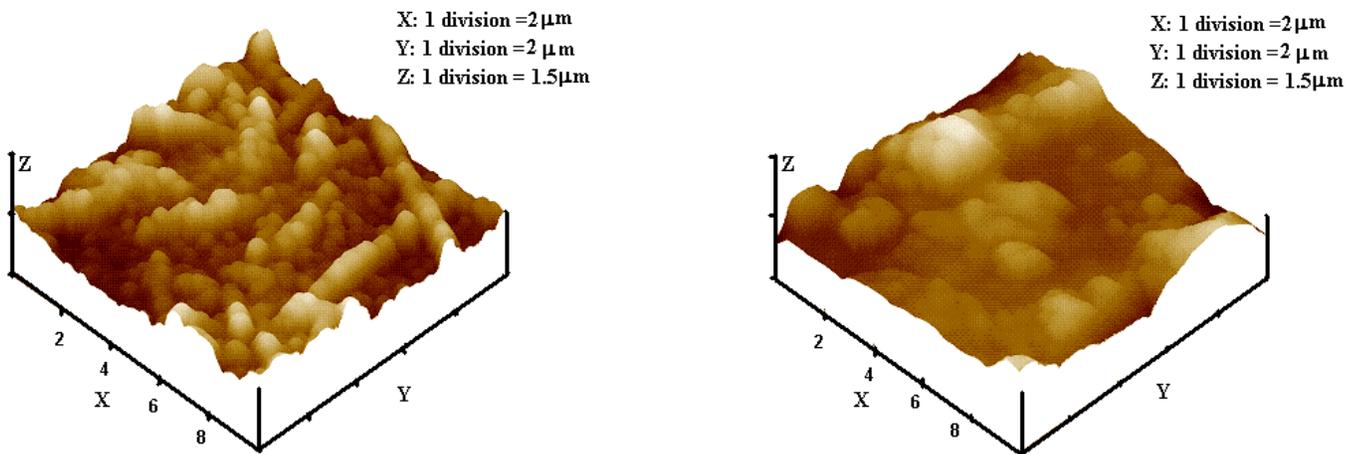


**Fig. (3).** Scanning Electron Micrograph of Cu rich CuInS<sub>2</sub> (CIS 1.5-5).

For CIS 1.0-2, the film obtained was S deficient (37.49 %). Also, this sample was Cu rich (35.98%), though we had kept the Cu/In ratio in the solution to be 1. Sulfur concentration increased to 46.54 % for the sample CIS 1.0-5. But no further significant increase was observed even after increasing the S/Cu ratio in the solution to 10. Chlorine was present in all the samples.

XRD pattern of the films, deposited with different Cu/In and S/Cu ratios, are depicted in Figs. (5, 6). The d values coincided with those of CuInS<sub>2</sub> (JCPDS data card 270159) with preferential orientation along (112) plane. Lattice constants were calculated to be a = 5.53 Å and c = 11.00 Å, which also matched well with the standard values a = 5.52 Å and c = 11.12 Å. No characteristic peaks corresponding to the chalcopyrite phase were observed.

Intensity of the peak corresponding to (112) plane increased with increase in Cu concentration, as shown in Fig.



**Fig. (4).** AFM images of Cu rich (left) and In rich (right) CuInS<sub>2</sub>.

(5). Grain size was calculated to be 25 nm for Cu rich films and decreased to 9 nm for indium rich films, which was evident from the broadening of maximum intensity peak. XRD peak corresponding to (109) plane of  $\text{In}_2\text{S}_3$  was observed in indium rich films (JCPDS data card 25-390).

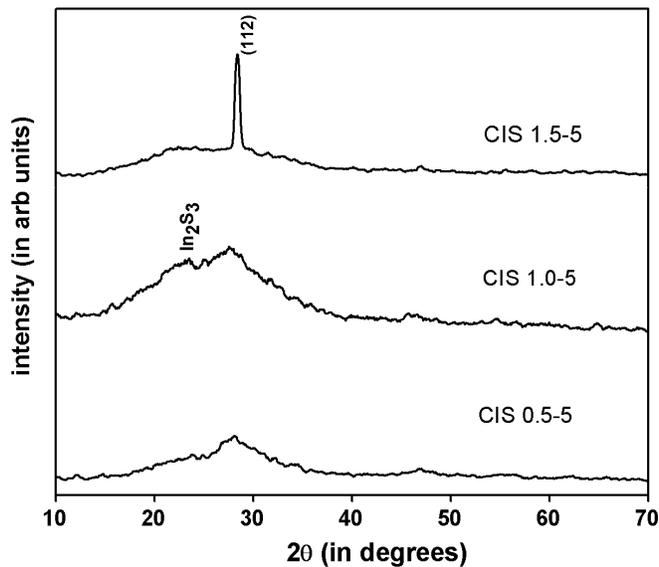


Fig. (5). XRD pattern of samples prepared with different Cu/In ratio keeping S/Cu = 5.

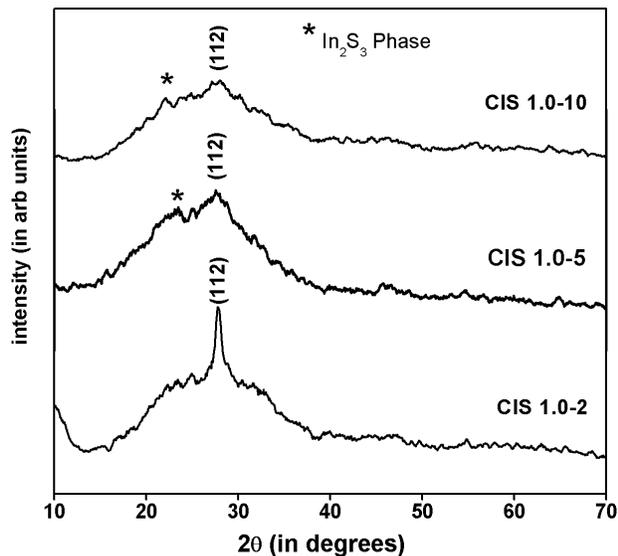


Fig. (6). XRD pattern of samples prepared with different S/Cu ratio keeping Cu/In = 1.

In sample CIS 1.0-2, there was an unintentional increase of Cu concentration (observed from EDAX), which might be the reason for the increase in intensity of (112) peak. It had been observed that Cu rich starting solutions promoted recrystallization and crystal growth in the film. Improvement of crystallinity of Cu rich films may be attributed to Cu mobility [9]. Samples CIS 1.0-5 and CIS 1.0-10 had broad peaks, indicating poor crystalline nature of these samples. Also,  $\text{In}_2\text{S}_3$  was present as secondary phase in these two samples.

Optical band gap of  $\text{CuInS}_2$  thin films were deduced from plot of  $(\alpha h\nu)^2$  vs  $h\nu$  by extrapolating the straight line from high absorption region (Figs. 7, 8). It was observed that the

band gap decreased with increase of Cu/In ratio. It was found to be 1.55 eV for the sample CIS 0.5-5, 1.44 eV for CIS 1.0-5, and decreased further to 1.35 eV, in the case of CIS 1.5-5. Carrier degeneracy in  $\text{CuInS}_2$  due to defects in the lattice was reported as a possible cause for this decrease in band gap [9].

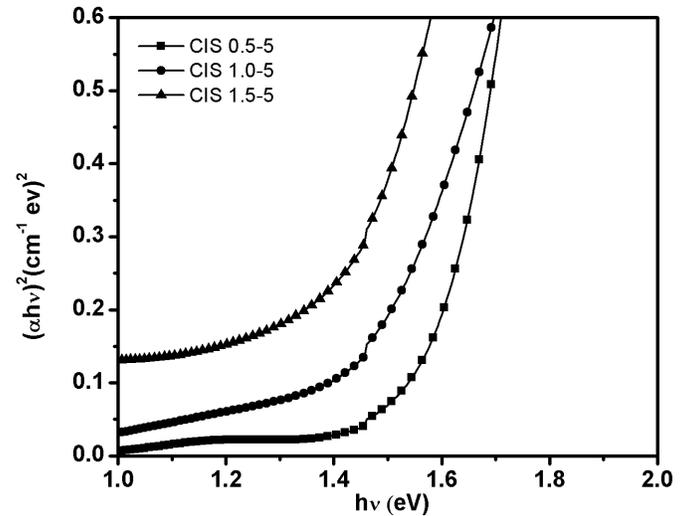


Fig. (7).  $(\alpha h\nu)^2$  vs  $h\nu$  graph of films prepared with different Cu/In ratio keeping S/Cu = 5 in solution.

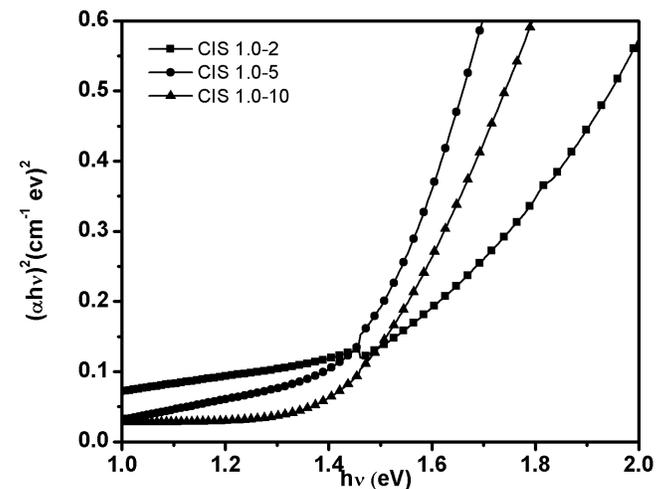


Fig. (8).  $(\alpha h\nu)^2$  vs  $h\nu$  graph of samples prepared with different S/Cu ratio keeping Cu/In = 1 in solution.

In the case of CIS 1.0-2, the band gap was found to be 1.34 eV. When S/Cu ratio increased to 5, this increased to 1.44 eV. Interestingly, no change in band gap was observed when the sulfur concentration was further increased to 10. This might be because there was no significant difference between the compositions of films with the increase in S/Cu ratio from 5 to 10, as seen from EDAX results.

Type of conductivity in the films was checked using 'hot probe method'. In hot probe or thermoelectric probe method, the conductivity type is determined by the sign of thermal emf generated by the temperature gradient between two probes kept in contact with the sample surface of which one is hot and the other cold. In a voltmeter whose positive ter-

terminal is connected to the hot probe and negative terminal to the cold probe is kept in contact with an n-type material, a positive voltage is detected. For a p-type material the voltage detected is negative [10]. CIS 0.5-5 was found to be n-type and CIS 1.0-5 and CIS 1.5-5 were p-type. It was observed that, as Cu/In ratio increased from 0.5 to 1.5, the resistivity decreased drastically by 5 orders (from 8000 ohm-cm to 0.023 ohm-cm) and photosensitivity decreased. This might be due to the fact that decrease of indium (which formed donor states) was causing increase of carrier concentration in p-type samples.

Sulfur deficient films (CIS 1.0-2) showed a fluctuating nature between n and p type i.e. the thermo emf developed changed between positive and negative. Sulfur deficient CuInS<sub>2</sub> usually tend to be n-type and variation of sulfur concentration over the sample area may be the cause of fluctuating nature. Resistivity was high for CIS 1.0-5 and CIS 1.0-10, compared to the one having S/Cu ratio 2. Interestingly photosensitivity of the sample with S/Cu = 5 was larger compared to the other two samples.

Dark conductivity of the films was measured as a function of temperature (100 K-450 K). Using this study, activation energies of intrinsic defect levels in sprayed CuInS<sub>2</sub> were obtained. This study opened up possibility of defect control in this type of samples, through intrinsic doping.

In low temperature range, conductivity increased slowly with temperature, while in high temperature region it increased more sharply. From  $\ln(\sigma)$  vs  $1000/T$  graph, activation energies were calculated (Figs. 9, 10). Two deep levels at 436 meV and 294 meV were obtained for CIS 0.5-5. Deep defects at 500 meV and 300 meV were reported for CuInS<sub>2</sub> in earlier works too, where films were prepared by a sequential process in which copper and indium were deposited by sputtering followed by annealing in S atmosphere [11]. When Cu/In ratio was increased to 1, conductivity also enhanced. Activation energies of 131 meV and 76 meV were obtained in this sample (CIS 1.0-5). These shallower levels were assigned to  $Cu_{in}$  and  $V_{Cu}$  respectively, which were acceptor defects. These defects were the most probable ones as the samples were p-type and EDAX measurements revealed a slight deficiency of copper. Since Cu and In had comparable sizes, this type of antisite defect formation was possible. Reported values of activation energies of  $Cu_{in}$  (150 meV) and  $V_{Cu}$  (80 meV) were also in agreement with our results [12]. When Cu concentration was further increased (CIS 1.5-5), only very shallow levels (~10 meV) were obtained.

In CIS 1.0-5 and CIS 1.0-10, the defect levels obtained were  $Cu_{in}$  and  $V_{Cu}$ . When S concentration was decreased (CIS 1.0-2), in addition to the acceptor level due to  $V_{Cu}$ , a level at 50 meV was obtained. This level was assigned to be  $V_s$ , (35-55 meV) which is a donor [13]. The EDAX results as well as type fluctuation in this sample also supported this analysis.

#### 4. CONCLUSION

From the present study it was observed that structural, electrical and optical properties of CuInS<sub>2</sub> thin films prepared using the CSP technique, could be controlled by varying the spray parameters and/or atomic ratio of the spray

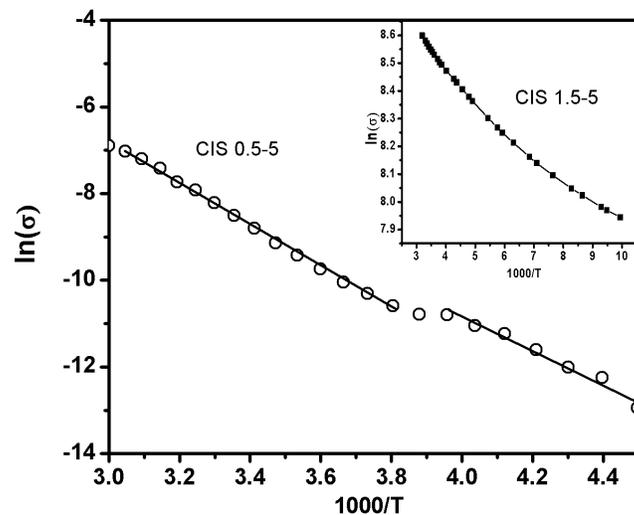


Fig. (9).  $\ln(\sigma)$  vs  $1000/T$  plot of In rich and Cu rich samples (inset).

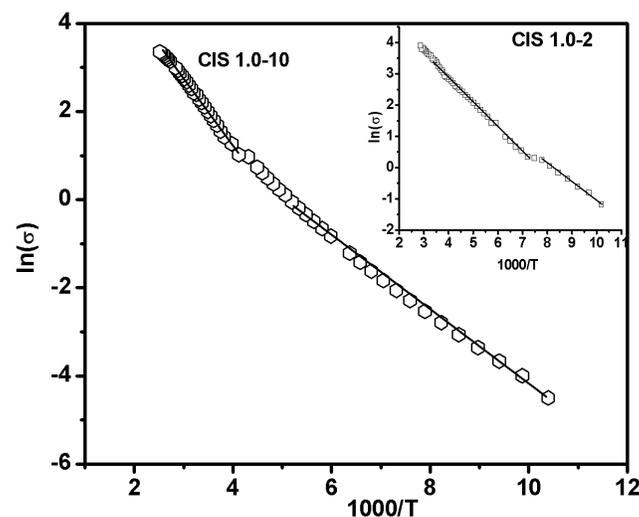


Fig. (10).  $\ln(\sigma)$  vs  $1000/T$  plot of S rich and S poor samples (inset).

solution. Systematic study of role of spray rate on the properties of the films formed revealed that smaller spray rate favoured formation of larger grains which resulted in better conductivity of the film. Films with good uniformity and lesser surface roughness were formed at smaller spray rates. Also, in addition to the widely studied Cu/In variation, effect of S/Cu variation was discussed. It was observed that though S-rich starting solution was required for obtaining stoichiometric films, increasing S beyond a limit did not result in its incorporation in the film and hence had no effect on the properties. Moreover, Cu rich films were good in terms of crystallinity and low resistivity, but these films had low photosensitivity and nonuniform composition over the surface. High resistivity and low crystallinity put limits on the use of In-rich films as absorber layer, inspite of their good photosensitivity. The sample with Cu/In = 1 and S/Cu = 5 (CIS 1.0-5) sprayed at small spray rate, which showed intermediate value of photosensitivity, crystallinity and resistivity, were better suited for device applications.

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