

Properties of CuInGaSe Thin Films Prepared by Chemical Spray Pyrolysis

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Abstract — Polycrystalline films of semiconducting Cu(In_{1-x}Ga_x)Se₂ (CIGS) quaternary alloy, one of the promising materials for photovoltaic applications, have been prepared by means of chemical spray pyrolysis (CSP). Copper, Indium and Gallium metal chlorides and Selenourea are used as constituent elements to prepare spray solution. Single phase CIGS films with chalcopyrite structure have been successfully grown on glass substrate at 350°C. The films have been characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Raman Spectroscopy and optical absorption in terms of deposition time from 5 minutes to 25 minutes. Hall studies were carried out to determine resistivity, mobility and carrier concentration in the film. All the deposited films were polycrystalline and showed single phase chalcopyrite structure with a preferred (112) orientation. Average grain size of 12.8 nm calculated from XRD spectra indicated that the films had a nanocrystalline structure. Chemical constituents present in the deposited CIGS films were identified using energy dispersive X-ray (EDX) analysis. The distinct peak in Raman spectra near 170 cm⁻¹ indicated the presence of CIGS. All the films exhibit direct band gap structure and their band gap values are found to be 1.40 to 1.64 eV. Optical absorption coefficients of the films are found to be over 10⁷ cm⁻¹. Resistivity of the films varied from 0.4 Ohm-cm to 4×10⁻² Ohm-cm with increase in thickness of the films.

Keywords — CIGS, CSP, EDX, Raman studies, SEM, XRD

I. INTRODUCTION

The ternary chalcopyrite semiconductors of the I-III-VI₂ group have attracted considerable attention over the last two decades because of their potential application in the optoelectronic devices, particularly in solar cells. Stuttgart researchers [1] have recently achieved 20.1 % efficiency using CIGS thin film as absorber layer. Among the several materials of this group, CuInSe₂ and CuGaSe₂ have proved to be effective and stable light absorbers for the fabrication of heterojunction solar cells [2]. However, the bandgap of CuInSe₂ (1.04 eV) is well below the optimum value suitable for efficient energy conversion. Alloying with Ga [3], S [4] or Al [5] increases the bandgap of CuInSe₂ making it more suitable for high-efficiency single junction and multijunction devices [2]. Incorporation of gallium into CuInSe₂ has demonstrated to shift the band gap towards a better match with the incident solar spectrum leading to

higher conversion efficiencies [3]. Although thin films of CIGS have been grown by a variety of techniques, devices fabricated using multisource elemental evaporation have shown better efficiencies compared to the devices prepared by other deposition techniques [6]. However, this method is not suitable for the economic production of CIGS layers on large scale due to the conflicting requirements associated with simultaneous deposition of different elements. Therefore it's a need to develop new techniques to grow high quality CIGS films which should be simple, low cost and suitable for large scale production [6]. The spray technique to disperse and deposit a precursor solution is very well suited for uniform large area coating [6]. Although spray pyrolysis technique is one of the best investigated non-vacuum deposition processes (mainly for CuInSe₂), only few reports are available for CIGS thin films [7, 8]. Spray pyrolysis is based on the decomposition and reaction of premixed precursors, generally metal-chlorides and a chalcogen compound (typically N, N-dimethyl selenourea or selenourea), on a heated substrate (300–400°C) [6]. Though there are reports [7, 8] on the deposition of CIGS films by this technique, this is the first report on preparation of these layers with different thicknesses by controlling the deposition time, which plays vital role in determining the efficiency of PV device. In the present study, CIGS thin films with different thicknesses were successfully synthesized by spray pyrolysis, and some results on the physical properties are reported.

II. METHODOLOGY

CIGS thin films with various film thicknesses were prepared by chemical spray pyrolysis using 20 vol. % aqueous solutions containing copper chloride (CuCl₂·2H₂O), gallium trichloride (GaCl₃), indium trichloride (InCl₃) and selenourea (all are analar grade from Aldrich, USA) as the starting solutions. The Cu:(Ga+In):Se atomic ratio in the solution was maintained as 1:1:3.5. An excess of selenourea was taken in the starting solution in order to compensate the loss of selenium during deposition due to its high vapour pressure. The concentrations of CuCl₂ and GaCl₃/InCl₃ were maintained at 0.0015 M while that of selenourea was 0.0055 M. Deposition time was varied starting from 5 minutes to 25 minutes in the interval of 5minutes. The solutions were sprayed onto soda-lime glass substrates maintained at a temperature of 350°C with an accuracy of ± 5°C measured using Eurotherm Model 840 temperature controller. The solution was sprayed at a flow rate of 5 ml min⁻¹. Nitrogen was used as the carrier gas at a flow rate of 6 l min⁻¹. The

source to substrate distance was maintained as 25 cm. The entire deposition process was carried out taking solution in dark container and also in the absence of electrical light inside deposition chamber to avoid the dissociation of selenourea into elemental selenium. The structural characterisation of deposited CIGS films was carried out using a PANalytical X-Ray Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5406\text{\AA}$). XRD spectra were recorded in the scanning range $20^\circ - 80^\circ$. The surface morphology of the films was examined by a JEOL JSM-6360 LV scanning electron microscope. The chemical composition of films was analysed by Energy Dispersive Analysis of X-rays (EDAX) attached to the scanning electron microscope. Raman analysis has been demonstrated using HoRiBa jobin yvan (Microscopy Olympus Bx41) with He-Ne Laser at a wavelength of 632nm. Transmittance spectra were obtained using SHIMADZU UV-VIS double beam spectrophotometer in the wavelength range 300-1100 nm. The film thickness was measured by a KLA Tencor P15 profilometer, etching an edge of the sample to make a reference step. Hall measurements were carried out by the Van der Pauw method using a Walker scientific HV-4H equipment.

III. RESULTS AND DISCUSSION

Physical observation revealed that, the deposited films were pin hole free and dark reddish brown in colour. Film thickness with respect to deposition time and the values of sheet resistance and resistivity calculated from the formula (1) are listed in Table. I.

$$\rho = R_s \times d. \quad (1)$$

Where ρ is the resistivity of film in Ohm-cm, R_s is the Sheet resistance in Ohm-Sq^{-1} and d is the thickness of sample.

A. Structural Analysis: XRD spectra shown in Fig. 1, revealed that all the CIGS films were polycrystalline with a reflection peak along the (1 1 2) direction, but other reflections corresponding to (2 2 0), (2 0 4), (3 1 2) and (1 1 6) can be seen, and splitting of (2 2 0)/(2 0 4) and (3 1 2)/(1 1 6) in CIGS can also be observed, which exhibit the presence of chalcopyrite structure [7, 8]. For short deposition times we can also notice an amorphous phase.

TABLE I
VARIATION OF THICKNESS, SHEET RESISTANCE AND RESISTIVITY WITH RESPECT TO DEPOSITION TIME

Deposition time (minutes)	Thickness, d (μm)	Sheet Resistance, R_s ($\text{K}\Omega\text{-Sq}^{-1}$)	Resistivity, ρ (Ohm-cm)
10	0.12	110	1.32
15	0.17	32	0.55
20	0.22	18	0.41
25	0.34	10	0.34

Lattice constants $a=5.65\text{\AA}$, $c=11.35\text{\AA}$ and $c/a=2$ were calculated for the 25 minutes deposited sample using the (2 2 0) and (1 1 2) lines. These values are similar to standard values given in Joint committee on Powder Diffraction Standards (JCPDS) no. 40-1488. The variation of 'a' and 'c' with deposition time for the films deposited in the present study is almost linear following the usual Vegard's behavior [7, 8]. The observed value of c/a, is slight deviated with the reported data is probably due to the change in the deposition method [7]. From Fig.1 it is clear that the amorphous phase (bump) decreased and crystallinity increased by increase in thickness of the film.

B. Surface morphology and composition: Fig.2 shows the surface morphology of deposited films. Films deposited for 10 minutes, the surface is found to be very smooth and no development of the grains could be observed as compared to other films. Selected area mapping has been done for 10 minutes deposited sample and the area in black circle is rich in Copper and Selenium.

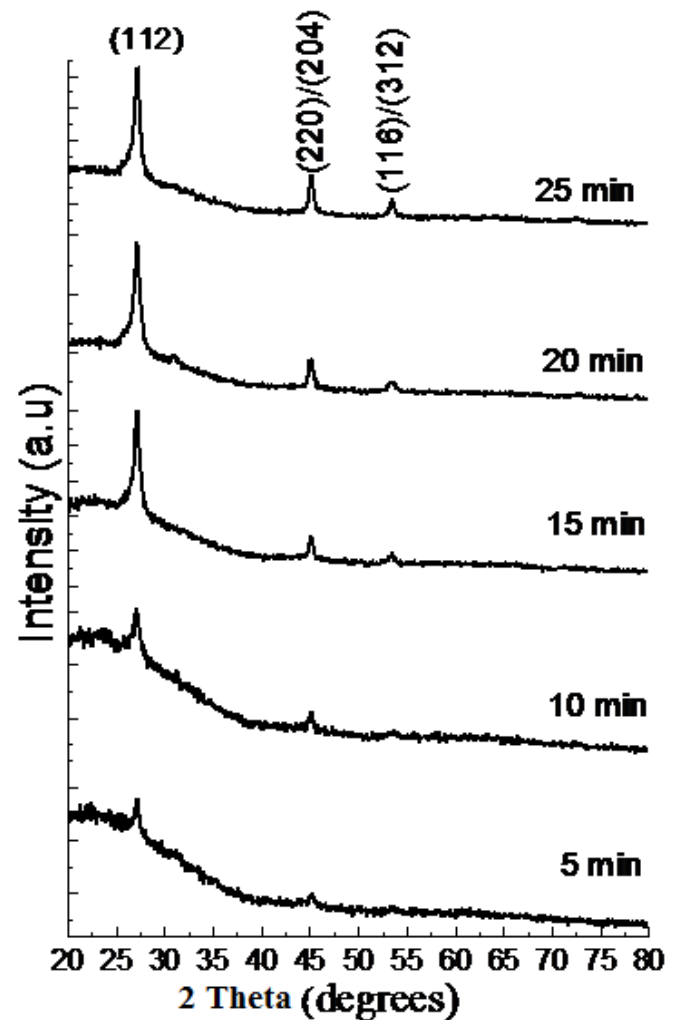


Fig.1 XRD pattern of CIGS thin films deposited for different time durations

These white spots in the film are probably γ -CuSe phase formed at the initial stage of the reaction because of less deposition time and incomplete reaction mechanism. A detailed explanation of growth of ternary and quaternary compounds was explained elsewhere [9]. Table II lists the atomic compositions of elements presented in CIGS thin films.

TABLE II
VARIATION OF Cu, In, Ga AND Se CONTENTS WITH DEPOSITION TIME

Deposition time (minutes)	Cu (at. %)	In (at. %)	Ga (at. %)	Se (at. %)	Molecular Formula	Cu/(In+Ga)
10	12.4	13.6	14.4	59.6	$\text{Cu}_{0.42}(\text{In}_{0.49}\text{Ga}_{0.51})_{0.94}\text{Se}_2$	0.44
15	13.7	10.5	15.4	60.2	$\text{Cu}_{0.45}(\text{In}_{0.41}\text{Ga}_{0.59})_{0.86}\text{Se}_2$	0.52
20	12.8	11.7	16.7	58.5	$\text{Cu}_{0.43}(\text{In}_{0.42}\text{Ga}_{0.58})_{0.97}\text{Se}_2$	0.44
25	12.3	11.4	18.0	58.2	$\text{Cu}_{0.42}(\text{In}_{0.39}\text{Ga}_{0.61})_{1.00}\text{Se}_2$	0.42

The deviation of the molecular formula from the expected $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ composition in the film is due to the chemical reaction during the deposition. Notice that all the films are strongly copper deficient, while the (In+Ga)/Se ratio is almost equal to $\frac{1}{2}$, as should be. Further experiments will be made with a higher Cu composition in the solution in order to achieve a composition with a higher Cu content in the film.

C. Raman analysis: Raman measurements have been made in order to study the phase composition and microstructure which cannot be obtained by X-ray diffraction measurements. Fig. 3 shows Raman Spectrum of the CIGS thin film deposited for 25 minutes. The distinct peak corresponding to a strong characteristic A1 mode phonon peak near 185 cm^{-1} indicates the presence of gallium rich CIGS films [8], which is in agreement with composition analysis given in table II. The Raman spectra ranging from 233 to 263 cm^{-1} is also noteworthy. These two peaks observed are due to the mixed $\text{B}_2(\text{TO})\text{-E}(\text{TO})$ mode at 233 cm^{-1} and the mixed $\text{B}_2(\text{LO})\text{-E}(\text{LO})$ mode at 263 cm^{-1} [8]. Usually for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ film, no peak will appear in this range but for the Ga rich films, a Raman peak was detected near 263 cm^{-1} [10, 11]. This peak confirms the existence of the binary compound Cu_{2-x}Se , which is reported to have a low resistance and degrade the performance of CIGS - based solar cells [10].

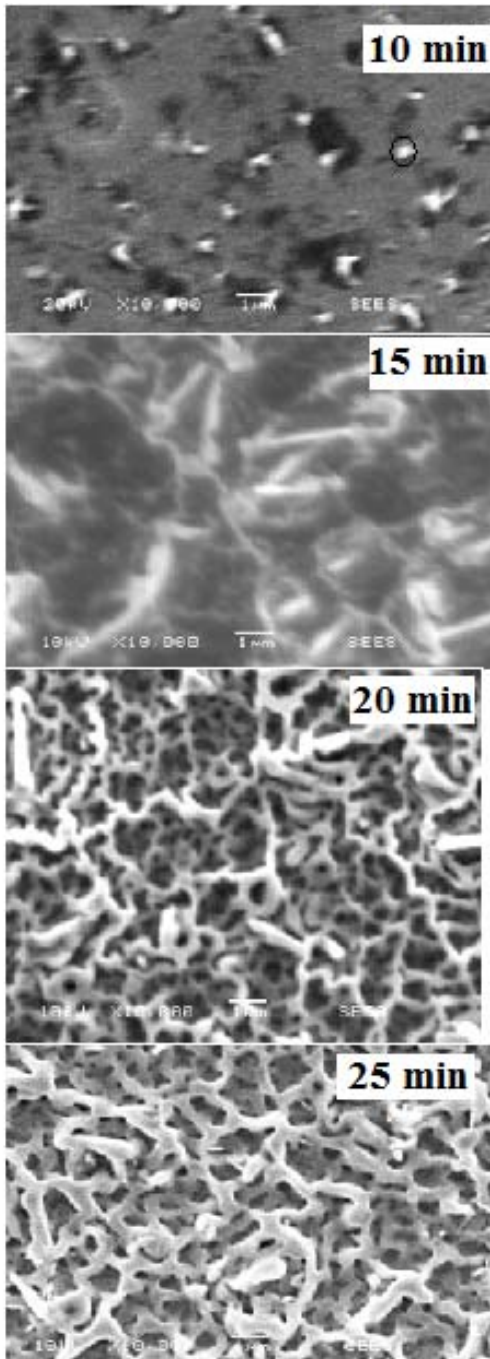


Fig. 2 SEM micrographs of CIGS thin films deposited with variation in thickness

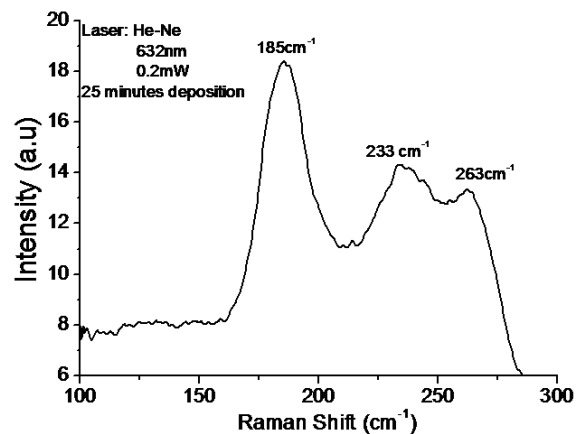


Fig. 3 Raman Spectrum for 25 minutes deposited CIGS thin films

D. Optical Properties: Fig.4 shows the plot of $(\alpha hv)^2$ versus hv and extrapolation of linear portion to the abscissa gives the band energy gap of deposited film. The absorption coefficient $\alpha = 10^7 \text{ cm}^{-1}$ for 25 minutes deposited CIGS film is estimated from the optical transmittance spectra using the relation,

$$\alpha = 2.303 \log (100/T)/t. \quad (2)$$

where T is the transmittance (in %) and t is the thickness of film. All such graph satisfies the condition for a direct transition in the excitation process that is

$$\alpha hv = A (hv - E_g)^{1/2}. \text{ for allowed direct transition,} \quad (3)$$

where A is an energy dependent constant, E_g is the band gap of respective material, hv is photon energy. All the films exhibit direct band gap structure [12]. The band gap energy of all the films are determined and tabulated in Table III. Just for comparison we have calculated the bandgap with equations (4) and (5). The optical bandgaps for near-stoichiometric $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ is smaller and exhibit a bowing behavior which follows the relationship

$$E_g = 1.011 + 0.664x + 0.249x(x - 1). \quad (4)$$

In comparison, Cu-poor films exhibit a linear variation with zero bowing given by [13]

$$E_g = 1.0032 + 0.71369(1-x). \quad (5)$$

where 'x' is the alloy composition of gallium.

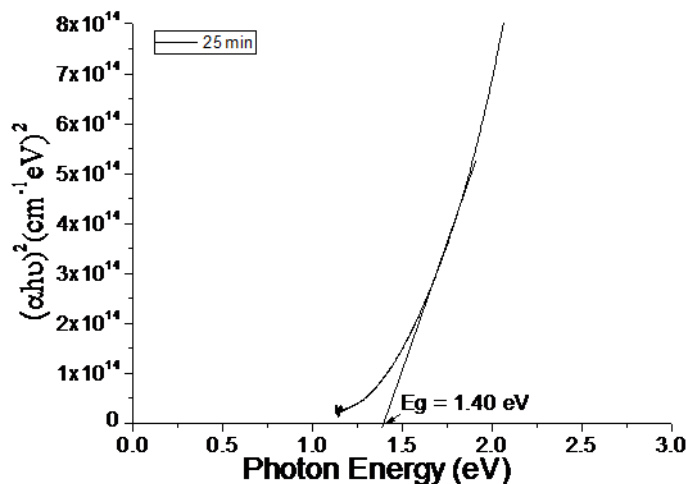


Fig. 4 Spectra of square of absorption coefficient for CIGS film deposited for 25 minutes

TABLE III
OPTICAL PROPERTIES OF CIGS THIN FILMS

Deposition Time (minutes)	Band gap, E_g (eV)	
	(from optical data)	(from equation 4)
10	1.64	1.34
15	1.57	1.29
20	1.50	1.30
25	1.40	1.27

E. Electrical Properties - Hall Effect measurements have been done using the Van der Pauw method. Fig. 5 shows the resistivity, mobility and carrier concentration of CIGS thin films as a function of film thickness. As the thickness of films increased resistivity decreased due to increase in carrier concentration. However, the mobility of films is very low, because the films are not dense as we see from SEM images. The resistivity of CIGS system depends on Cu/(In + Ga) ratio [8].

V. CONCLUSION

Thin polycrystalline films of Cu(In, Ga)Se_2 were grown successfully by CSP on a glass substrate at 350°C using the aqueous solutions of metal-chlorides and a chalcogen compound and the structural, optical and electrical properties were studied. The important results obtained in this study are as follows: (i) good controllability of thickness was achieved, (ii) all films exhibited the chalcopyrite structure and lattice constants a and c obeyed Vegard's law, (iii) the optical band gap changed from 1.40 to 1.64 eV with alloy composition, and (iv) the $A1$ mode phonon exhibited a single-mode behavior and the phonon frequency from 230 to 265 cm^{-1} revealed the Ga-rich CIGS thin films. These results and discussions led us to conclude that Cu(In,Ga)Se_2 films grown by CSP may be useful for solar cell application due to the simplicity of the technique. We are carrying out further experiments such as annealing of the films to achieve the best performance of these films as absorber layer in CIGS based solar cells.

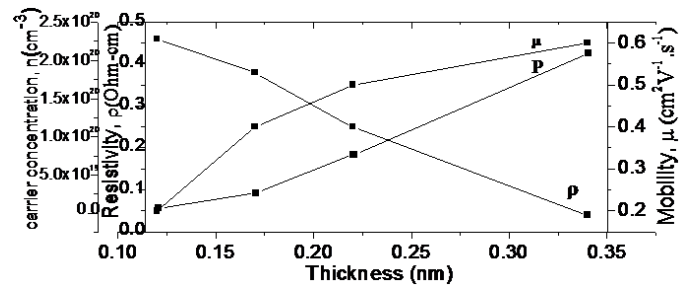


Fig. 5 Electrical Parameters of CIGS thin films

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