

## Synthesis and Characterization of CIGS ink for Solar Cells

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### ABSTRACT

CIGS is proved to be a better candidate as absorber layer in thin film solar cells. However, mostly vacuum based expensive techniques have been used to prepare CIGS thin films. We have used inexpensive and reliable sol gel technique for the synthesis of CIGS inks for ink jet printed solar cells. Chlorides of all the metals are used as precursors whereas DI water along with some organic liquids is used as solvents. Synthesized solutions are refluxed at 80 °C for 15 -75 minutes. Centrifugation is done at 4000 rpm for 10 minutes. Nanoparticles are characterized by using SEM and XRD. Optimized nanoparticles are dispersed in appropriate solution to prepare inks. Optical properties of thin films, prepared by CIGS ink, are measured using variable angle spectroscopic ellipsometer. These films found to be good absorber in 900-1000 nm wavelength.

### 1. INTRODUCTION

Solar cells based on single crystal silicon wafers have been produced with high efficiencies but there are many disadvantages of wafer based solar cells. These are high production cost, indirect band gap of silicon and low conversion efficiency (Gu 2012). For this reason, the single crystal silicon solar cells were replaced with thin film solar cells. The advantage of using thin films is the low production cost and their potential high solar to electricity-conversion efficiency, reliability, and stability (Park 2009).

The most promising materials as absorbers in thin film solar cells are the Chalcopyrites. The band gap of  $\text{CuInSe}_2$  is  $E_g=1$  eV and that of  $\text{CuGaSe}_2$   $E_g= 1.7$  eV (Voorwinden 2003, Faraj 2012). Therefore, a manipulation of the band gap between these two extremes is possible. It allows a large amount of light to be absorbed in the material (Baji 2013).

Polycrystalline  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  (CIGS) is used as absorber layer in thin film solar cells due to its high absorption coefficient, tunable direct band gap, and excellent optoelectronic qualities (Liang 2012, Park 2009).

There are a number of methods to prepare CIGS absorber films. These methods include evaporation techniques, such as co-evaporation, sputtering and selenization, and electro-deposition (Mitzi 2009, Faraj 2012). Wu (2012) reported a simple modified Polyol route to synthesize chalcopyrite of CIGS nanoparticles. The reactants were  $\text{CuCl}$ ,  $\text{InCl}_3$ ,  $\text{GaCl}_3$  and Se powder with tetra ethylene glycol (TEG) used as a solvent which

act both as a reducing agent and solvent and are harmless. The average grain size and characteristics were investigated with SEM, TEM, EDS and XRD. The diameter of the spherical CIGS nanoparticles in the range of 40-100 nm can be achieved by varying temperatures from 200-280°C for 6 h with increasing Ga content. Gu (2012) adopted Solvothermal route to synthesize the CIGS powder for solar cell applications. The method was known to produce a lot amount of powder and manage particle traits easily. The particle shapes and phase change were noticed with the variation of reaction time and temperature. CGS and CIS were obtained at low reaction temperature of 210°C. As the temperature increased to 230°C, CuInGaSe<sub>2</sub> phases of dissimilar compositions emerged, however at 250°C only one stoichiometry composition was formed. As the reaction time was increased at 250°C, the three phases coexist and the phase ratio did not vary significantly.

Mousavi (2012) prepared the CIGS nanoparticles by using wet chemical technique which is found to be a non-vacuum thermal process without selenization. The influence of source materials, growth conditions and temperature on the grain size and phase were examined. The main phase tetragonal structure of CIGS was confirmed by XRD patterns. The morphology and grain size ranges from 20-80 nm were achieved by SEM and TEM. The optical characteristics determined the band gap of the prepared samples to be about 1.44 eV, which matches to a suitable wavelength region for absorber layers in photovoltaic applications.

In this study efforts are made to synthesize surfactant-free CIGS nanoparticles by controlling their size via refluxing through a simple chemical method. During our experiments it was observed that refluxing time has great influence on particle size. The effect of refluxing time on samples has been analyzed. Five samples were prepared with reflux time of 15, 30, 45, 60 and 75 min. Finally, optimized sample at reflux time of 60 minutes is discussed in this paper.

## **2. EXPERIMENTAL DETAILS**

### *2.1. Chemicals*

Chlorides of Copper, Indium, Gallium and Selenium were used as precursors. De-ionized water (DI) and ethanol were used as solvents.

### *2.2. Synthesis of Cadmium Sulphide Nanoparticles*

In a typical procedure, CuCl<sub>2</sub>.2H<sub>2</sub>O, InCl<sub>3</sub>, Al<sub>2</sub> Cl<sub>2</sub>.18H<sub>2</sub>O, GaCl<sub>3</sub> and SeCl were dissolved in DI water. Aqueous solution of each InCl<sub>3</sub>, GaCl<sub>3</sub>, AlCl<sub>2</sub> and SeCl was stirred for 5 hours at 70 °C for in 3-neck flask, separately. The solution was refluxed for 3 hours by keeping the temperature constant at 70 °C. Color of the solution was turned into bottle green with dark brownish-red color precipitates. Excess ethanol was added to the sample and centrifuged at 5000 rpm for 10 min. The resultant precipitates were dried. Experimental set up, for the synthesis of CIGS nano-ink, is shown in Fig. 1.

### *2.3. Spin Coating*

Films were spin coated onto 1x1cm<sup>2</sup> glass slides using a Süß Microtech Delta 6RC spin coater at 3000 rpm for 30 sec. The glass slides were firstly washed with detergent and then ultrasonically cleaned in acetone and IPA for 10 and 15 minutes respectively.

#### 2.4. Characterization

X-ray diffraction patterns of dried nanoparticles and films were studied by using Rigaku D/Max II-A X-Ray Diffractometer (XRD). Size and morphology of nanoparticles were observed by using Hitachi S-3400N scanning electron microscope.



Fig. 1 Experimental set-up for the synthesis of CIGS nano ink

## 2. Results and Discussion

CIGS nanoparticles after centrifugation was characterized for phase formation and crystal structure. XRD patterns of CIGS nanoparticles, as-synthesized and annealed, are shown in the Fig. 2. In order to analyze the crystal size, the samples were targeted by CuK $\alpha$  source with wavelength 1.54060Å. Annealing was performed at 100°C, 200°C, 300°C, and 400°C for 30 minutes for the strengthening of as synthesized compound and /or the elimination of byproducts. These XRD patterns correspond to different temperatures for the formation / strengthening of CIGS from its constituent elements of Cu, Ga, Al and Se according to the composition Cu(In,Ga)<sub>2</sub>Se<sub>2</sub>. The main diffraction peaks of all compositions based on the XRD database for (200) phase of crystal structure of CIGS (JCPD # 40-1488).

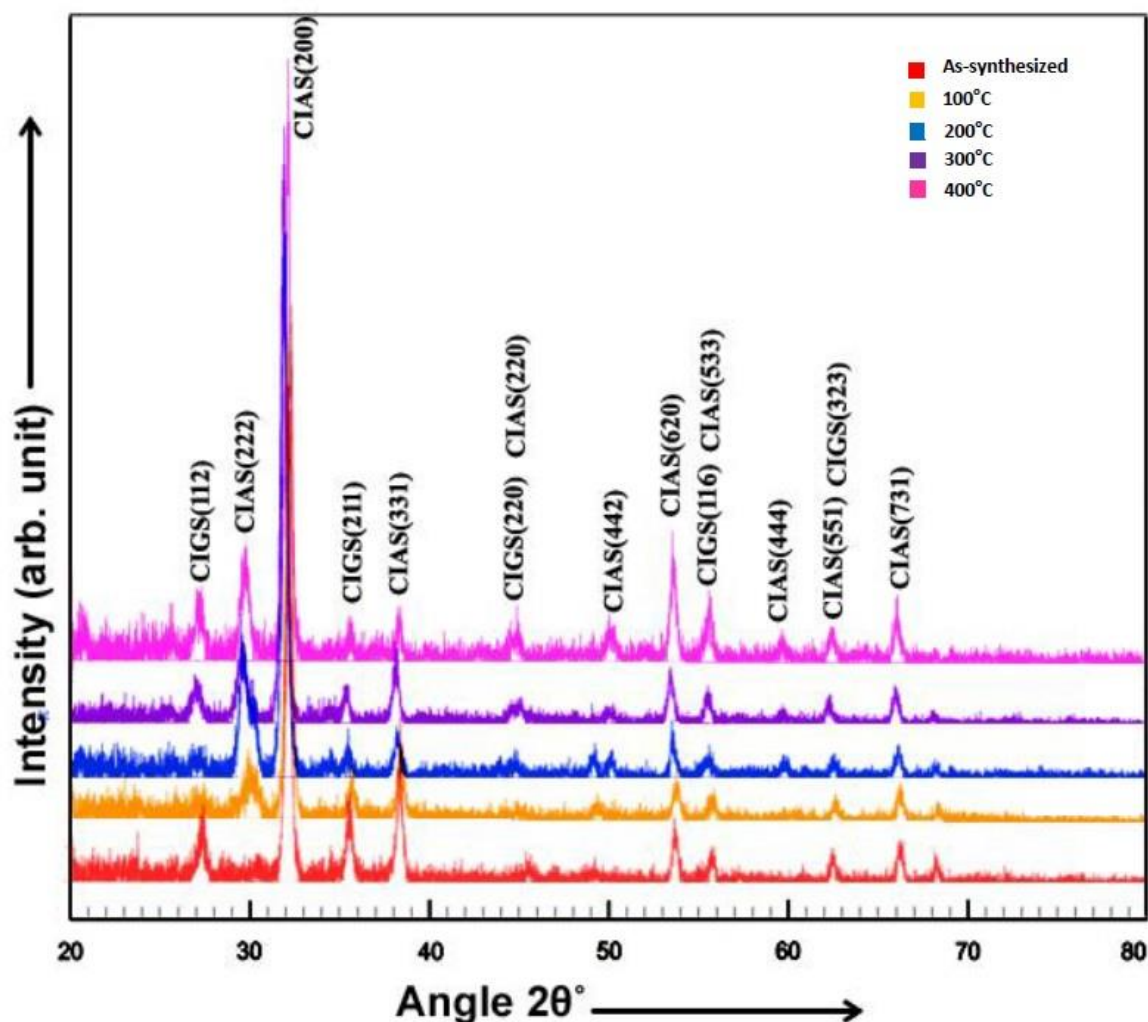


Fig. 2 XRD patterns of CIGS films

Crystallite size, shown in Fig. 3, was determined using Scherer equation given in Eq. (1)

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

Where B is the full width at half maximum (FWHM) of the peak,  $\lambda$  is the wavelength of the X-ray (1.5406 Å) and  $\theta$  is the peak position. The main diffraction peaks at an angle of  $2\theta=32.04^\circ$ .

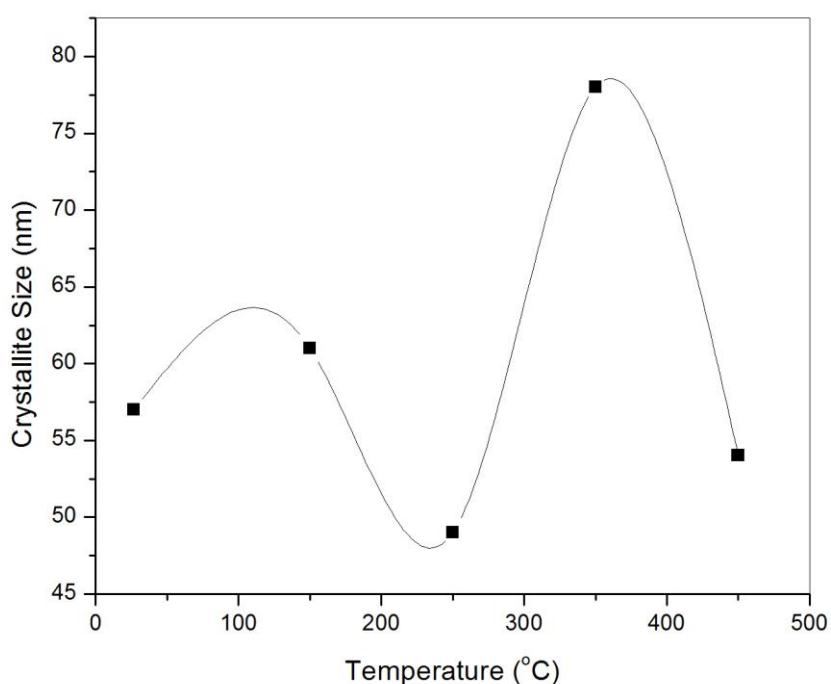


Fig. 3 Crystallite size as a function of Temperature

The crystalline sizes for as-synthesized CIGS nanoparticles were 57 nm. Almost a constant behavior was observed at a temperature of 150°C. However, a decrease in crystallite size values up to 48nm was observed at 250°C. This decreasing trend confirmed the chemical shift in the material thus moving towards the compound formation, as observed in XRD patterns.

SEM results of the optimized CIGS nanoparticles at reflux time for 60 minutes and then annealed at 250°C are shown in Fig 4. SEM images shows spherical particles show several colonies of nanoparticles with an average size of ~40 - 50nm. It is observed that after further increase in time the particle size diameter kept growing from ~50nm to ~85nm for samples annealed at 300°C and 400°C. This shows that as the

reaction time increases the particle size also increases due to the Ostwald ripening growth mechanism i.e. during the growth the total amount of particles decreases slowly due to dissolution of small ones and the larger particles will continue to grow resulting in a defocusing of size distribution.

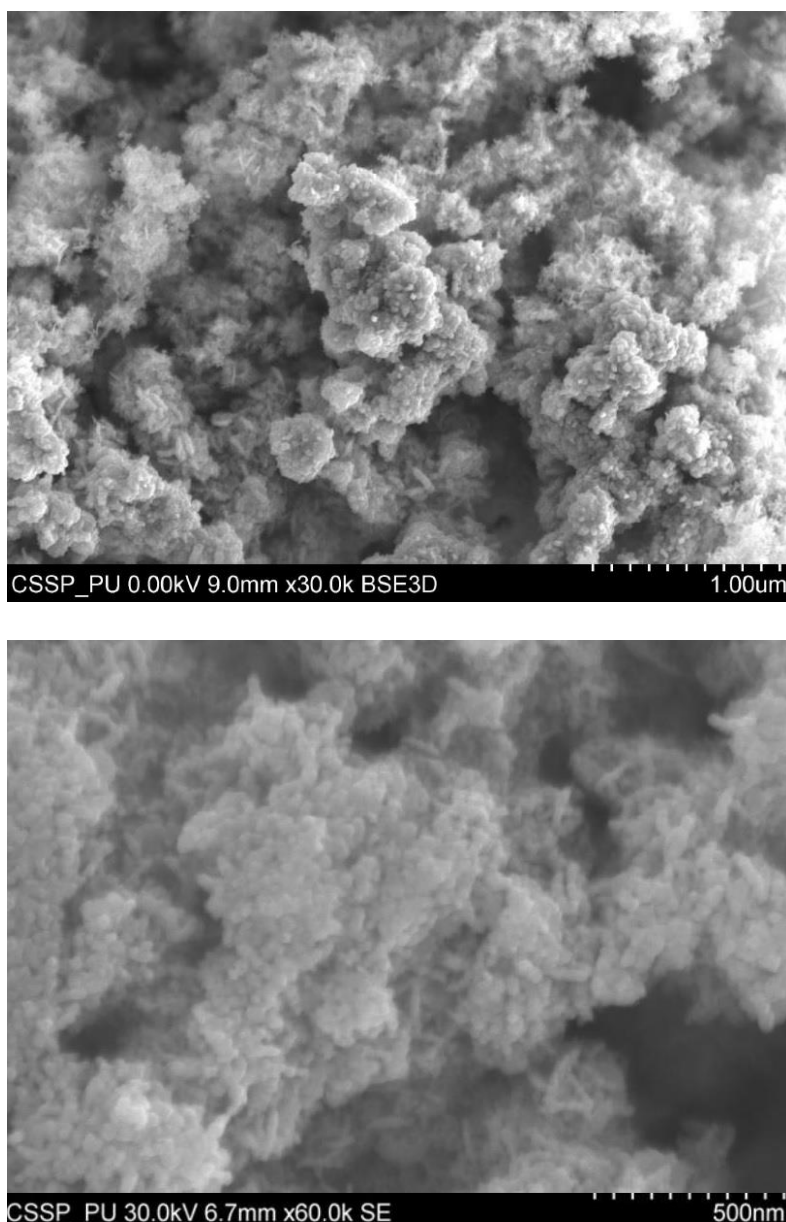


Fig. 4 SEM images of CIGS nanoparticles for 60 minutes reflux time

Fig. 5 shows absorption spectra of CIGS films prepared from nano ink. The films are highly absorbing in the visible region and UV region. As these films are further intended to be utilized for solar cell applications for which high absorption of the films is an

important requirement. The high absorption of the films in our case indicate their potential use as an absorber layer in solar cells.

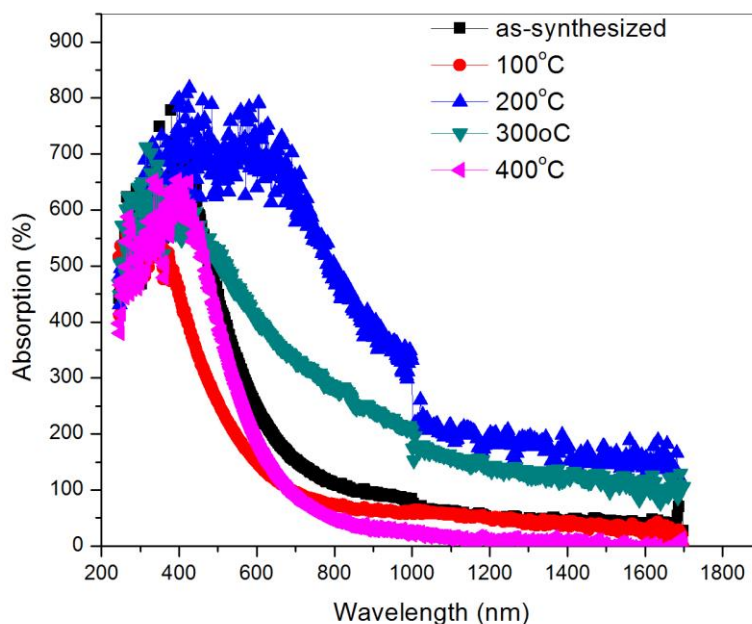


Fig. 5 Absorption spectra of CIGS thin films

The band gaps of the films are calculated using transmission curves and is plotted as a function of annealing conditions in Fig. 6. Almost constant trend in band gap value  $\sim 1.37$  was observed for all the samples.

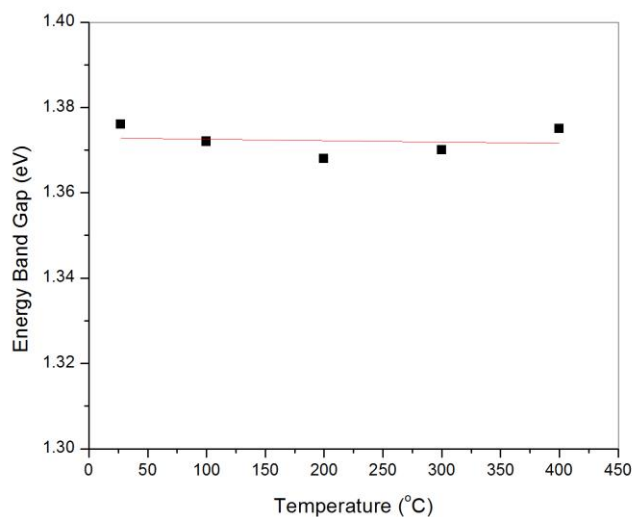


Fig. 6 Energy Band Gaps of CIGS thin films

### 3. CONCLUSIONS

Cu(In,Ga)Se<sub>2</sub> nanoparticles were synthesized using simple and cost effective chemical route. Nanoparticles were characterized structurally by XRD whereas as size and shape was determined by SEM. CIGS peaks were observed even in the as-synthesized samples. Crystallite size remained almost constant ~ 56nm for as-synthesized and 150°C annealed samples. Whereas, decrease in the crystallite size ~ 46nm was observed at 250°C which indicated the presence of chemical shift in the compound. This chemical shift lead to the formation and stabilization of CIGS compound as was observed by XRD patterns. Spherical nanoparticles ~45nm were observed by SEM when the samples were annealed at 250°C. These nanoparticles were then used for the synthesis of CIGS nano ink. The films are highly absorbing with high values of refractive index and extinction coefficient. Energy band gap ~ 1.37 eV was observed for all of the samples.

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