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Parametric optimization of mechanochemical process for synthesis of $Cu(In, Ga)_{0.5}Se_2$ nanoparticles

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ABSTRACT

Copper indium gallium diselenide (CIGS) is a promising photovoltaic material. Non-vacuum deposition of CIGS is a recommended strategy to produce cost effective solar cells. Amongst various non-vacuum deposition techniques, nanoparticle based deposition methods have gained major impetus due to their economic benefits, simplicity and flexibility to scale up. In the present work, CIGS nanoparticles are synthesized by a mechanochemical process and the effect of milling parameters (ball to powder ratio (BPR), milling speed (rpm) and milling time) on the structural, morphological and compositional properties have been studied. CIGS nanoparticles are synthesized with BPR of 15:1, 20:1 and 25:1 for different milling times ranging from 1 to 6 h and milling speeds from 200 to 400 rpm. The synthesized CIGS nanoparticles have been characterized using XRD, FESEM, HRTEM and EDAX analysis. XRD analysis showed the formation of chalcopyrite CIGS nanoparticles without any secondary phase within 2 h of milling time with a BPR of 25:1 at 400 rpm. The influence of milling parameters on morphology and agglomeration has been studied using FESEM. It is observed that the nanoparticles synthesized at higher BPR with shorter milling time, are less agglomerated. The compositional study performed by EDAX analysis showed that the synthesized CIGS nanoparticles are in good match with the desired stoichiometry of $Cu(In,Ga)_{0.5}Se_2$.

1. Introduction

The photovoltaic (PV) has made striking growth over the past decades due to meagre non-renewable energy resources. The emerging thin film PV technology has the potential for reducing module cost due to less consumption of semiconductor material. Among thin film materials, CIGS is reckoned to be promising absorber material for large area PV applications. CIGS is a semiconductor material having tunable direct bandgap (1.04–1.68 eV) [1] and high absorption coefficient (10^5/cm) in wide absorbing spectrum [2]. In addition, CIGS solar cells have shown high radiation stability [3] with PV conversion efficiency of 21.7% [4].

Vacuum deposition techniques such as co-evaporation [5] and sputtering [6] are well known for obtaining device quality CIGS thin films. However, vacuum based deposition methods have difficulties owing to soaring process cost [7], process complexity, problems in scale up of vacuum equipment and material wastage [8,3]. Developing non-vacuum techniques to obtain device quality CIGS thin films

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can be a key to overcome the limitations of vacuum methods. Non-vacuum techniques are broadly classified into molecular precursor approach including electrodeposition, spray pyrolysis and nanoparticle approach [9]. Nanoparticle approach involves synthesis and deposition of nanoparticle based precursor material onto a substrate using cost effective simple methods such as spin coating [10], spraying [11], screen printing [12] and doctor blade [13]. Nanoparticle approach is regarded as a feasible method due to good control over atomic concentrations [13], high material usage and simplicity in scale up [3].

There is plethora of chemical methods including a colloidal process [14], solvothermal process [15] and hot injection [16] to synthesize CIGS nanoparticles. But the chemical processes are either time consuming or requires schlenk-line techniques [17]. The mechanochemical process is a powder processing technique, which involves milling powders of metals, alloy or compounds together. During this process material transfer will take place to acquire homogenous alloy [18]. Owing to the potential to have mass production of nanoparticles from non-toxic precursor materials with high energy efficiency in short processing time makes the mechanochemical process a favourable technique to synthesize CIGS nanostructures [2]. Despite this fact, the mechanochemical process is an intricate process. It involves various parameters, such as ball to powder ratio (BPR), milling time and milling speed (rpm) which needs to be optimised to synthesize nanoparticles of desired properties.

Several groups have reported synthesis of CIGS nanoparticle by the mechanochemical process [19–21]. The structural studies of mechanically alloyed CIGS nanoparticles from elemental Cu, In, Ga and Se have been reported by Benslim et al. [19]. The role of milling time on material phase formation and crystallite size of CIGS nanoparticles is recently reported by Rehani [20]. Fu et al. have reported that increased rotational speed is beneficial for pure CIGS formation [21]. In the present work, we synthesized CIGS nanoparticles by the mechanochemical process from elemental precursor materials and studied the importance of milling time, milling speed and BPR on single phase CIGS nanoparticle formation with reduced agglomeration and desired composition. To the best of our knowledge the importance of BPR on mechanochemical synthesis of CIGS is not well investigated. We observed that higher BPR helps to reduce milling time required for the formation of single phase CIGS. Morphology and composition of the mechanochemically synthesized CIGS nanoparticles were also influenced by BPR.

2. Experimental details

The precursor materials used in this work were elemental copper granules (> 99.90 pure, Aldrich), gallium granules (> 99.99 pure, Aldrich), powders of indium (> 99.99 pure, Aldrich) and selenium (> 99.99 pure, Aldrich). The raw material mixture, Cu (0.9408 g), In (0.8495 g), Ga (0.5158 g) and Se (2.3370 g), was taken in a tungsten carbide vial. A planetary ball mill (PM 400, Retsch, Germany) was used with the tungsten carbide vial. Tungsten carbide balls weighing 7.738 g and 10 mm diameter were used as milling media. The reaction undergone in a ball milling process is as follows:

$$Cu + 0.5In + 0.5Ga + 2Se \rightarrow Cu(In, Ga)_{0.5}Se_2 \quad (1)$$

Table 1
Experimental design of the mechanochemical process.

Experimental number	Ball to powder ratio (BPR)	Milling time (h)	Milling speed (rpm)
1	15:1	2	400
2	20:1	2	400
3	25:1	2	400
4	25:1	1	400
5	25:1	6	400
6	25:1	2	200
7	25:1	2	250
8	25:1	2	300
9	25:1	2	350

In order to study the effect of milling time, milling speed and BPR on the reaction, the milling parameters were varied systematically (Table 1). To start with, a BPR of 15:1 was selected while the other parameters such as milling time and milling speed were fixed at 2 h and 400 rpm respectively. Eventually, the BPR was increased to 20:1 and further to 25:1 to find out the minimum BPR for synthesizing single phase CIGS in 2 h. Subsequently, the effect of milling duration was investigated by varying time from 1 to 6 h. Eventually, the effect of milling speed on structural, morphological and compositional properties was studied by varying speed from 200 to 400 rpm with an interval of 50.

X-ray powder diffraction (XRD) analysis performed on a Smart Lab Diffractometer (Rigaku) using Cu Kα radiation ($\lambda = 1.504$ Å) was the main tool used to confirm the formation of CIGS as well as binary compounds. Measured diffraction intensity was in the 2θ range between 20° and 90° with a step size of 0.02° for 6 s per point. Dependence of structural properties of mechanochemically synthesized sample on milling parameter was also deduced from the XRD spectrum. Morphology of the CIGS nanoparticles was analysed using Carl Zeiss Auriga Field emission scanning electron microscopy (FESEM). Composition of the CIGS nanoparticle was analysed by Bruker Ser 5010 X flash Scanning electron microscopy (SEM)-energy dispersive X-ray analysis (EDAX). JEM-ARM200F High resolution transmission electron microscopy (HRTEM) was used to analyse the lattice structure of CIGS.

3. Results and discussion

3.1. Effect of ball to powder ratio

BPR was the first process variable of milling to be investigated. In general higher BPR shortens the milling time required to form single phase of desired material [22]. The BPR was initially set as 15:1 whilst other parameters such as milling time and milling speed were kept as 2 h and 400 rpm respectively. The XRD results of samples as a function of BPR is shown in Fig. 1. It was observed that single chalcopyrite phase CIGS formation took place at BPR of 25:1. The sample obtained with 15:1