Research Article

Synthesis of CIS (CuInSe_2) Based Materials for Solar Applications

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Nanopowders of copper indium diselenide were produced with five different organic solvents: ethylenediamine, triethanolamine, oleylamine, oleic acid, and polyetheramine. We successfully synthesized pure CIS nanopowders at a temperature of 240°C at three different durations of 10 h, 20 h, and 40 h with a one-step process. This shorter time method offers important cost advantages in manufacturing. Polyetheramine and oleic acid were used for the first time in literature for CIS synthesis in an autoclave.

1. Introduction

Copper indium diselenide (CIS), CuInSe_2 , is one of the most important semiconductor materials used in thin film photovoltaic (PV) cells. CIS is becoming a promising candidate material for solar cell applications due to its high optical absorption coefficient, suitable direct band gap energy, and long term stability [1]. This semiconductor is a crucial material as an absorber layer and offers an important advantage. It enables production of low cost flexible thin film solar cells. CIS nanostructures and thin films were in the past produced using magnetron sputtering [2], co- evaporation [3], laser deposition [4], electron beam deposition [5], and also non-vacuum based methods. It is known that processes based on vacuum technology have some disadvantages such as high energy consumption, high processing temperature, necessity of ultrapure materials, and limitation in total area of films [6]. Other types of methods of synthesis involve methods such as electrodeposition [7], chemical deposition [8, 9], hydrothermal process [10], and solvothermal process [11, 12]. It appears from earlier work that the solvothermal method is the simplest low-cost process for manufacturing and suitable for PV industry. The solvothermal process conditions for synthesizing CIS nanopowders influence its

structure and surface properties [13]. Processes with multiple steps were experimented using different types of solvents such as ethylenediamine [6, 14–16], triethanolamine [10, 16], oleylamine [17–20], oleic acid [13], polyetheramine [21], citric acid, butylcarbitol, hydrazine [22], ammonium bromide [23], and hexadecylamine [24].

In this study, we used the solvothermal method based on dissolving metals or metal salts with organic solvents in an autoclave at low temperatures with a single-step process. Nanopowders were produced with five different organic solvents: ethylenediamine, triethanolamine, oleylamine, oleic acid and polyetheramine. We successfully synthesized pure CIS nanopowders at a temperature of 240°C, at three different durations of 10 h, 20 h, and 40 h with a one-step process.

2. Experimental Method

All chemicals (A. Aesar Co.) were used as received without further purification. Copper chloride (CuCl_2 anhydrous 98%), indium chloride (InCl_3 anhydrous 98%), gallium chloride (GaCl_3 anhydrous 99%), and selenous acid (H_2SeO_3 anhydrous 98%) were used as precursors and anhydrous ethylenediamine, triethanolamine, oleylamine, polyetheramine, and oleic acid were used as organic solvents.

In the experimental process, CuCl_2 , InCl_3 , GaCl_3 , and H_2SeO_3 (chemical mixture) were weighed according to the stoichiometric ratio of 1:0.7:0.3:2 in an argon filled glove box. All samples were prepared separately according to solvent characteristics.

2.1. Sample Prepared with Anhydrous Ethylenediamine. For preparation of sample with anhydrous ethylenediamine, 17.5 ml anhydrous ethylenediamine and 2.5 ml ethanol were added to chemical mixture in a glove box and dissolved for 30 minutes with magnetic stirring and then held for 5 minutes in an ultrasonic bath. Sample was loaded into a Teflon-lined stainless steel autoclave with 45 ml capacity. The autoclave was sealed and maintained at 240°C for 10 h, 20 h, and 40 h in an electric oven. After the reaction, the autoclave was allowed to cool to room temperature. CIS nanoparticles in a black colored ethylenediamine organic solution were subject to centrifugation at 6000 rpm repeated four times and rinsed with distilled water and ethanol to remove the byproducts. The final black slurry was dried at 80°C for 8 hours in a drying oven.

2.2. Sample Prepared with Triethanolamine. For preparation of triethanolamine sample, 18 ml ethanol, 2 ml distilled water, and TEA were added to chemical mixture in a glove box and dissolved for 30 minutes with magnetic stirring before keeping in ultrasonic bath for 5 minutes. Sample was loaded into a Teflon-lined stainless steel autoclave with 45 ml capacity. The autoclave was sealed and maintained at 240°C for 10 h, 20 h, and 40 h in an electric oven. After the reaction, the autoclave was allowed to cool naturally to room temperature and CIS nanoparticles, in black color ethylenediamine organic solution, were collected after centrifugation at 8000 rpm repeated 4 times and rinsed with distilled water and ethanol to remove byproducts. The final black slurry was dried at 80°C for 8 hours in a drying oven.

2.3. Sample Prepared with Oleylamine. For preparation of oleylamine sample, 20 ml oleylamine was added to chemical mixture in a glove box and dissolved for 30 minutes with magnetic stirring before keeping in ultrasonic bath for 5 minutes. Sample was loaded into a Teflon-lined stainless steel autoclave with 45 ml capacity. The autoclave was sealed and maintained at 240°C for 10 h, 20 h, and 40 h in an electric oven. After the reaction, autoclave was allowed to cool naturally to room temperature and CIS nanoparticles, in black color ethylenediamine organic solution, were collected after centrifugation at 8000 rpm repeated 4 times and rinsed with acetone to remove byproducts. The final black slurry was dried at 80°C for 24 hours in a drying oven.

2.4. Sample Prepared with Oleic Acid. For preparation of oleic acid sample, 20 ml oleic acid, 2 ml ethanol, and 1 ml distilled water were added to chemical mixture in a glove box and dissolved for 30 minutes with magnetic stirring before keeping in ultrasonic bath for 5 minutes. Sample was loaded into a Teflon-lined stainless steel autoclave with 45 ml capacity. The autoclave was sealed and maintained at 240°C for 10 h, 20 h, and 40 h in an electric oven. After the

reaction, autoclave was allowed to cool naturally to room temperature and CIS nanoparticles, in black color ethylenediamine organic solution, were collected after centrifugation at 8000 rpm repeated 4 times and rinsed with acetone to remove byproducts. The final black slurry was dried at 80°C for 24 hours in a drying oven.

2.5. Sample Prepared with Polyetheramine. For preparation of 20 ml polyetheramine sample 2 ml ethanol and 1 ml distilled water were added to chemical mixture in a glove box and dissolved for 30 minutes with magnetic stirring and then for 5 minutes at ultrasonic bath. Sample was loaded into a Teflon-lined stainless steel autoclave with 45 ml capacity. The autoclave was sealed and maintained at 240°C for 10 h, 20 h, and 40 h in an electric oven. After the reaction, autoclave was allowed to cool naturally to room temperature and CIS nanoparticles, in black color ethylenediamine organic solution, were collected after centrifugation at 8000 rpm repeated 4 times and rinsed with distilled water, acetone, and ethanol mixture to remove byproducts. The final black slurry was dried at 80°C for 24 hours in a drying oven.

The crystal structure was characterized by X-ray diffraction (XRD). The morphology and size of synthesized CIS nanoparticles were characterized by scanning electron microscopy (SEM) equipped with an EDAX.

3. Results and Discussion

The oleylamine plays several roles during the synthesis of CIS. It enables control of the growth rate of the nanoparticles during reactions by forming a liquid-metal complex. It plays the role of a capping agent for the nanoparticles. It is thought to reduce the reactivity between Cu, In, Ga, and Se reactants [19]. Also, it has a high boiling point and nitrogen containing compound. Because of these characteristics, it is a very good candidate solvent for synthesizing CIS nanopowders. The XRD patterns of synthesized CIS nanopowders for three different hours are shown in Figure 1. Resolved peaks became sharp and cleaner as the process time increased from 10 h to 40 h.

3.1. Oleylamine. Figure 1 represents X-ray diffraction patterns of CuInSe_2 nanopowders synthesized at 3 different times (10, 20, and 40 hours) at constant temperature (240°C) conditions. XRD data shows that synthesized powders are comprised of tetragonal CIS materials (JCPDS card number 040-1487). Each sample shows five major diffraction peaks located in the expected position for the (112), (204/220), (116/312), (008/400), and (228/424) crystal planes.

Pure tetragonal CIS powder was synthesized during the reaction at 10 hours; when time was increased to 20 hours a second phase tetragonal CuGaSe was observed. At 40 hours process time, the peak intensity was lower and CuGaSe phase disappeared. According to Hahn et al. [19], the atomic percentages of Se decrease with increasing reaction time, while that of Ga continuously increased. This could be explained by the slow vaporization of Se in solution with increasing reaction time because of its relatively high vapor pressure compared to other elements. Thus, the balance of

FIGURE 1: XRD pattern of synthesized CIS powder at 240°C for 10, 20, and 40 hours with oleylamine solvent.

FIGURE 2: SEM micrographs of synthesized CIS powder at 240°C for (a) 10 h, (b) 20 h, and (c) 40 h with oleylamine solvent.

content shifted from Se to Ga during long reaction times. At 40 hours of reaction time, CuGaSe phase was not observed, but the intensity for CuInSe₂ peak decreased.

To investigate the morphological properties of CIS nanoparticles, SEM images from the synthesized CIS powder were gathered and provided in Figure 2. Figure 2(a) shows agglomerated particles with the sizes 150–200 nm. When the reaction time increased, particle sizes enlarged at 20 h (Figure 2(b)) and at 40 hours; the particle size becomes 1.5–2 microns. When the reaction time is prolonged, particle agglomeration was clearly observed as was also described in another study [19].

3.2. Triethanolamine (TEA). In Figure 3, XRD data shows that the synthesized powders were mainly comprised of CIS tetragonal chalcopyrite materials (JCPDS card number 40-1487). In a study by Wu et al. [10], it was indicated that cubic particles were observed at 160°C, cubic shape particles decreased at 170°C, and CIS tetragonal shape was formed at 200°C.

In this study, based on XRD data from Figure 3 at 10 h, pure CIS phase is observed with 0.5–1 micron spherical particles, worm-like, irregular shaped nanoparticles as shown

in Figure 4(a). At 20 hours' time reaction, 200–400 nm range, worm-like, irregular shaped nanoparticles are observed (Figure 4(b)). From XRD data for 40 hours' time reaction, the orthorhombic and the cubic structures occurred with low intensity CIS phase and woolen ball shape particles similar to described by Khanaki et al. [17] were observed on SEM images in Figure 4(c).

3.3. Oleic Acid. CIS nanoparticles were synthesized with oleic acid as a solvent, which has a similar molecular structure to different functional group as Hahn et al. [13] described earlier. Figure 5 shows the XRD patterns of CIS particles prepared in an oleic acid solution at 240°C for 10, 20, and 40 hours. XRD data shows that the synthesized powders were comprised of tetragonal CIS materials (JCPDS card number 040-1487). Each sample shows three major diffraction peaks located in the expected position for (112), (204/220), and (116/312) crystal planes. Figure 6 provides information about microstructures of synthesized CIS powder at 240°C for 10 h, 20 h, and 40 h.

At 10 h process time, three different phases were observed. They were tetragonal CuGaInSe, tetragonal CuInSe₂, and tetragonal Cu₃Se₂ phases. At 20 h process, pure tetragonal

FIGURE 3: XRD pattern of synthesized CIS powder at 240°C for 10, 20, and 40 hours with triethanolamine solvent.

FIGURE 4: SEM micrographs of synthesized CIS powder at 240°C for (a) 10 h, (b) 20 h, and (c) 40 h with triethanolamine solvent.

FIGURE 5: XRD pattern of synthesized CIS powder at 240°C for 10, 20, and 40 hours with oleic acid.

FIGURE 6: SEM micrographs of synthesized CIS powder at 240°C for (a) 10 h, (b) 20 h, and (c) 40 h with oleic acid.

CIS phase was observed. At 40 h process, tetragonal CIS particles were observed with lower intensity compared to 20 h process. Hahn et al. [13] synthesized CIS powder with oleic acid in a three-neck flask at 250–300°C. Polygonal and octahedral shape particles were obtained. In this study, all CIS powder had tetragonal shapes. From the SEM images, first 10 hours' time CIS and umangite (Cu_3Se_2) were observed at 1–2 micron size; at 20 hours' time reaction plate-like shape CIS was observed similar to reported by Gu et al. [14]. The morphology changes from polygonal to octahedral plate-like shape with increasing reaction temperature. At 40 hours' reaction time, only CIS phase was observed with agglomerated large particles with the long process time. When the reaction time increased, the intensity of CIS gets decreased because it is thought that In leaves the structure. For this study, the optimum condition was 20 h reaction time.

3.4. Polyetheramine. Polyetheramine is a rare solvent with double amine-capped polymer with a high boiling point resulting in strong chelation. Wang et al. [21] used polyetheramine solvent for CIGS synthesizing at 250°C in three-neck flask for 20 hours' time. In this study, all the reaction occurred in an autoclave for 10 h, 20 h, and 40 h.

Figure 7 illustrates the X-ray diffraction patterns of CuInSe_2 powders synthesized at 240°C for 10 hours in an autoclave. It shows that tetragonal CIS 40-1487 and CGS 031-0456 phases were observed with large plate-like and irregular small particles (Figure 8(a)). When the time increased to 20 h, both CIS and CGS powders intensity get decreased besides particle growing with agglomeration (Figure 8(b)). X-ray data at 40 h shows In and Se released from the structure to form CuSe_2 and InSe phases with agglomerated big plate-like particles. A particle size of 200–300 nm is observed for longer reaction time of 40 h at Figure 8(c).

3.5. Ethylenediamine (EDA). EDA is most preferred solvent for synthesizing CIGS, CIS powders with solvothermal method. Zhang et al. [15] produced CIS nanopowders with EDA at 210–230°C range for 20 hours. In addition, Chen et al. [16] obtained pure CIS phase at 200°C for 15 hours.

The tetragonal CGS, hexagonal GaSe, Se and CuSe phases with 150–200 nm agglomerated particles were observed at processing time of 10 h, based on Figures 9 and 10(a). Advancing process time to 20 hours yielded CIGS and CuSe_2 .

FIGURE 7: XRD pattern of synthesized CIS powder at 240°C for 10, 20, and 40 hours with polyetheramine.

However, at 40 hours' process only second phases such as indium selenide and copper selenite were observed. Chen et al. [16] comment that if longer time of solvothermal process was employed, the peak belonging to the CIS chalcopyrite phase was strengthened and longer reaction time does favor the crystallization of CuInSe_2 phase and high purity can be obtained. But in this study, in a longer time reaction CIS peak has disappeared. Parallel to work done by Gu et al. [14], CGS seed was obtained up to 230°C for 20 hours' process but disappeared at 40 hours' reaction process.

4. Conclusions

Five different solvents such as oleylamine, oleic acid, triethanolamine, polyetheramine, and ethylenediamine were successfully used to synthesize tetragonal CIS powders with solvothermal method in an autoclave in the same conditions. It has been found that oleylamine is the best solvent based on the X-ray data from processing at 240°C for 10, 20, and 40 hours. CIS phase was successfully synthesized using five different solvents. According to results at these processing

FIGURE 8: SEM micrographs of synthesized CIS powder at 240°C for (a) 10 h, (b) 20 h, and (c) 40 h with polyetheramine.

FIGURE 9: XRD pattern of synthesized CIS powder at 240°C for 10, 20, and 40 hours with ethylenediamine.

FIGURE 10: SEM micrographs of synthesized CIS powder at 240°C for (a) 10 h, (b) 20 h, and (c) 40 h with ethylenediamine.

conditions, best desirable properties were obtained in this order: (1) oleylamine (10 hours), (2) triethanolamine (20 hours), (3) oleic acid (20 hours), (4) polyetheramine (10 hours), and (5) ethylenediamine (20 hours). Polyetheramine and oleic acid were used for the first time in literature for CIS synthesis in an autoclave. Other methods were studied in

the literature; the chemical reaction occurs in a three-necked flask which takes much long time for a successful synthesis.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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