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SYNTHESIS AND CHARACTERIZATION OF $CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) BULK COMPOUND AND HOT WALL DEPOSITED THIN FILM ABSORBER LAYER FOR SOLAR CELL APPLICATIONS

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ABSTRACT

$CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) alloyed compound was prepared from the mixtures containing appropriate amounts of high quality elemental copper, indium, gallium, and selenium by direct melting. The chemical composition and phase evolution were analyzed by x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) measurements. High resolution transmission electron microscopy (HRTEM) micrographs show the lattice spaces of the prepared CIGS powder. Cu (In, Ga)Se_2 thin films were deposited onto well cleaned glass substrates under a vacuum of $2x10^{-6}$ torr using hot wall deposition technique. Transmittance spectra of the prepared CIGS films were obtained in the wavelength range of 190 nm to 2500 nm using a double beam spectrophotometer. From the plot of hν versus $(\alpha h\nu)^2$, the band gap of the hot wall deposited CIGS thin film is estimated to be1.18 eV by extrapolating the linear portion of the curve to the hν axis. The atomic force microcopy (AFM) images revealed that the average grain size was 20 nm and the surface roughness was about 8 nm for the prepared thin films.

Keywords: CIGS; direct melting method; absorber layer; hot wall deposition technique; thin film solar cells.

INTRODUCTION

Chalcopyrite $CuInGaSe_2$(CIGS), related to ternary and quaternary compounds is belonged to semiconducting I-III-VI_2 family of materials are realistic candidates for a variety of optoelectronic devices such as solar cells, photo-image sensors and light emitting devices etc. In fact, several photovoltaic research is progressing that can make this technology more cost effective from a commercial point of view to compete with Si-based solar module.[1] Chalcopyrite CIGS has emerged as one of the most important polycrystalline semiconducting material in solar industry due to its high absorption coefficient ($10^5 cm^{-1}$), direct band gap and their stability against photo-degradation.[2] Thin layers of CIGS are most efficient light-absorbing materials next to $CuInSe_2$(CIS) that find application as thin film solar cells. The maximum quantum efficiency obtainable from the solar spectrum in the energy range of 1.15 – 1.35 eV is very close to the band gap of CIGS thin film absorber layer.

To enhance the optical properties of the cell, it is experimentally evidenced that grading the band gap of the absorber material improves the device performance.[3] The addition of gallium (Ga) to $CuInSe_2$offers many advantages. It increases the band gap of the material, thus increasing the open- circuit voltage. Based on the [Ga]/ [In+Ga] ratio, the band gap of the CIGS can be varied continuously between 1.04 eV ($CuInSe_2$) and 1.68 eV ($CuGaSe_2$). The short circuit current (Isc) decreases with increasing amount of Ga, as expected from the corresponding increase in the band gap with the Ga content. The maximum short circuit current is obtained for a gallium content of [Ga/ (In+Ga)] =0.37. The open circuit voltage Voc increases with gallium content however not as much as would be expected from the corresponding

increase in the band gap energy.[4] The maximum conversion efficiency obtained in CIGS solar modules with gallium (Ga) content varies between 30 to 37 %.[4]

The efficiency of photovoltaic (PV) cell strongly depends on many factors including stoichiometry, microstructure, presence of impurity phases and surface roughness for a given area of the deposited film. The methods generally used for deposition of CIGS thin films include co-evaporation, selenization and electro-deposition.[5] Since the last decade, various studies have continued in order to enhance the economical competitiveness of the CIGS cells. [6-12] The main problems associated with these materials are that all preparation technologies for these alloy materials are expensive. Therefore, a reliable and a simple process for preparing high purity CIGS functional materials is desirable. To our knowledge, very few reports available in direction till date. Our results demonstrate that, through careful optimization of processing parameters, the single-step hot wall deposition technique can produce stoichiometric CIGS films with good crystalline quality. In this present work reports structural and optical properties of prepared CIGS thin films by hot wall deposition technique for solar cell applications.

EXPERIMENITAL

i. Preparation of bulk $CuIn_{0.7}Ga_{0.3}Se_2$ alloy

$CuIn_{0.7}Ga_{0.3}Se_2$ (CIGS) alloyed compound was prepared from the mixtures containing appropriate amounts of high quality elemental copper, indium, gallium, and selenium (all chemicals from Sigma Aldrich – purity 99.99%) by direct melting. The appropriate amount of elements were cut and crushed into small pieces. Subsequently, these elements were sealed in a quartz ampoule under 10^{-5} Torr and kept in a rotating furnace. The furnace temperature was raised in steps of 100 °C/hr and maintained at 1050 °C for 8 hours. Then the furnace temperature was brought to room temperature at the cooling rate of 50 °C/hr.

The prepared CIGS compounds were crushed and ground to produce the powders. In the present study Leica S-440i EDAX spectrometer was used to determine the elemental contents present in the as-prepared bulk compound. The crystallographic orientations of the powders were determined using Bruker X-ray diffractometer with monochromatic Cu-Kα radiation of wavelength of 1.54056 Å in the scanning range of 20-80° and the step size was 0.02°.

ii. Preparation of hot wall deposited $CuInGaSe_2$ (CIGS)thin films

Thin films of Cu (In, Ga)Se_2 were deposited on to well-cleaned glass substrates by hot wall deposition technique in a base vacuum of 2 x 10^{-6} Torr. The cleanliness of the substrate surface plays a decisive role on film growth and adhesion. A thoroughly cleaned substrate is a pre-requisite for the preparation of films with reproducible properties. The substrates were cleaned with detergent solution, distilled water and acetone for about 30 minutes each in an ultrasonic bath so as to increase the rate of contaminant removal. In ultrasonic cleaning, dissolution of residues is enhanced by intense local stirring action of the shock waves created in the solvent. The substrates were then subjected to isopropyl alcohol vapour degreasing, in which the rising vapour condenses on the glass substrates to be cleaned, thereby heating it and increasing the rate of dissolution of substrate contaminants. Finally, the wet-cleaned glass substrates were dried in a clean oven maintained at about 100 ºC.

Figure-1 shows the schematic of hot wall deposition system used in the present study that consists of a quartz tube of 5.5 cm length and 1 cm diameter with one end open. The end of the quartz tube is shaped in such a way that it rests inside the tungsten conical basket (source heater). Kanthal wire is wound on the quartz tube with equal spacing to provide uniform temperature along the length of the tube (Fig.-2). A glass substrate is held at a distance of less than 1mm with the help of a substrate holder placed exactly above the open end of the quartz tube as a lid closing the tube. The whole arrangement is placed in a vacuum chamber (Hind Hivac Model 12A4, Bangalore, India). The prepared bulk CIGS compound of about 10 mg was taken in the quartz tube as the source material to deposit the CIGS thin films. The wall heating supply voltage and filament current were maintained at 20 V and 1.6 A respectively.

The optical transmittance spectra of the CIGS thin films was recorded in the wavelength range of 190 to 2500 nm using a double beam UV-VIS-NIR spectrophotometer (JASCO,V-570). The substrate absorption

has been corrected by introducing an uncoated polished and clean glass substrate in the path of the reference beam. The surface topography of the prepared CIGS thin films have been studied using Multimode Nanoscope IIIa (Digital instruments – Veeco) atomic force microscopy (AFM).

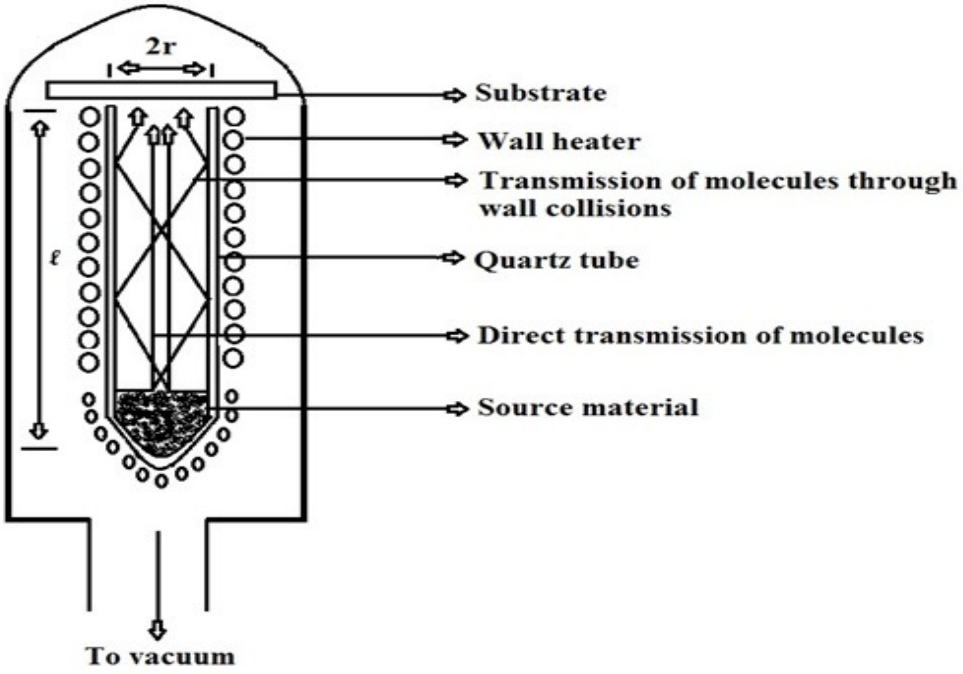

Fig.-1: Schematic of hot wall deposition system for CIGS film preparation

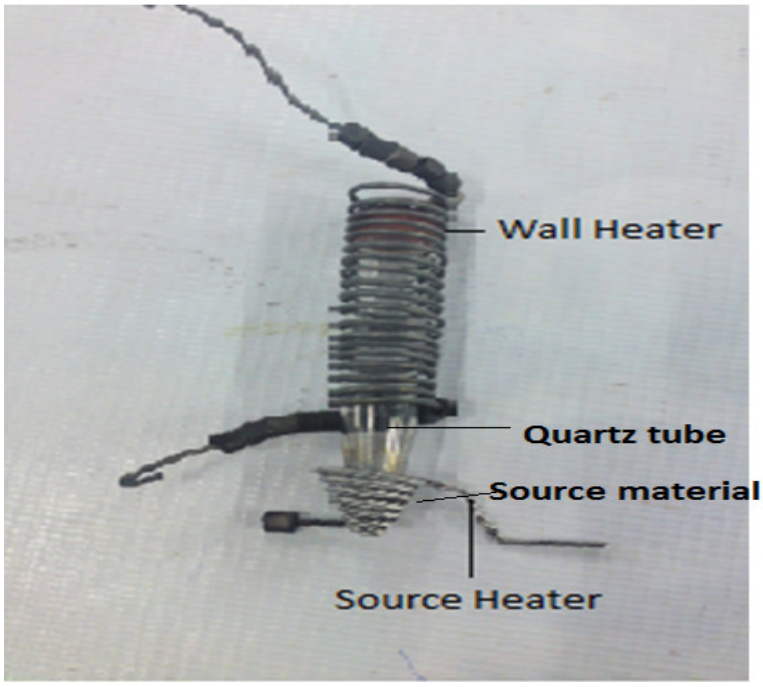

Fig.-2: Wall and source heater arrangements

RESULTS AND DISCUSSION

Chemical composition studies

Bulk $CuIn_{0.7}Ga_{0.3}Se_2$ compound was synthesized using the direct melt method at 1050°C temperature. It is observed that the phase formation sequence of indium and selenium first involves the formation of In_2Se_3 (PDF 00-023-0294) followed by the formation of InSe (PDF 01-080-2272). The following lists the possible reactions during the heating process at the temperature range 100-250 °C.[13]

$$2In + 3Se \rightarrow In_2Se_3 \quad (1)$$
$$In + Se \rightarrow InSe \quad (2)$$
$$Cu + Se \rightarrow CuSe \quad (3)$$
$$Se(s) \rightarrow Se(liq.) \quad (4)$$
$$Ga + Se \rightarrow GaSe \quad (5)$$

These reactions produce the binary compound products which dominate in the temperature range below 400 °C. When the reaction temperature is raised to 500 °C, In_2Se_3 phase disappears while the peaks of $CuIn_{0.7}Ga_{0.3}Se_2$ (1 1 2) and $CuInSe_2$ (2 2 0)/ (2 0 4) start to appear. The related reactions in the temperature range of 350-550 °C can be summarized as follows:

$$CuSe + ½\ In_2Se_3 + ½\ Se \rightarrow CuInSe_2 \quad (6)$$
$$(Cu\text{-}Se) + (0.7)\ (In\text{-}Se) + (0.3)\ (Ga\text{-}Se) \rightarrow CuIn_{0.7}Ga_{0.3}Se_2 \quad (7)$$

The co-existence of predominant binary and ternary phases disappear beyond 725 °C.[14] The energy dispersive x-ray analysis spectra of the prepared bulk CIGS compound were observed and is presented in Fig.-3. The chemical composition of the prepared bulk CIGS compound was found to be copper: 22.23 atomic%, indium: 18.3 atomic%, gallium: 10.18 atomic% and selenium: 49.29 atomic%. [15]

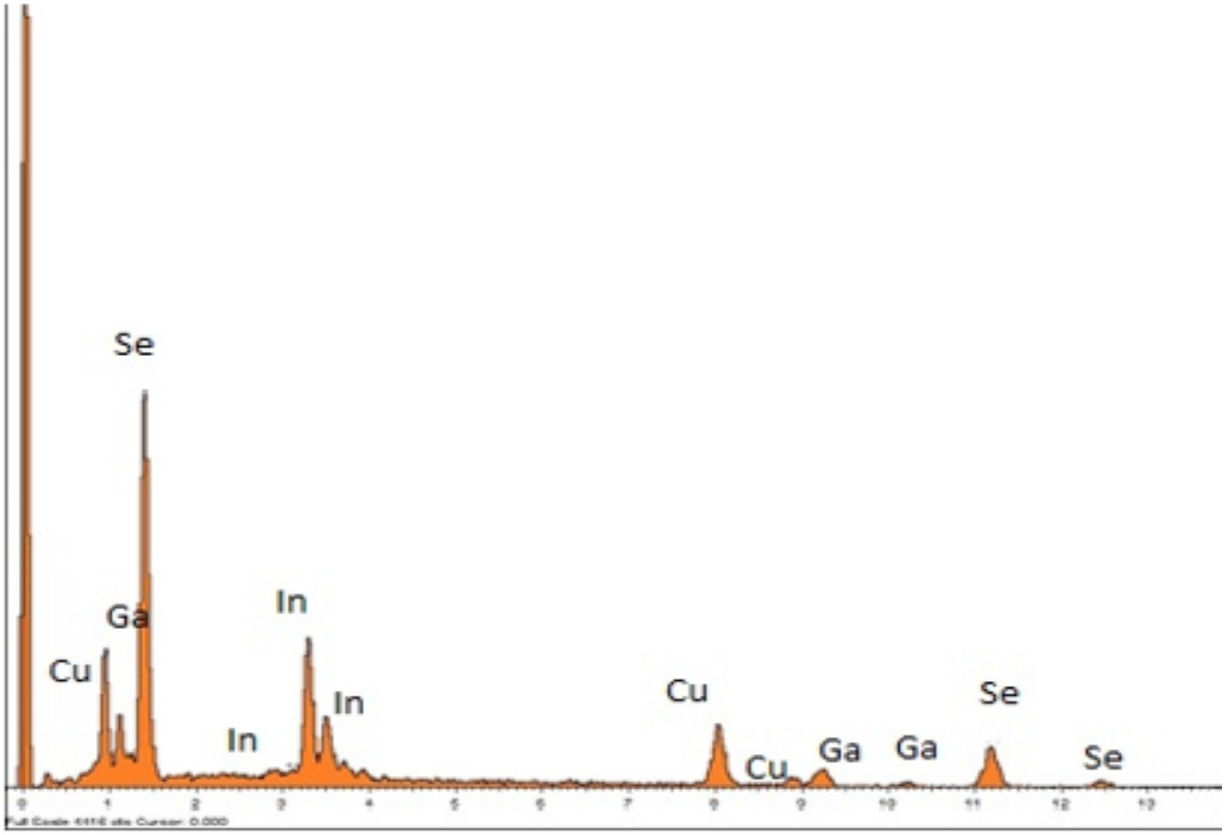

Fig.-3: EDAX pattern as prepared bulk $CuIn_{0.7}Ga_{0.3}Se_2$ compound

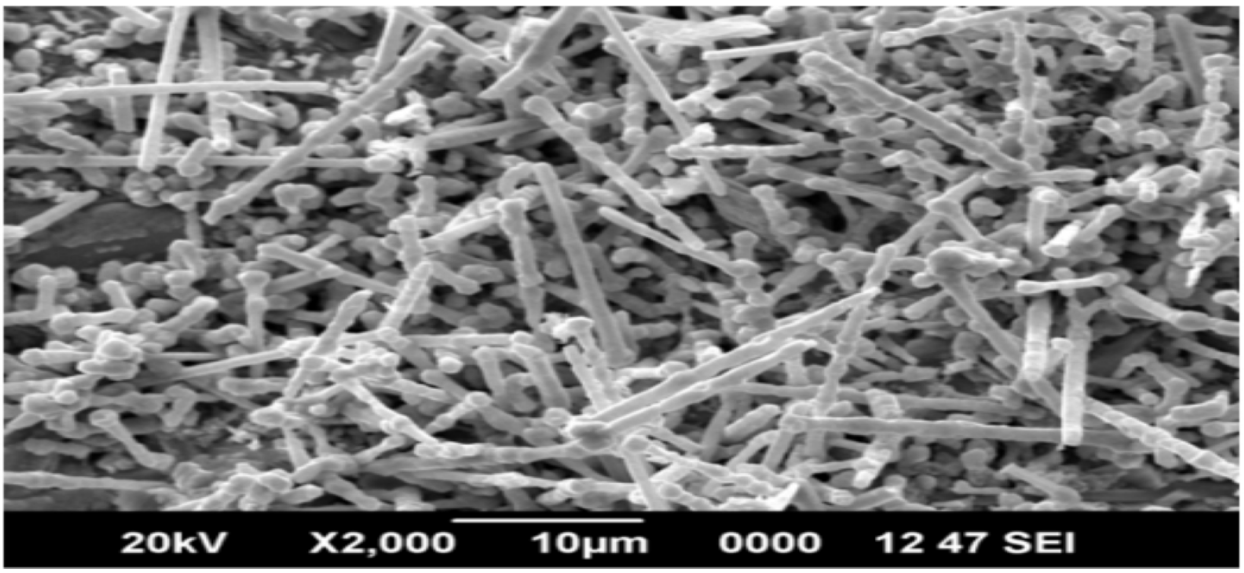

Fig.-4:Scanning electron micrograph (SEM) of bulk $CuIn_{0.7}Ga_{0.3}Se_2$ compound

Figure-4 shows the SEM surface morphology of the prepared bulk CIGS compound.The image revealed that the crystallites are oriented randomly. The stoichiometric compound exhibited rod like morphology as evidenced by the SEM picture.

X-ray diffraction(XRD) analysis

From the X-ray diffraction pattern of the bulk Cu (In,Ga)Se_2 as shown in Fig.-5, the crystalline nature is confirmed. Based on the XRD database (JCPDS #35-1102) these peaks can be assigned to those of CIGS alloy. The most intense peak at 26.7confirmed the existence of chalcopyrite structure. The ratio of peak height intensities of (112) to (220/204) is used as a measure of the preferred orientation. The bulk CIGS compound exhibits chalcopyrite crystal structure with lattice parameters a= 5.73 Å, c= 11.66 Å. $\alpha = \beta = \gamma = 90°$.

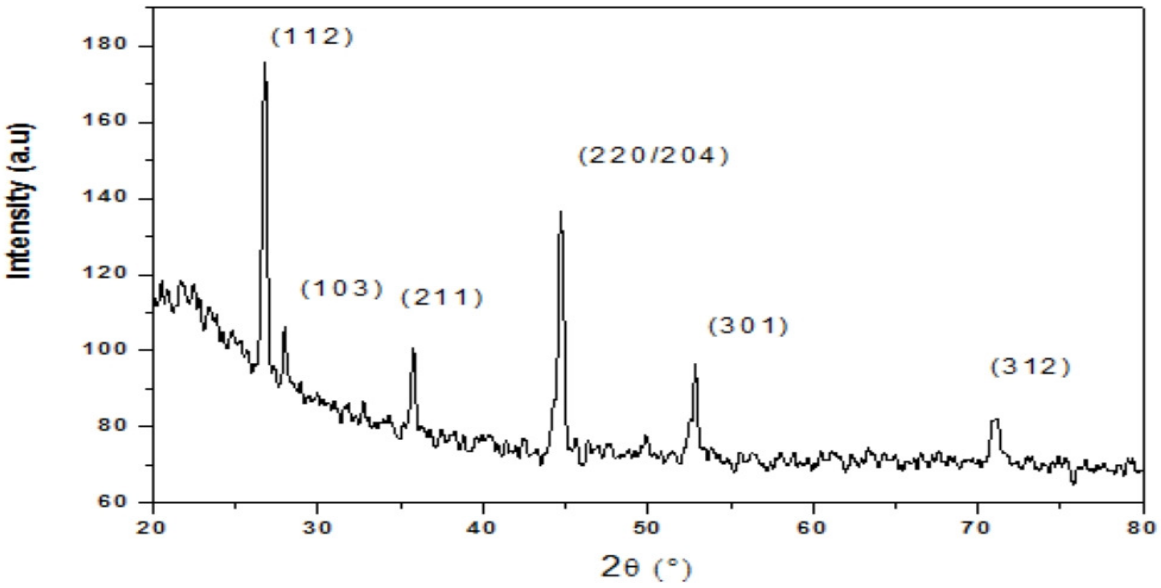

Fig.-5: X-ray diffraction pattern of prepared CIGS bulk powder

The crytal structure of the powders was further confirmed by high resolution tranmission electron microscope. HRTEM images and corresponding selected area electronic diffraction (SAED) patterns arepresented in Fig.-6. HRTEM image indicates that CIGS exhibit large agglomerate states that are composed of super-lattice nanocrystals.The TEM image of the CIGS powder revealed atomic rows spaced about 0.33 nm.[16] The value is comparable to those obtained from XRD analysis shown in Fig.-7. The scanninng transmission electron microscopy (STEM) analysis revealed the composition expected slightly increase in copper content due to the use of TEM copper grid.[17] The expected chalcopyrite structure with the preferential orientation along (112), (220/ 204) and (312) was observed.

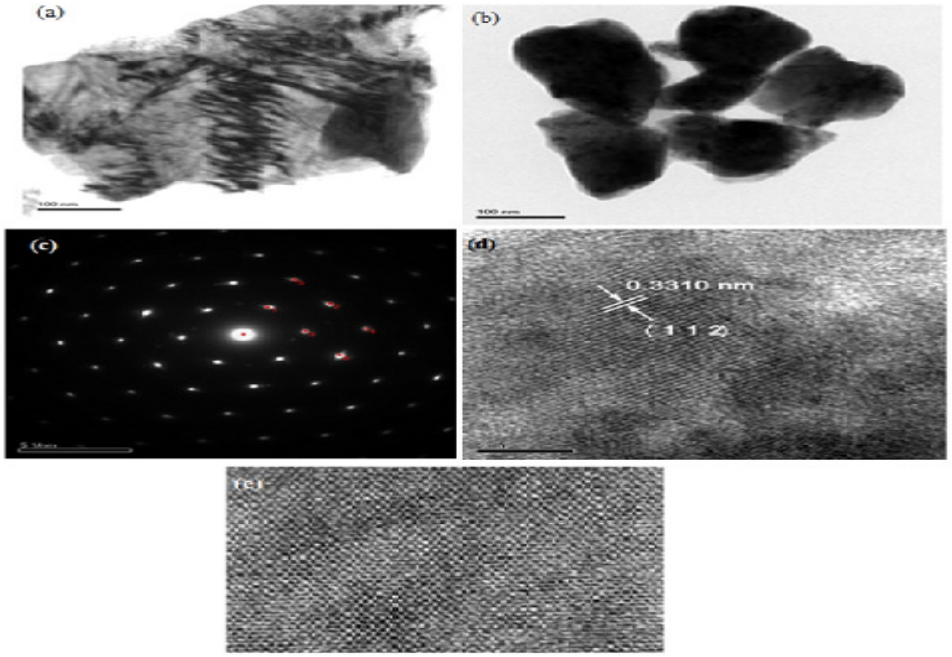

Fig.-6: HRTEM image of the bulk CIGS compound powder

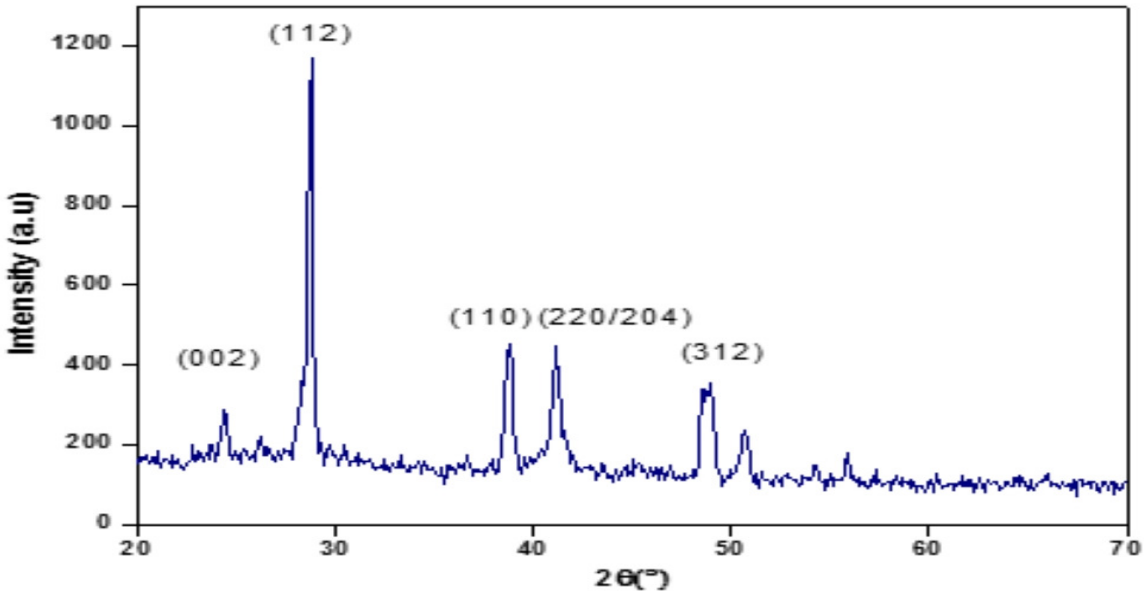

Fig.-7: XRD pattern of hot-wall deposited CIGS thin films

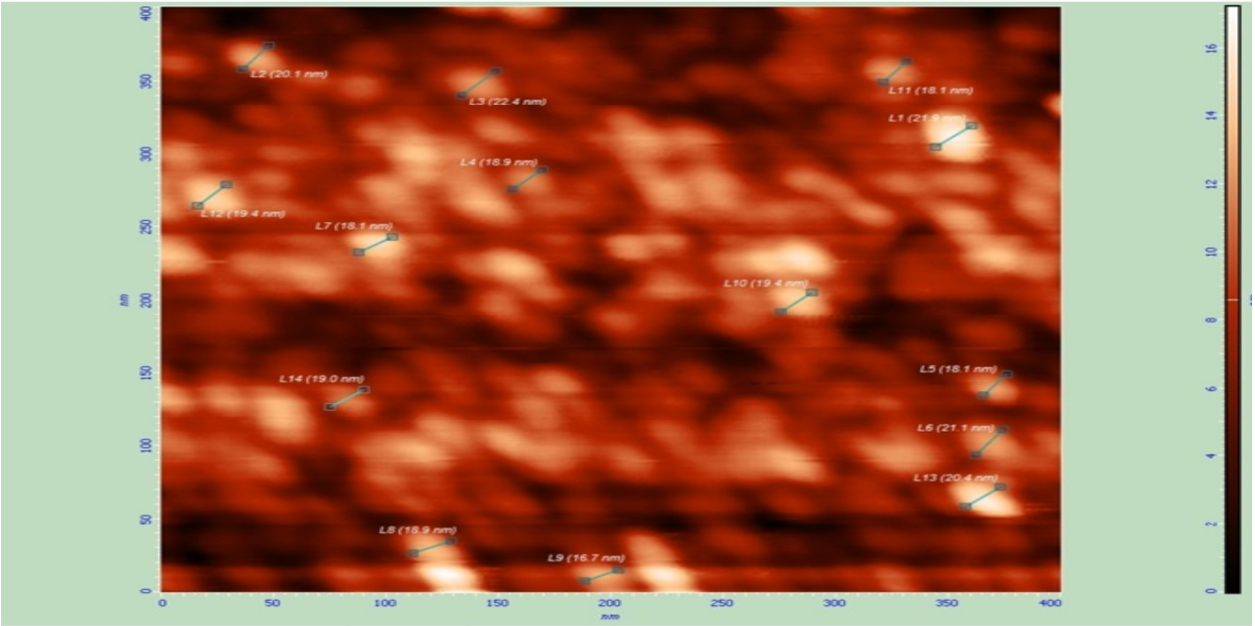

Fig.-8: 2D – image of atomic force microcopy (AFM) of the hot wall deposited thin films of thickness 480 nm.

Surface morphological analysis on the hot wall deposited CIGS thin film has been carried out using an atomic force microscope (AFM). Figure-8 shows the densely packed grains with uniform distribution to the film surface. The AFM image revealed that the average grain size and surface roughness was 20 nm and 8 nm respectively. The improvement in crystallinity of the film occurs by the coalescence of the neighboring islands driven by the thermal energy acquired from the glass substrate.

Optical studies

Fig. 9 shows the transmission spectra of hot wall deposited as-prepared CIGS thin films in the wavelength range between 190 to 2500 nm. All the films show low transmission in the region 300-600 nm. It can be demonstrated that the presence of excess Se will deteriorate the optical properties of the CIGS films, because excess Se increases the residual absorption[13]. The absorption coefficient (α) of the hot wall deposited CIGS thin films can be determined from the transmittance data. The absorption coefficient of the films is relatively high in the order of 10^4 cm^{-1} which demonstrate suitable candidate as it as a photon absorbing material. The optical band gap (E_g), for a direct allowed transition is determined by plotting hν versus $(\alpha h\nu)^2$ (Fig.-10) and by extrapolating linear curve to the hν axis. The band gap was found to be 1.18 eV.[18]

CONCLUSION

Stoichiometric $CuIn_{0.7}Ga_{0.3}Se_2$ compound was synthesized by direct melting method at high temperature. The tetragonal chalcopyrite structure with preferred orientations along the crystallographic planes (1 1 2), (2 2 0/ 2 0 4) was confirmed by XRD pattern for the prepared CIGS compound powder. XRD analysis has been observed for the hot wall deposited CIGS thin film onto a Mo coated glass substrate. The CIGS films exhibit strong preferential orientation along the (1 1 2) plane. The small- angle electron diffracton (SAED) pattern of a three dimensional superlattice consists of nanocrystals of 0.24 nm over a few microns in (211) crystallographic plane of the array. The AFM image revealed that the average grain size and surface roughness was 20 nm and 8 nm respectively. Stoichiometric $CuIn_{0.7}Ga_{0.3}Se_2$ with chalcopyrite structure and preferential orientation (1 1 2) with good crystalline quality and a band gap of 1.18 eV is obtained. Our work suggests that CIGS films prepared by hot-wall deposition process will be suitable candidates for solar cell applications.

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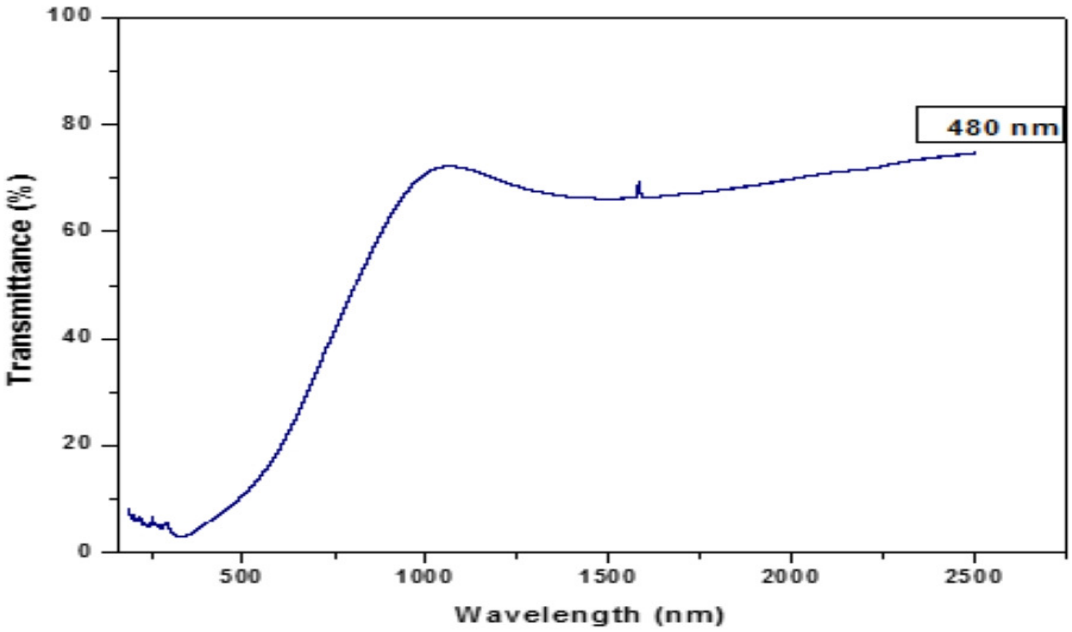

Fig.-9: Transmittance spectra of CIGS thin films of thickness 480 nm

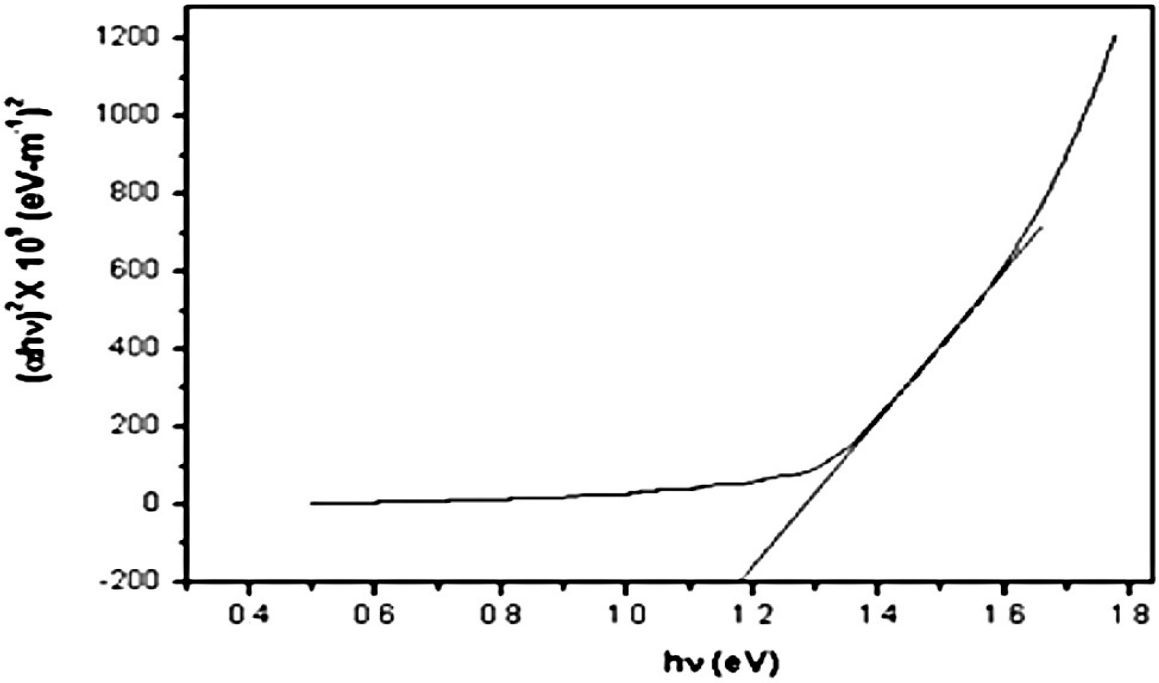

Fig.-10: Graph of hν versus $(\alpha h\nu)^2$

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