

Mechanochemically Synthesized CIGS Nanocrystalline Powder for Solar Cell ApplicationBharati Rehani^{1,*}, J.R. Ray², C.J. Panchal², Hamza Master¹, R.R. Desai³, P.B. Patel⁴¹ *Metallurgical and Materials Engineering Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara-390001, Gujarat, India*² *Applied Physics Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara-390001, Gujarat, India*³ *Department of Chemistry, Sardar Patel University, Vallabh Vidhyanagar-380120, India*⁴ *Department of Electronics, Sardar Patel University, Vallabh Vidhyanagar-380120, India*

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Copper Indium Gallium Diselenide (CIGS) is a compound semiconductor material from the group of III-VI. The material is a solid solution of copper, indium and selenium (CIS) and copper, gallium and selenium with an empirical formula of $\text{CuIn}_{(1-x)}\text{Ga}_x\text{Se}_2$, where $0 < x < 1$. CIGS has an exceptionally high absorption coefficient of more than 10^5 cm^{-1} for 1.5 eV. Solar cells prepared from absorber layers of CIGS materials have shown an efficiency higher than 20 %. $\text{CuIn}_{(1-x)}\text{Ga}_x\text{Se}_2$ ($x = 0.3$) nanocrystalline compound was mechanochemically synthesized by high-energy milling in a planetary ball mill. The phase identification and crystallite size of milled powders at different time intervals were carried out by X-ray diffraction (XRD). The XRD analysis indicates chalcopyrite structure and the crystallite size of about 10 nm of high-energy milled CIGS powder after two and half hours of milling. An attempt for preparing the thin film from CIGS nanocrystalline powder was carried out using the flash evaporation technique. Scanning electron microscopy (SEM) reveals uniform distribution of CIGS particles in thin film.

Keywords: Mechanochemical synthesis, Nanocrystalline powder, XRD, SEM, Flash evaporation.

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1. INTRODUCTION

The application of nanotechnology is regarded as an important factor for photovoltaic application. It will achieve broad economic acceptance through considerable cost savings and increase in efficiency. This development is based on new materials and solar cell types with simpler production processes [1]. However, the conventional vacuum based evaporation methods have drawbacks such as the process complexity, high production costs and issues regarding the scaling up. Before the commercialization of the solar cells, these factors need to be considered.

In this regard, a nanoparticle based preparation of the CIGS material and the absorber layer is believed to be a promising process due to a relatively low cost simple preparation method and flexibility for scaling up supports the recent advances in nanoparticle synthesis technologies. The various processes for the synthesis of CIGS nanoparticles/nanocrystalline powder are colloidal process [2], precipitation [3], thermolysis [4] and mechanical alloying [5]. The advantage of the nano size effect of particles is that it lowers the melting temperature of the material [6] and therefore an exothermal reactive sintering occurs.

Pure metal powders in desired stoichiometry are generally milled in planetary ball mill. The particles are repeatedly flattened, fractured and rewelded during the process of milling. The kinetic energy of alloying with phase transformation during milling depends upon energy transferred by balls to the powder [8]. Copper Indium diselenide (CIS) nanocrystalline powder is very easy to prepare without mechanical milling. Addition of Gallium (Ga) in the CIS could make this process diffi-

cult, due to the low melting temperature of Ga. Thus, mechanochemical synthesis is considered as a suitable method. The major advantage of Ga addition is that band gap is increasing from 1.02 to 1.66 eV, as the content of Ga increases from 0 to 1. In CIGS based thin film solar cell highest efficiency reported was 20.3 % [7] for addition of 0.3 of Ga.

In this work the CIGS nanocrystalline powder was synthesized by mechanochemical process, i.e. ball milling process. Effect of milling time on the material phase formation, and crystallite size has been discussed. The phase identification and crystallite size measurement were carried out using the X-ray Diffraction (XRD) method. In addition to this an attempt was made to prepare CIGS thin film on glass substrate using flash evaporation technique. The surface morphology of the CIGS thin film was studied using Scanning Electron Microscopy (SEM).

2. EXPERIMENTAL

Copper (Cu), Indium (In), Selenium (Se) and Gallium (Ga) are taken in stoichiometric quantities according to $\text{Cu}_1\text{In}_{(1-x)}\text{Ga}_x\text{Se}_2$ where $x = 0.3$. The mixed powder was blended in a rolling milling for 30 min prior to high-energy milling. High-energy milling was carried out in a 250 ml capacity twin-bowl type planetary ball mill of M/s. Insmart Systems, Hyderabad. The milling was carried out in tungsten carbide lined stainless steel vial using tungsten carbide balls of 10 mm and 6 mm diameters as grinding bodies. The photograph of twin-bowl type planetary ball mill system is shown in Fig. 1.

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Fig. 1 – Twin-bowl type planetary ball mill system. Inset figure shows the tungsten carbide (WC) lined stainless steel vial and WC balls

The mill was operated at a speed of 400 rpm and ball to charge ratio of 10 : 1. Argon gas was purged inside the jars before milling to avoid any oxidation during high-energy milling. During the course of milling, powder samples were drawn at an interval of 30 minute for characterization by X-ray diffraction (XRD). The powder diffraction profiles were obtained using Bruker AXS, D8 advance diffractometer, within the 2θ range of 20° - 80° at a scan speed of 3° per min using Cu target and Cu-K α radiation of 0.154056 nm wavelength at a power rating of 40 kV and 40 mA.

The thin film of CIGS was prepared on glass substrate by flash evaporation technique from CIGS nanocrystalline powder in vacuum coating unit of HIND HIVAC, Bangalore (model no. 15F6). The surface morphology of thin film was studied using Scanning Electron Microscope model JEOL JSM-5610 LV at different magnifications [9].

3. RESULTS AND DISCUSSIONS

3.1 XRD Analysis

XRD profile of milled powder samples at different milling time is shown in Fig. 2. Main peaks appear at (112), (220)/(204), (116), and (400) planes indicating tetragonal chalcopyrite structure of Cu(In, Ga)Se₂ (CIGS) compound. Peaks appear to be sharp indicating crystalline phase of compound. With the CIGS phase and additional CuSe phase is also observed as milling time increases, particularly after 2 h milling time. The d -values of CuSe phase match with the PDF-ICDD no. 26-0556, which shows its hexagonal structure. At room temperature, CuSe exists as hexagonal phase but at 48°C , it is converted to orthorhombic form and reverts back to hexagonal form at 120°C [10]. The presence of CuSe in this case after 2 h milling may be due to increase in temperature during high-energy ball milling. During milling the frictional forces between jar and grinding media leads to moderate increase in tem-

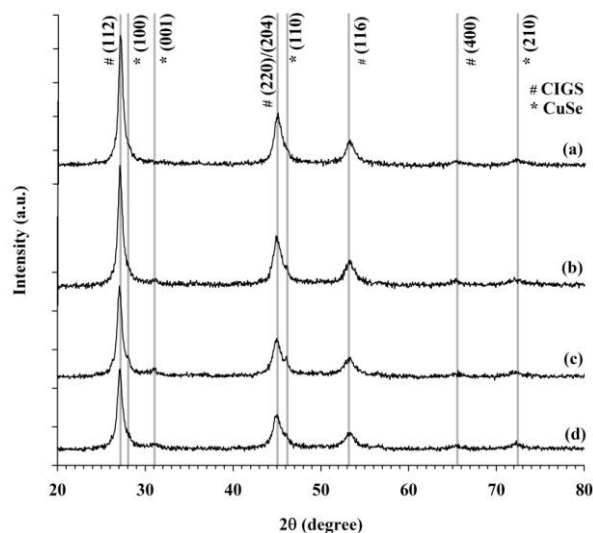


Fig. 2 – XRD spectra of CIGS powder prepared by ball milling having a different milling time 1 h (a), 1.5 h (b), 2.0 h (c), and 2.5 h (d)

perature during milling. In Fig. 2 the crystalline planes for CuSe are (100), (001), (110), and (210) as indicated.

The broadening of major peak i.e. (112) is clearly observed from the XRD spectra. This indicates that the crystallite size reduces with increase in milling time from 1 h to 2.5 h. Relatively broad X-ray peaks were obtained for 2.5 h ball milling time, which are indicative of crystallite size in nano size regime. Crystallite size was calculated using Scherrer's equation for different milling time as given in Table 1. The Table 1 also give the interplanar distance (d), corresponding 2θ values and Full-width half maximum (FWHM) of CIGS nanocrystalline powder at different milling time.

Table 1 – Crystallite size and interplanar distance of CIGS nanocrystalline powder at different milling time

| Milling time (h) | 2θ ($^\circ$) | FWHM (radians) | Crystallite Size, D (nm) | d – spacing (nm) |
|------------------|------------------------|----------------|----------------------------|--------------------|
| 1 | 27.05 | 0.01047 | 13.62 | 0.3295 |
| 1.5 | 27.05 | 0.01134 | 13.62 | 0.3295 |
| 2 | 27.05 | 0.01134 | 12.58 | 0.3295 |
| 2.5 | 27.1 | 0.01309 | 10.9 | 0.3289 |

The XRD spectra shown in Fig. 2 have been compared to standard data, PDF-ICDD no. 35-1102, it shows a slight shift of the peaks towards higher 2θ angles. Shifting to the higher diffraction angles may due to lattice distortion and internal stresses induced during the course of milling [5]. The internal stresses modify the lattice parameters and consequently produce an angular shift of XRD peak. The XRD profiles when compared for different milling times reveal minor shift of peaks towards higher 2θ angles, especially for 2.5 h of milling. This shift is possibly due to integration of gallium atom in place of indium and thus changes in lattice parameters. When relatively smaller gallium atoms substitute for indium atoms in the lattice, it results in gradual change in lattice parameters (d – spacing) [11]. The Lattice parameters 'a' and 'c' were calculated using Equation 1.

$$\frac{1}{d^2} = \left[\frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \right] \quad (1)$$

The 'a' and 'c' values obtained match closely with the standard data i.e. PDF-ICDD no. 35-1102. Vegard's law states that there is a linear relationship between the lattice parameter 'c' and the composition x of gallium. The value of lattice parameter 'c' decreases linearly with gradual decrease in indium content [4]. As milling duration increases values of lattice parameter 'c' decreases as shown in Table 2. This result supports the fact that milling does improve the composition of CIGS compounds by increasing gallium rich phases. Also, it reduces the probability of generation of the secondary crystalline phases.

CIGS compound possess tetragonal chalcopyrite structure with Bravais lattice values given as $\{x, y, z\} = \{1, 1, 2\}$. Each group I element (Cu) and group III element (In/Ga) atoms has four bonds to group VI element (Se). In turn each Se atom has two bonds to Cu and two bonds to In/Ga. As the strength of the group I-VI and group III-VI bonds are in general different, the ratio of the lattice constants c/a is not exactly '2' [11]. The c/a ratios for CIGS nano-crystalline powder is in good agreement with the literature as shown in Table 2. Quantity 'U' equals to $(2 - c/a)$ is a measure of the tetragonal distortion in chalcopyrite materials.

Table 2 – FWHM, lattice constants 'a' and 'c', with the tetragonal distortion factor (U) of CIGS nanocrystalline powder at different milling time.

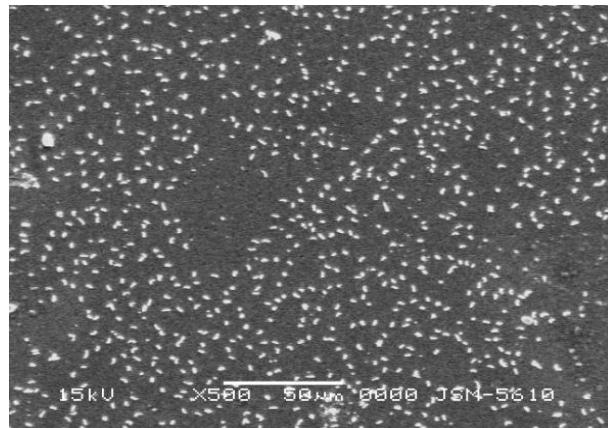
| Milling Time (h) | FWHM (radians) | a (Å) | c (Å) | c/a (Å) | U = 2 - c/a |
|------------------|----------------|-------|-------|---------|-------------|
| 1 | 0.01047 | 5.698 | 11.47 | 2.012 | -0.0129 |
| 1.5 | 0.01134 | 5.715 | 11.39 | 1.993 | 0.0070 |
| 2 | 0.01134 | 5.698 | 11.46 | 2.011 | -0.0112 |
| 2.5 | 0.01309 | 5.698 | 11.40 | 2.007 | -0.0007 |

As seen from the Table 2 the tetragonal distortion factor is near to zero at 2.5 h milling time i.e. -0.0007. This indicates the minimum stress is present in the CIGS powder prepared at higher milling time.

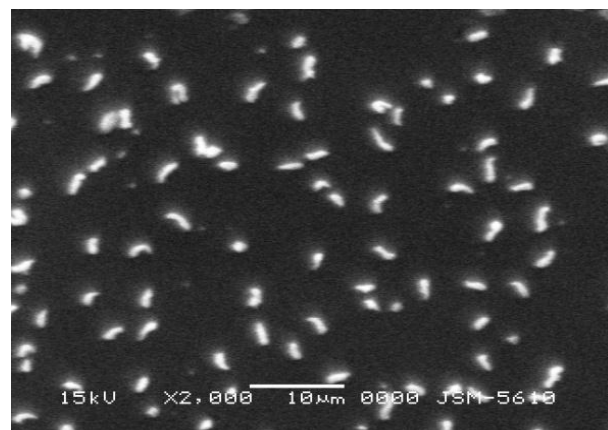
3.2 SEM Analysis of CIGS Thin Film

SEM micrographs of flash evaporated CIGS thin film prepared from nanocrystalline powder at different magnifications are shown in Fig. 3a and 3b. The thin films are deposited on glass slide of 7.5 cm \times 2.5 cm at a pre-deposition temperature of 523 K. The thickness of the film was kept near to 250 nm. The film thickness was measured using the quartz crystal thickness monitor. The film is quiet dense with average distance between grains is 0.5 to 1 μ m as seen in Fig. 3. Grains shown in SEM images are worm shaped with approximately 0.5 μ m in length and 0.08-0.1 μ m in width. These worms like grains possess a white shining appearance. In the early stages of deposition, adsorption occurs at discrete nucleation sites. As atoms approach the surface, islands are formed which grows in size until they merge with neighboring islands to form a continuous film. The probability of migration for adsorbed atom on the surface is relatively less at lower substrate temperature.

Deposition at lower substrate temperature leads to formation of small isolated grains with large number of voids. Surface migration increases at higher substrate temperature resulting in enhanced interaction of adsorbed atoms to form large grains [13]. This will have a major effect on the size and number of voids present in the film. At higher substrate temperatures, i.e. 573 K, grain distribution becomes uniform and dense as shown in Fig. 3. The surface morphology shows nearly uniform distribution of grains.



a



b

Fig. 3 – SEM microphotograph of CIGS thin film (thickness 250 nm) deposited at 523 K substrate temperature prepared from nanocrystalline powder at 500X (a) and 2000X (b).

4. CONCLUSIONS

High-energy ball milling of elemental of Copper, Indium, Gallium and Selenium appears a suitable process for the production of Cu(In, Ga)Se₂ (CIGS) nanocrystalline powder having tetragonal chalcopyrite structure. Minor secondary CuSe phase appears after 2 h milling. The milled CIGS powder has crystallite size less than 10 nm after two and half hours (2.5 h) of milling. Scanning Electron Microscopy (SEM) of as-deposited CIGS thin film by flash evaporation technique at a substrate temperature of 523 K shows shining white worm like grains uniformly distributed on the surface.

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