Conference Paper

Synthesis of CZTS in Aqueous Media Using Microwave Irradiation

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Copper-Zinc-Tin-Sulfide (CZTS), a promising material for absorber layer application in thin film solar cells, has been synthesized in aqueous media by microwave irradiation technique. Compared to conventional synthesis methods, microwave irradiation is highly efficient, reliable, and less time consuming. The synthesized nanopowders were characterized for particle size by dynamic light scattering (DLS), phase by X-ray diffraction (XRD), and band-gap by UV-Vis-NIR spectroscopy. Various atmospheric processing methods are being evaluated for the deposition of absorber layers from CZTS nanopowder based ink.

1. Introduction

Solar cells have been an important area of research owing to the ever increasing energy demand and depleting fossil fuel resources. Though, at present, Silicon (Si) based solar cells dominate the Photovoltaic market, very recently, thin film solar cell (TFSC) technologies have been acknowledged as an alternative to Si technology. Si being an indirect band gap material requires $\sim 300\ \mu\text{m}$ layer of Si to absorb efficiently the incoming radiation. The relatively thick layer increases the chances of recombination of the carriers and to avoid the same highly crystalline Si is mandated by the Si based PV cells which increases the cost per watt of energy produced. TFSCs address these issues as they have absorber layers with direct band gaps and high absorption coefficients ($10^4\ \text{cm}^{-1}$). Hence, very thin layer of about $1\text{--}2\ \mu\text{m}$ is sufficient to absorb 99% of the incident radiation.

Copper-Zinc-Tin-Sulfide (CZTS) is a multicomponent chalcogenide semiconductor material which, in recent days, has been recognized as an alternative to Copper Indium Gallium chalcogenide (CIGS) and Cadmium Telluride (CdTe) based absorber layers in TSFCs. Though CIGS and CdTe

technologies have proven themselves to be promising in terms of efficiency, the scarcity of In, Ga, and Te, and the toxicity of Cd have led to search alternative materials. Owing to the earth abundance and nontoxicity of its constituents, CZTS promises to be an inexpensive alternative to CIGS and CdTe.

Currently, the record power conversion efficiency for vacuum-deposited CZTS is 6.8% [1] on an active cell area of $0.15\ \text{cm}^2$. Nonvacuum based approaches to synthesize and deposit CZTS have been active areas of research in the recent years owing to the high cost of the vacuum deposition processes like sputtering and evaporation. In this line, many solution based approaches like electrodeposition, sol gel method, and various other ink based processes have been developed. These processes invariably use a post Sulfur/Selenium/Hydrogen sulfide/Hydrogen selenide/Sodium Selenide atmosphere heating which make these processes hazardous to deal with. The present highest record efficiency of 9.7% [2] was achieved using a hydrazine-based solution deposition approach with mixed sulfur/selenium anions on a device area of $0.45\ \text{cm}^2$. The same research group later improved the efficiency to 10.1% [3]. But the hydrazine used

in the process is highly toxic and is also highly reactive and hence easily erodes away the equipment used for its handling.

The synthesis of inorganic colloidal nanocrystals usually involves complex and time consuming processing of precursors in the presence of solvents, ligands, and/or surfactants at elevated temperatures. But, in recent years, it has been rendered easy due to the use of microwave irradiation as a nonclassical energy source [4]. Microwaves provide sufficient instantaneous energy to the resonance stabilized intermediate to cross the activation energy barrier to form products [5]. Due to this, the reactions get completed sooner than in a conventionally heated reaction. This is the guiding principle for this microwave assisted synthesis. Recently, Flynn et al. [6] described a method in which CZTS nanoparticles were synthesized in ethylene glycol using microwave irradiation. Nevertheless, synthesis of CZTS in aqueous media is definitely an interesting turn in the history of its development [7]. The present paper discusses the same using microwave irradiation. The process, apart from alleviating the need to use hazardous postdeposition heating in Sulfur/Selenium containing vapors, also eliminates toxic solvents usually used in the synthesis of semiconductor nanoparticles.

2. Experimental Details

For CZTS of stoichiometry $\text{Cu}_2\text{ZnSnS}_4$, the required amounts of Copper Chloride, Zinc Chloride, Tin (II) Chloride, and Thiourea were taken in a microwave vessel (Microsynth) along with DI water and a few mL of ammonium hydroxide. Initially the mixture was stirred for 15–30 min. Then, the sealed reaction mixture was subjected to microwave irradiation using a Microsynth System operating at 800 W and a frequency of 2.45 GHz. The reaction was carried out at constant temperature in the range of 150–220°C for 60–90 min. The precipitate thus obtained was collected using centrifuge and is heated for 2–5 hrs in an atmospheric oven. The resultant nanopowders were characterized for phase by X-ray diffraction, for particle size by Dynamic light scattering technique, and for band gap by UV-Vis-NIR spectroscopy.

3. Results and Discussions

Figure 1 shows the X-ray diffraction data of the powder obtained after centrifugation. All the peaks which are seen clearly match with the standard CZTS JC PDS 26-0575—the major peaks being at diffraction angle $2\theta = 28.5^\circ$, 47.33° , and 56.17° corresponding to (112), (220), and (312) planes of kesterite structure. Other minor peaks in the XRD spectrum also correspond to CZTS. The crystallinity of the formed CZTS powder is substantiated by the sharp peaks of the XRD spectrum.

Figure 2 is the UV-Vis-NIR spectroscopy of the obtained CZTS nanopowder. For obtaining the spectrum, the powder was dispersed in Isopropanol and sonicated for 30–45 min in a cold water bath. The absorption of the liquid is recorded. The absorption starts at around 970 nm (~ 1.3 eV). The corresponding energy is within the ideal range to absorb most of the incoming radiation of the solar energy.

FIGURE 1: The X-ray diffraction spectrum of CZTS.

FIGURE 2: The UV-Vis NIR spectrum of CZTS.

FIGURE 3: Particle size distribution of CZTS obtained using the dynamic light scattering technique.

The particle size distribution of the powder is measured using Dynamic Light Scattering technique (DLS) and it is shown in Figure 3. For this, a small amount of nanopowder is dispersed in DI water and ultrasonicated for 60 min. This solution is immediately used for the particle size analysis as this will deagglomerate the particles and will give us a correct picture of the size of the particles in the powder. Addition of any dispersant might result in a deviation in

the measurement of actual size of the particle. The result shows that the synthesized nanoparticles are between 150 and 500 nm with majority of them at around 290 nm.

The novelty of the present work is the synthesis of CZTS in aqueous media [8]. The base for this innovative method is that Copper, Zinc, and Tin being d-block elements from the periodic table form complexes with the ammonium ion. The ammonium hydroxide also helps in the reduction of sulfur to S^{2-} ion. This results in the in situ formation of sulfides which further react to form CZTS. The complexes help in reducing the amount of metals going out of the solution in the form of sulfides by retaining considerable amount of metals in the form of complexes.

4. Conclusion

CZTS has been prepared using microwave irradiation in aqueous media in the presence of ammonium hydroxide [8]. The described microwave synthesis of CZTS is highly reliable and reproducible. The XRD results obtained clearly indicate a crystalline kesterite phase of CZTS. The UV-Vis spectrum data provided in Figure 2 shows the band gap of the synthesized powder to be 1.3 eV. The particle size distribution shows that the majority of the particles have a size of 290 nm. The obtained powder can be used to make absorber layers in CZTS based thin film solar cells by spin coating, ink jet printing, and so forth.

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