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# Preparation and study of structural and optical characterization of Cu (In,Ga)$Se_2$ (CIGS) thin film on polyethylene terephthalate substrate by screen print technique

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Chalcopyrite copper indium gallium diselenide Cu ($Ga_{0.3}$ $In_{0.7}$) $Se_2$ (CIGS) nanoparticles were prepared by using dissolve copper, indium, gallium acetylacetonate and Se powder in oleylamine using hot injection methods. The CIGS nanoparticles are deposited on polyethylene terephthalate (PET) substrates using screen print technique. X-ray diffraction (XRD) showed a chalcopyrite type structure with crystallite grain size of about 43.8 nm. The chemical constituents present in the deposited CIGS thin films on PET substrates have been identified using energy dispersive X-ray analysis (EDX), the surface topographical study on the film has been performed by AFM. Optical properties of CIGS thin films deposit on PET substrates were characterized using an ultraviolet-visible spectrophotometer. Optical constants such as absorption coefficient and energy gap were determined from transmittance spectrum. The band gap of CIGS absorber layer is estimated to be 1.25 eV.

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*Keywords:* Cu ($Ga_{0.3}$ $In_{0.7}$) $Se_2$, Polyethylene terephthalate, Chalcopyrite, Screen print, Thin film, Solar cells

## 1. Introduction

Copper indium gallium diselenide (CIGS) is member of I-III-$VI_2$ group of chalcopyrite semiconductors [1]. It is used as light absorber material for thin-film solar cells.The major advantage of Cu(InGa)$Se_2$ over other photovoltaic materials arise due to its unique combination of properties such as, high absorption coefficient, direct band gap, moderate surface recombination velocities and radiation hardness[2]. The band gap of the material can be tailored to suit photovoltaic device requirements by altering the composition of the material. For example by varying the In/Ga ratio the band gap can be raised from 1.0 eV to about 1.7 eV.

Various techniques have been reported for the deposition of CIGS thin films such as vacuum evaporation [3] spray pyrolysis deposition [4], Electrodeposition [5], close-spaced vapor transport deposition [6], sputtering deposition[7], electron beam deposition [8], screen print deposition [9], etc.

The development of CIGS films on flexible substrates is interesting due to the light weight, small volume, easy to carry and damage free nature of the devices. Light weight CIGS solar cells on flexible polymer substrates can be attractive for space applications [10, 11].

In this paper, CIGS nanoparticles ink synthesizes using commercial grade copper, indium, gallium acetylacetonate, selenium powder and oleylamine. The basic principles of preparation CIGS nanoparticles ink in this work is given in the literature [12-16].

CIGS nanoparticles ink was deposited on polyethylene terephthalate (PET) substrates by screen print technique. The structural and optical properties of CIGS thin films deposited on PET substrate were studied.

## 2. Experimental detail

### 2.1 Materials

Copper (II) acetylacetonate (Cu(acac)$_2$; 98%), selenium powder (Se; 99.99%) and oleylamine (approximate C18-content 80-90%) from Acros Organics.Gallium(III) acetylacetonate (Ga(acac)$_3$; 99.99%) and indium (III) acetylacetonate (In(acac)$_3$; 99.99%) from Sigma-Aldrich, methanol and toluene.

### 2.2 Chemical instruments

A vacuum pump (temperature up to 90 $^0$C), round-bottom flask, condenser, test tube, $N_2$ atmosphere cylinder, centrifuge, heating mantle and magnetic stirrer.

A round three necked flask was placed in heating mantle. One neck was connected to condenser which is connected to $N_2$ atmosphere cylinder and the two others were sealed by a septum, as seen in Fig. 1.

### 2.3 Preparation of CIGS nanoparticles inks

A typical procedure of CIGS synthesis follows (52.4 mg of Copper (II) acetylacetonate (Cu $(acac)_2$ )), (36.7 mg of Gallium(III) acetylacetonate ($Ga(acac)_3$)) and (41.2 mg of Indium (III) acetylacetonate ($In(acac)_3$)) are mixed and added to 5 mL of oleylamine at room temperature. This solution was kept at 80 $^0$C under vacuum pump for a 30 min to complete dissolve. This solution was marked solution (1).

31.6 mg of Selenium powder was added to 8 mL of oleylamine in separate flask. This solution was kept at 90 $^0$C under vacuum pump for a 1 hour, and then put under $N_2$ atmosphere. This solution was then heated to 260 $^0$C over 20 min period and kept at that temperature. Over the course of a hour, the solution gradually changed from colourless, to orange, and to brownish red .This solution was completely dissolved and marked solution (2).

5 mL of solution (1) was added to solution (2) under vigorous stirring using magnetic stirrer. The solution turned immediately to deep black; the heating mantle was then turned off to provide slow cooling of the reaction vessel. After 30 min the temperature decreased to 100 $^0$C, at which point the solution was heated again to 260 $^0$C for 1hour. Then, the reaction mantle was removed and the solution was allowed to cool to room temperature. The solution was then transferred to test tube and 5mL of methanol was added to the mixture; then the mixture was centrifuged at 3300 for 8min.

The clear supernatant was discarded and its precipitate was redispersed in10 mL of toluene. A 5 mL of methanol was added to the solution and again and the nanoparticles were again isolated by centrifuged at 3300 for 8 min. The supernatant was again decanted; the precipitates were redispersed in 8 mL of toluene. The suspension was centrifuged at 3300 for 15 min. This process is done four times to obtain a high-purity product, yielding the final product of CIGS nanoparticles ink.

### 2.4 Characterization of the thin films

The PET substrates were washed by alcohol and then ultrasonically cleaned for 10 min. The deionised water was used to rinse the PET substrate. The PET substrate was dried by nitrogen gas. CIGS thin films were prepared on PET substrates by the Screen Print technique. The film was fully dried by placing the substrate in a vacuum chamber at room temperature for 4 h. The thickness of CIGS thin film deposited on PET substrate is of the order of 300 nm, which was determined by using optical reflectometer (Model: Filmetrics F20) .The surface morphology of each CIGS thin films was performed by atomic force microscopy(AFM) (Model: Ultra Objective). The compositions of the CIGS thin films were estimated using Energy Dispersive Analysis of X-rays (EDX) (Model JSM – 6460 LV).The crystallographic structure of CIGS deposited PET substrates was determined using high resolution X-ray diffractmeter system (model: Panalytical X' Pert PRO MRD PW3040). The optical properties of CIGS thin films deposited PET substrates were characterized by UV Spectrophotometer (Model: U-2000 HITACHI).

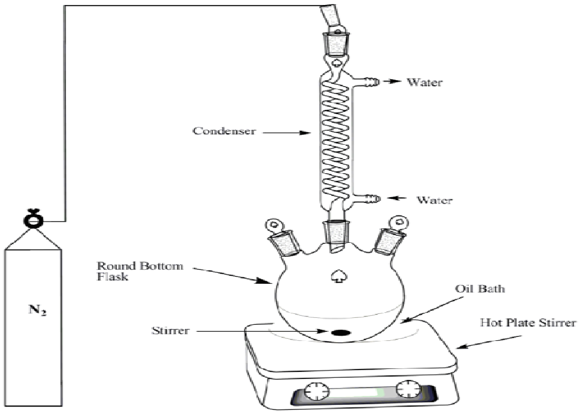

*Fig. 1. Experimental Set-up of Chemical Apparatus.*

## 3. Results and discussion

### 3.1 Structural properties

To determine the crystal structures of CIGS thin films deposited on PET substrate, the XRD pattern was examined as shown in Fig. 2. The main peak corresponding to the PET substrate was observed at 2θ angle 26 $^0$, it has very high intensity. This means that the materials which have peak at the same position is submerged in a very strong peak of the PET substrate [17-19]. Four prominent XRD peaks were identified as being due to the Cu ($Ga_{0.3}$ $In_{0.7}$) $Se_2$ crystal planes of (220), (400), (424) and (440), which give a chalcopyrite tetragonal structure with lattice constants of a= 0.57360 nm, c= 1.14480 nm and c/a=1.9958, consistent with the standard values of the reported Cu ($Ga_{0.3}$ $In_{0.7}$) $Se_2$ data [20].This XRD result confirm the proper phase formation of CIGS thin films.

The crystalline grain size (t) of the CIGS thin films was determined by using Sherrer formula

$$t = \frac{0.9\lambda}{\beta\cos\theta} \tag{3.1}$$

Where β is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening, λ is the wavelength of the X-ray, 1.5406 A$^0$ and θ the peak position.

Based on the line width of the (220) diffraction peak, the crystalline grain size calculated of as deposited CIGS thin films were 43.8 nm.

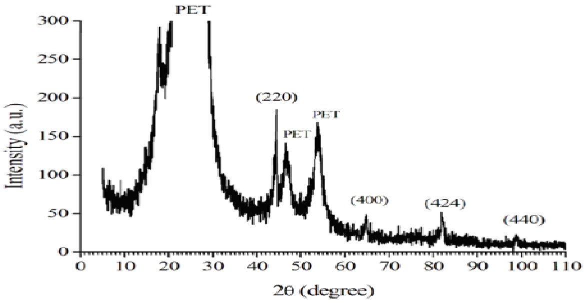

*Fig. 2. XRD patterns of CIGS thin films on PET substrate.*

AFM images for surface morphologies of CIGS thin films deposited on PET are given in Fig. 3. From Table 1, the root mean square (RMS) for CIGS thin films on PET substrate is 13.05 nm. Another parameter that is skewness is a measure of symmetry, or more precisely, the lack of symmetry. The skewness for CIGS thin films on PET substrate is 3.76. Fig. 3 shows the peaks are scattered over the substrate tends to be equally distributed. Kurtosis is a measure of whether the data are peaked or flat relative to a normal distribution. That is, data sets with high kurtosis tend to have a distinct peak near the mean, decline rather rapidly, and have the heavy tails. Data sets with low kurtosis tend to have a flat top near the mean rather than a sharp peak. Fig. 3 shows a very sharp peak out of majority flat area. Obviously, the surfaces of the CIGS thin films deposited on PET substrate were smooth. Smoother films show not only reduced light trapping at the surface, but also lowers the number of interface states between the absorber layer and the window layer in the device [21].

*Table 1. Shows the Parameters AFM for CIGS thin films deposited on PET substrate.*

| No. | Parameters | |
|---|---|---|
| 1 | Max Height Diff. | 152.63 nm |
| 2 | Mean (nm) | 24.23 nm |
| 3 | Root Mean Square (nm) | 13.05 nm |
| 4 | Average Deviation (nm) | 7.88 nm |
| 5 | Skewness | 3.76 |
| 6 | Kurtosis | 24.72 |

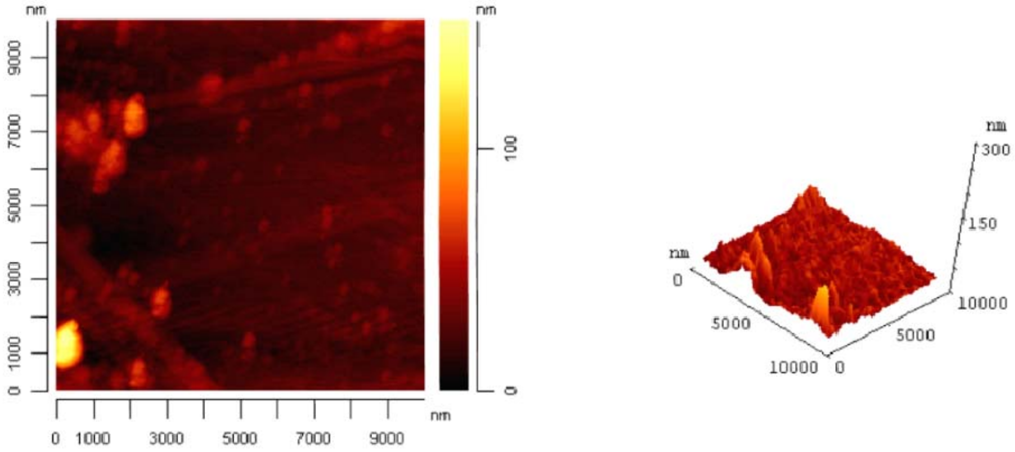

*Fig. 3. AFM analysis of CIGS thin films deposited on PET substrate.*

Fig. 4 shows the EDX result of CIGS thin films deposited on PET substrate .EDX analysis confirms the composition of Copper, Indium, Gallium and Selenium in CIGS film. The presence of C and O peaks in Fig. 4 is due to the PET substrate. These results are in good agreement with XRD study.

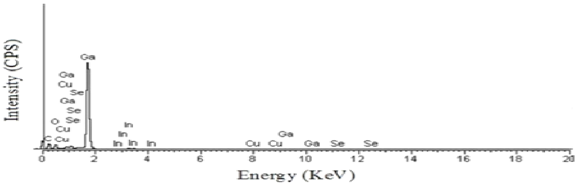

*Fig. 4. EDX result of CIGS thin film deposited on PET substrate.*

### 3.2 Optical properties

The transmittance spectra of CIGS thin films deposited on PET substrate is shown in Fig. 5.

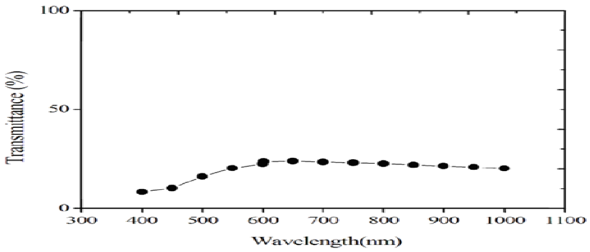

*Fig. 5. Transmission spectra of CIGS thin films deposited on PET substrate.*

Using transmission measurements, the absorption coefficient (α) was calculated using the following expression:

$$\alpha = -\ln\left(\frac{1}{T}\right)/d \tag{3.2}$$

Where d refers to the estimated thickness of the thin film and T is the transmittance. The result absorption coefficient is found to be of the order of exceeding ($10^4$ cm$^{-1}$).This is in accordance with the reported values [22, 23].

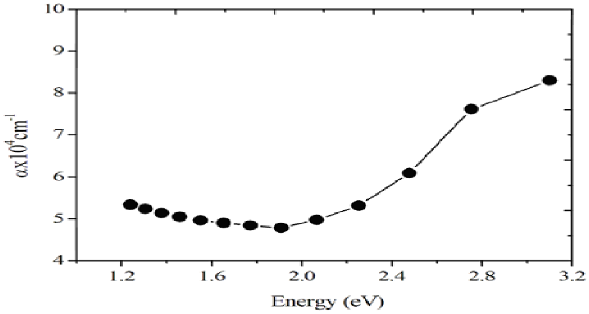

*Fig. 6. Spectral absorption coefficient of CIGS thin film versus photon energy.*

It is well known that CIGS is a direct gap semiconductor, the absorption coefficient in the region of strong absorption obeying the equation.

$$\alpha = \frac{k}{hv}\left(hv - E_g\right)^{\frac{1}{2}} \tag{3.3}$$

h the Planck constant, ν the radiation frequency, E$_g$ the bandgap energy and A the constant, which depends on the nature of the radiation. The extrapolation of the linear portion of the $(\alpha h\nu)^2$ versus Energy graph at α = 0 yields the band gap value of the material. As indicated in Fig. 7, the band gap of the deposited material was determined to be 1.25 eV and agrees well with the values generally reported in the literature [24-26]. It corresponds to the optimal value for good performances of solar cells.

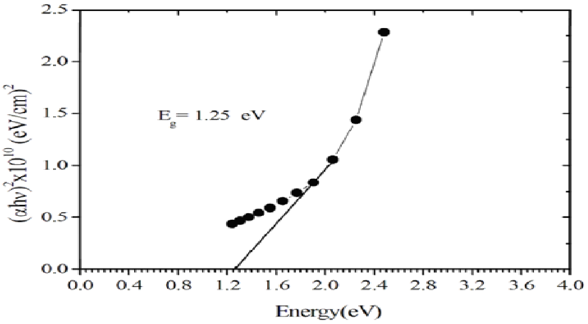

*Fig. 7. Relation between (αh□)$^2$ and photon energy for CIGS thin film.*

## 4. Conclusion

Preparation of CIGS nanoparticles in oleylamine with narrow size distribution using commercial grade copper, indium, gallium acetylacetonate, and Se powder and then deposited on PET substrates by the screen print technique. X-ray diffraction patterns confirm the proper phase formation of the CIGS thin films. AFM surface study shows the surfaces of the CIGS thin films deposited on PET substrate a smother with root mean square 13.05 nm. Calculations of the band gape value for CIGS thin films deposited on PET substrate 1.25 eV.

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