Effect of Milling Time on Mechanically Alloyed Cu(In,Ga)Se 2 Nanoparticles

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Effect of Milling Time on Mechanically Alloyed Cu(In,Ga)Se_2 Nanoparticles

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***Abstract*— Copper indium gallium diselenide alloy powders were synthesised by mechanical alloying of elemental Cu, In, Ga and Se in a planetary ball mill. Effect of milling time on structure of CIGS nanoparticles was studied using X-ray diffraction measurements. Influence of milling time on phase evolution, cell parameters and crystallite size was reported in detail. FESEM analysis provided information on the morphological changes of CIGS particle during milling. EDAX results revealed dependence of milling time on composition of product particles. A tendency of increasing Cu and decreasing Se concentration with milling time was observed. Cu and Ga rich CIGS nanoparticles were obtained after milling for 6 h. The sample obtained after 6 h of milling showed homogeneous composition.**

Keywords*— *$CuIn_{0.5}Ga_{0.5}Se_2$ nanoparticle, mechanical alloying, FESEM, EDAX.

I. INTRODUCTION

Copper indium gallium diselenide (CIGS), a quaternary semiconductor alloy, has gained attraction as an absorber material in photovoltaic devices. CIGS exhibits high absorption coefficient (10^5/cm). A 1-2 µm thick CIGS layer is able to absorb 90% of the incident sunlight [1]. More over this direct bandgap material has shown good radiation stabilities [2]. A tunable bandgap (1.02 -1.66 eV) [2, 3] with varying concentration of gallium is another important physical property which makes CIGS a promising absorber material from the chalcogenide family. Recently, CIGS based solar cell has shown highest efficiency (20.4%) among thin film photovoltaics [4].

Vacuum techniques such as co evaporation [5] and sputtering [6] are considered to be the best to produce good quality CIGS thin films. But the initial equipment cost [7] and further maintenance expenses make them uneconomical. In addition, there exist issues in scaling up of sophisticated vacuum equipments and wastage of material utilization [8, 2]. Research on non-vacuum techniques acquired interest to prevail over the limitations of vacuum methods. Among various non-vacuum techniques such as electrodeposition [9], spray pyrolysis [10], paste coating [11], etc, deposition of nanoparticle based precursor material on to a substrate is regarded as a feasible method due to good control over atomic concentrations [12], high material usage and simplicity in scale up [9].

There are variety of methods including colloidal process [13], solvothermal process [14] and mechanical alloying to synthesise CIGS nanoparticles. Mechanical alloying involves milling powders of metals, alloy or compounds together. During this process material transfer will take place to acquire homogenous alloy [15]. The potential to obtain bulk CIGS nanoparticles from non toxic precursor materials with high energy efficiency in short processing time makes mechanical alloying advantageous over other techniques [1]. Despite this fact, mechanical alloying is an intricate process involving various parameters, such as ball to powder ratio (BPR), milling time, milling velocity (rpm) and milling medium, which needs to be optimised to synthesize nanoparticles of desired properties.

Benslim et al. have reported the structural studies of mechanical alloying of CIGS nanoparticles from elemental Cu, In, Ga and Se [16].The effect of milling time on material phase formation and crystallite size of CIGS nanoparticles is recently reported by Rehani [3]. Influence of milling time on composition and uniform stoichiometry of CIGS alloy is not well studied yet. In the present work, we have analysed the effect of milling time on the structural, morphological and compositional properties of mechanically alloyed CIGS nanoparticles.

II. EXPERIMENTAL

Copper indium gallium diselenide nanoparticles were synthesised using high energy mechanical alloying process. Elemental copper granules (>99.90 pure), gallium granules (>99.99 pure), powders of indium (>99.99 pure) and selenium (>99.99 pure) were weighed according to the molar ratio of $CuIn_{0.5}Ga_{0.5}Se_2$. This precursor material mixture was taken in a tungsten carbide vial. Tungsten carbide balls of 10 mm diameter were also used. In order to study the effect of milling time on the structural, morphological and compositional properties of CIGS alloy, mechanical alloying process was carried out with a BPR of 15:1 at milling speed of 400 rpm for 2,4 and 6 h.

Structural properties of the prepared CIGS alloy was investigated using X-ray powder diffraction (XRD) analysis performed on a Smart Lab Diffractometer (Rigaku) using Cu Kα radiation (λ= 1.504Å). Measured diffraction intensity was

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in the 2θ range between 20◦ and 90◦ with a step size of 0.02◦ for 6 s per point. Morphology of the CIGS powders was analyzed using Carl Zeiss Auriga Field emission scanning electron microscopy (FESEM). Composition of the CIGS nanoparticle was analyzed by Bruker Ser 5010 X flash Scanning electron microscopy (SEM)-energy dispersive X-ray analysis (EDS).

III. RESULTS AND DISCUSSION

A. Structural properties

X ray diffractogram of CIGS alloy particles obtained after ball milling for 2 h to 6 h with BPR of 15:1 at 400 rpm was shown in figure 1. It showed formation of single phase CIGS chalcopyrite structure with increasing milling time. At a milling time of 2 h, the product obtained was a mixture of CIGS and secondary phases such as Cu_2O, $CuInO_2$, Cu_2Se, and Ga_2O_3. As the milling time progressed, intensity of (112), (220)/(204),(312)/(116) planes of CIGS chalcopyrite structure increased and planes corresponding to secondary phases decreased. As intensity of peaks in X- ray diffractogram is directly proportional to density of crystalline planes in the sample, we confirmed the formation of single chalcopyrite phase CIGS alloy particles at milling time of 6 h. During mechanical alloying process, the precursor materials will undergo various steps such as cold welding, fracturing and rewelding along with increase in temperature due to collision of high energy balls among each other and with the wall of the vial. We assume that oxide and selenide secondary phases dissociated with increase in temperature and led to the formation of single CIGS phase.

A shift in peak position to lower diffracting angle was observed with increasing milling time. The lattice parameters "a" and "c" were calculated using "(1)".

$$1/d^2 = (h^2+k^2)/a^2 + l^2/c^2 \qquad (1)$$

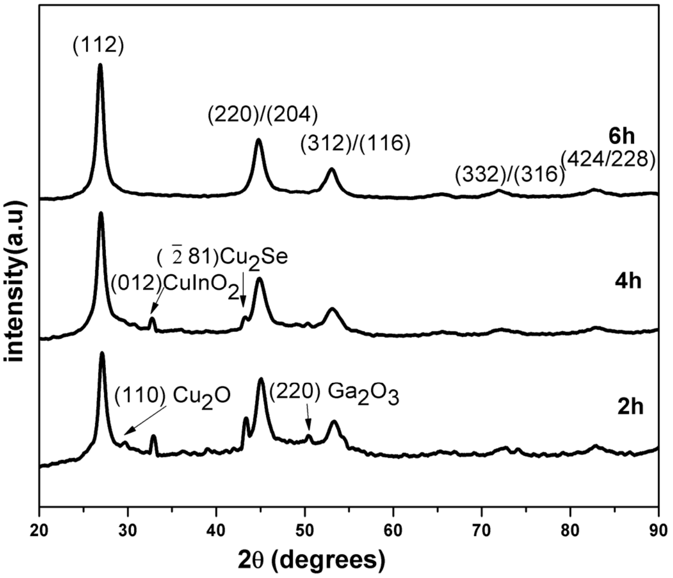

Fig. 1 X-ray diffractogram of synthesized CIGS alloy powder milled for 2, 4 and 6 h.

Where, h, k and l are miller indices, d is the atomic lattice spacing, a and c are lattice parameters of CIGS crystal structure.

It was observed from the fig.2 that lattice parameter "c" increased with milling time while "a" showed a slight change. It may be due to either increasing Cu or decreasing Ga with milling time. CIGS exhibit chalcopyrite crystal structure in which each Cu and In/Ga atom have four bonds to Se atom while each Se atom has two bonds to each Cu and In/Ga atoms. Lattice parameters "a" and "c" are dependent on the bond strength between each atom. Since strength of Cu-Se, In-Se and Ga-Se bonds are different, c/a will be slightly different from 2 [17]. Tetragonal distortion parameter U= 2-c/a (table 1) was found to be increasing from positive to negative value showing occurrence of dilation of crystal structure with milling time rather than compression [18].

We could notice from table 1 that there is an increase in full width half maximum (FWHM) of (112) plane. Crystallite size was calculated using Scherrer's formula. Figure 3 showed decrease in crystallite size from 8.8 nm to 8.08 nm with increasing milling time. A rapid decrease in crystallite size occurred from 2 to 4 h of milling. But after 4 h, only a slight decrease in crystallite size occurred. This result emphasized the importance of milling time in reducing crystallite size [19].

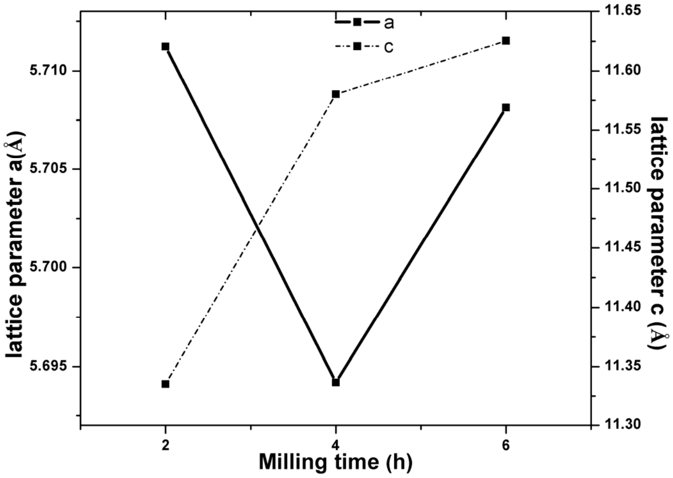

Fig. 2 Variation of lattice parameters "a" and "c" with milling time.

Table 1. Full width half maximum (FWHM), d spacing and tetragonal distortion factor U of CIGS powder at different milling time.

Milling time (h)	D spacing (Å)	FWHM	U=2-c/a
2	3.288	0.889	0.015
4	3.305	0.910	-0.033
6	3.315	0.913	-0.036

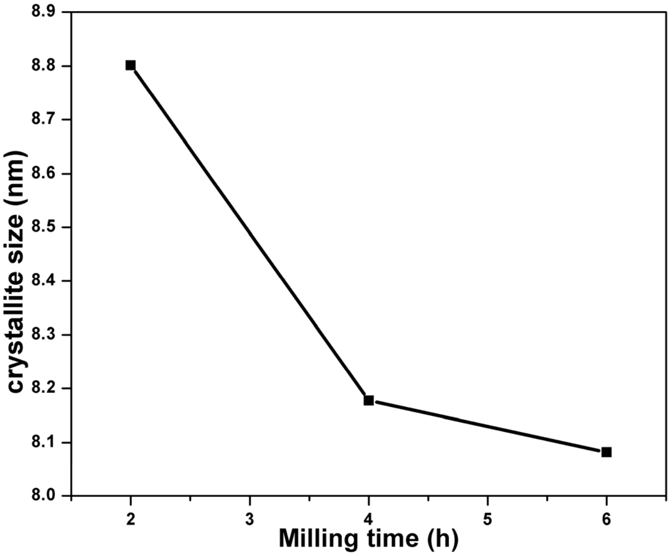

Fig. 3 Variation of crystallite size with milling time.

B. *Compositional properties*

The EDAX analysis (table 2) showed that the compositions of ball milled particles are close to initial $CuIn_{0.5}Ga_{0.5}Se_2$ composition. It was observed that atomic percentage of Cu increased with milling time. While Se atomic percentage decreased. This was in accordance with the results reported by Vidhya et al. [20]. Loss of Se at higher milling time may be due to either volatilization with increased temperature inside the vial or contamination from the container and balls. An increase in In content from 10.33 to 12.40 at% was noted by varying milling time from 2 h to 4 h. A decrease in Ga content was noted with longer milling time as Ga is a soft material and it is very facile to stick onto the walls of the vial. This was in good agreement with increase in lattice constant “c” with milling time. The CIGS nanoparticles obtained after 6 h of milling time was copper rich with Cu/In+Ga ratio to be 1.19. Hence, the influence of milling time on the composition of product was verified.

EDAX analysis performed at multiple points for the CIGS alloy obtained after 6h of milling time was shown in fig.4 and obtained data enlisted in table 3. It was observed that CIGS has good homogeneity in composition.

Table 2. Atomic percentage of Cu, In, Ga and Se in the synthesised CIGS milled for 2, 4 and 6 h.

Milling time (h)	**Atomic percentage of elements (at %)**				**Cu/In+Ga**	**Ga/In+Ga**
	Cu	***In***	***Ga***	***Se***		
2	21.9	10.3	15.3	52.37	0.857	0.596
4	25.7	12.4	12.8	49.02	1.018	0.509
6	28.7	11.1	12.9	47.24	1.197	0.537

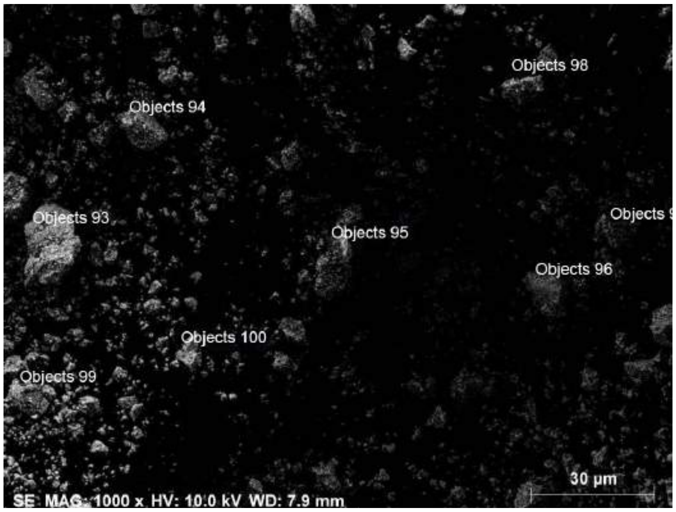

Fig. 4 EDAX analysis at multipoint on CIGS alloy powder obtained after milling time of 6 h.

Table 3. Distribution of constituent elements in CIGS alloy milled for 6 h obtained from EDAX performed at multiple points.

Points	**Atomic percentage of elements (at %)**			
	Cu	***In***	***Ga***	***Se***
93	29.88	9.14	14.35	46.63
94	29.48	9.24	13.92	47.36
95	29.82	9.34	13.32	47.52
96	30.00	8.30	14.16	47.21
97	29.80	9.58	13.18	48.37
98	29.80	8.87	13.55	47.78
99	25.97	12.31	12.78	48.95
100	30.05	8.75	14.12	47.09

C. *Morphological properties*

FESEM images of the CIGS alloy powder obtained after 2, 4 and 6 h of milling time were shown in fig. 5. It was found that surface morphology of product changed with milling time. During ball milling process, the initial precursor materials will undergo ball-powder-ball collision and pass through a flattening stage due to the force exerted by collisions. Upon continuous collisions with balls, the flattened structures will be cold welded. Because of welding process particle morphology have the appearance of flat agglomerated particles (fig. 5-2 h). Cold welded particles will fracture owing to prolonged collisions (fig.5-4 h). The tendency of agglomeration increases as fractured particles have gained high surface energy (fig.5-6 h). High surface energy and cohesion among particles with decreasing particle size account for agglomeration. The fracturing and cold welding mechanisms continue as milling time prolongs [19]. Hence, it is clear that milling time has profound influence on morphology of synthesised particles.

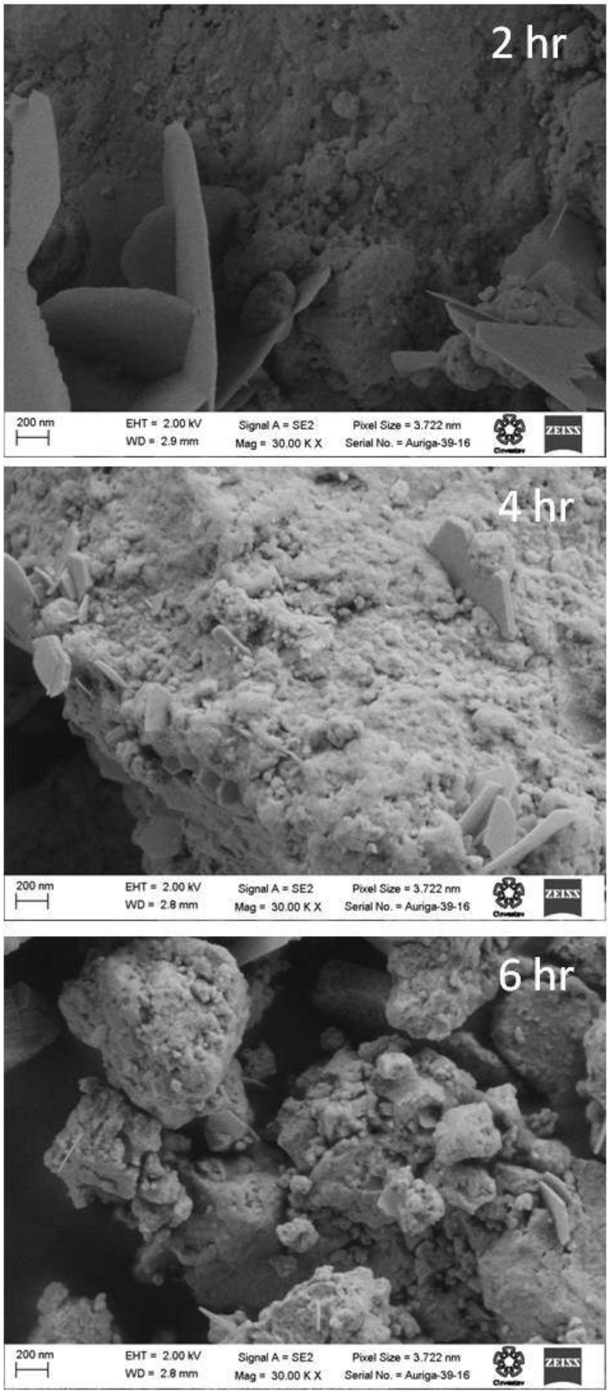

Fig. 5 FESEM images of mechanically alloyed CIGS alloy obtained after 2, 4 and 6 hr of milling.

IV. CONCLUSION

Quaternary chalcopyrite phase $CuIn_{0.5}Ga_{0.5}Se_2$ alloy powder was prepared successfully using mechanical alloying process. CIGS nanoparticles with crystallite size of 8nm were obtained by mechanical alloying for 6 h. A shift in XRD peak to lower diffracting angles and changes in lattice parameters were observed with increasing milling time. Composition of CIGS alloy was greatly affected with change in milling time. CIGS alloy obtained after 2 h of milling time was slightly copper poor and Se rich. On the other hand, Cu rich and Se poor CIGS alloy were formed after milling for 6 h. Dependence of milling time on morphology of alloyed particle was clearly understood from the SEM analysis. CIGS alloy powder mixture obtained at the end of 2 h of milling was found to be flat due to cold welding. While agglomerated CIGS alloy powders were observed after milling for 6 h owing to repeated fracturing and re-welding processes took place during mechanical alloying. Further work on mechanical alloying process to reduce synthesis time and agglomeration of CIGS alloy particles by increasing BPR is under investigation.

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