



Influence of the $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles size on solar cell performance

Balakrishna Ananthoju^{a,b}, Jeetikanta Mohapatra^c, D. Bahadur^{a,d}, N.V. Medhekar^{a,e},
M. Aslam^{a,b,f,*}

^a IITB-Monash Research Academy, IIT Bombay, Powai, Mumbai-400076, India

^b Department of Physics, IIT Bombay, Powai, Mumbai-400076, India

^c Centre for Research in Nanotechnology and Science (CRNTS), IIT Bombay, Powai, Mumbai-400076, India

^d Department of Metallurgical Engineering and Materials Science, IIT Bombay, Powai, Mumbai-400076, India

^e Department of Materials Engineering, Monash University, Clayton, VIC-3800, Australia

^f National Centre for Photovoltaic Research and Education, IIT Bombay, Powai, Mumbai-400076, India

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ABSTRACT

Controlling the semiconductor nanoparticles (NPs) size can alter their optical and electronic properties, which is an important feature for many optoelectronic device applications. In this study, we demonstrated a simple and economical approach to synthesize size-controlled $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) NPs and their application as an absorber layer in solar cells. The size of the CZTS NPs has been controlled from 2.5 to 8 (± 0.5) nm by variation of the amine to the precursor mole ratio. The impact of the particle size on the structural, optical, and electrical performance of the devices are studied systematically. XRD and Raman spectroscopy measurements reveal the formation of pure kesterite phase of the CZTS. Moreover, the UV–vis spectroscopy data show that the CZTS NP films have a high optical absorption coefficient (10^4 cm^{-1}) in the visible region, and its optical band gap is in the range of 1.50–1.62 eV. The power conversion efficiency of a solar cell fabricated using CZTS NPs is enhanced considerably from 3.6% to 4.8% with an increase of nanoparticles size, within an active area of $1.0 \pm 0.1 \text{ cm}^2$. The maximum external quantum efficiency of 59% is obtained for the solar cell with CZTS thin film comprising 8 nm particles. The observed changes in the device performance parameters might be due to the variation of the thin film microstructure.

1. Introduction

Thin film solar cells based on the compound semiconductor absorber layers have emerged as the most promising alternative due to an ideal band gap (1.4–1.6 eV) and high absorption coefficient (10^4 cm^{-1}) as compared to silicon [1–5]. However, the current thin-film solar cells are based on rare-earth and toxic elements such as cadmium and indium [1,2]. Hence, during the past decade, there has been a rapid increase in the interest to develop CZTS thin film solar cells based on all non-toxic and earth-abundant elements in order to substitute with the traditional toxic absorber layers [3–7]. CZTS demonstrates a high optical absorption coefficient (10^4 cm^{-1}), a suitable band gap (1.4–1.6 eV) and a high electrical conductivity, making it an ideal platform for solar energy conversion applications [3–7]. The record CZTS nanoparticle device had an efficiency of 6% [3], while for the vacuum-based pure-sulfide device is 11% [4], which is still less than that of CZTSSe ($\approx 12.6\%$) [5]. The observed enhancement in the efficiency is due to the incorporation of selenium which significantly

decreases the surface defects and helps to grow bigger grains and offers a substantial improvement in the device performance [5,8]. Moreover, it has been observed that the band gap of CZTS decreases with selenium doping, this results in a decrease in the open circuit voltage of the devices [5,8].

The development of low-cost alternatives for the fabrication of high-efficiency thin film solar cells is essential to make solar energy a major source of electricity in comparison to other sources. To make the large area, low-cost, and improve the efficiency of CZTS solar cell, one potential approach would be to use CZTS NPs. Nanoparticles have already been demonstrated as high efficiency and low-cost alternative material for solar cells [8]. Most highly-efficient CuInGaSe_2 (CIGS) and CZTS solar cells are deposited using vacuum-based techniques [9,10]. However, these vacuum-deposition techniques are very expensive and have issues (phase and stoichiometry) in the fabrication of devices with large scales [9,10]. The high-efficiency thin-film solar cells reported so far in the literature are mostly small area devices and have better device performance because of better control over film morphology and

* Corresponding author. Department of Physics, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India.
E-mail address: m.aslam@iitb.ac.in (M. Aslam).

uniformity but limited practical applications [3,5,8–10]. Therefore, there is a growing interest in the development of low-cost and large-area-solution-based techniques. The solution-based process offers a suitable method for the formation of size and shape controlled quaternary chalcogenide nanoparticles with a desired stoichiometry and phase [8,11,12]. CZTS thin film solar cells are expected to have a maximum theoretical efficiency of 30% and efficiencies have already reached as high as 8.4% at laboratory scale using vacuum-deposition techniques [3,13]. Various hurdles, from the perspective of the material and the devices have to be overcome in order to make the CZTS technology competitive in commercial solar cell modules [14]. The main difficulty in perspective of CZTS material synthesis is to achieve single phase without any secondary phases (Cu_2S , Cu_2SnS_3 , ZnS , and etc). These secondary phases act as charge carrier recombination centres and collection barriers that limit the number of generated charge carriers, thus, results in low performance of the device [14]. Moreover, the charge carrier mobility ($\sim 6\text{--}30\text{ cm}^2/\text{V}$) and diffusion lengths ($\sim 350\text{ nm}$) are poor in CZTS absorber layers fabricated using CZTS NPs which results in poor device performance [14].

Recently, several synthesis processes for the CZTS NPs have been reported, the majority of which has demonstrated the formation of the kesterite phase of CZTS with tetragonal crystal structure [8,15–17]. However, the concerns such as phase purity, stoichiometry, shape, and size control of the CZTS NPs have not been addressed properly in the literature so far. The size and shape control is a necessary requirement for not only fundamental research but also for the effective appliance in electronic devices [18]. So far, there are only limited reports on the fabrication of size-controlled CZTS NPs [19,20]. Recently, Safdar et al. reported the synthesis of ultrafine CZTS NPs by a solution process, wherein, they studied the structural, optical and morphological properties of CZTS NPs [19]. In addition, Eray S. Aydil and co-workers demonstrated the fabrication of size-controlled CZTS NPs by varying the reaction temperature, wherein, they observed the quantum confinement effect for particles diameter less than 3 nm [20]. However, these reports are mainly focused towards synthesis, structural and optical properties of the NPs: a clear correlation between the CZTS NPs size and the device performance of CZTS is scarce in the literature. Thus, further research is necessary to understand the effect of particle size effect on the solar cell performance to achieve high-efficiency solar cells. Moreover, from the industry standpoint, an economic, simple, and scalable method needs to be designed for the synthesis of CZTS NPs with controlled size, uniformity and pure phase.

Herein, we demonstrated a simple and cost-effective approach to prepare 2–8 nm CZTS NPs and have studied the influence of nanoparticles size on the structural, optical properties, and electrical device performance of the CZTS thin film solar cells. We have performed a detailed structural and morphological analysis using XRD, Raman spectroscopy, XPS and UV–visible absorption spectroscopy to confirm the quality and stoichiometry of the CZTS NPs. Furthermore, a scalable, binder-free ink has been prepared using toluene as the dispersal solvent. After optimization of ink parameters and annealing processes, dense and uniform CZTS thin films are produced. Finally, we have fabricated the large area ($1.0 \pm 0.1\text{ cm}^2$) solar cells with glass/Mo/CZTS/CdS/i-ZnO/AZO/Ni/Al structure and the effect of particle size on device performance has been studied.

2. Experimental section

2.1. Materials

Copper chloride (CuCl_2), zinc chloride (ZnCl_2), stannous chloride (SnCl_2), sulfur powder, oleylamine, acetone, hexane, and toluene were used for the synthesis of CZTS nanoparticles. All chemicals were bought from Sigma-Aldrich and were used without any additional purification.

2.2. Preparation of size-controlled quaternary $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles

We demonstrated a simple and high yield ($\sim 20\text{ g}$) approach for the synthesis of CZTS NPs using oleylamine as the solvent, surfactant, and reducing agent. In a representative synthesis of 2.5 nm CZTS NPs, 50 mmol of CuCl_2 , 25 mmol ZnCl_2 , and 25 mmol SnCl_2 were added to 1.5 moles of oleylamine (amine-to-precursor mole ratio of 1:15) in a European style three-neck round bottom flask. Initially, the reaction mixture was heated at $120\text{ }^\circ\text{C}$ for 15 min under the continuous flow of nitrogen gas to form the metal-amine complex. Immediately, 100 mM of sulfur was added to the reaction mixture, which instantly changes the color of the reaction mixture to light brown. After adding sulfur, the temperature was increased to $220\text{ }^\circ\text{C}$ at a ramp rate of $5\text{ }^\circ\text{C}/\text{min}$ and the reaction was allowed to continue at $220\text{ }^\circ\text{C}$ for 2 h with continuous stirring. Thereafter, the flask was allowed to cool to room temperature. The obtained nanoparticles were collected from the growth solution by precipitation with acetone, followed by centrifugation and then re-dispersion in hexane. After several hexane/acetone extractions, the final product was dried under vacuum at $60\text{ }^\circ\text{C}$ in a vacuum oven. The size of CZTS NPs was controlled with the variation of precursor to amine mole ratios as 1:15 (2.5 nm), 1:12 (3.5 nm), 1:9 (5 nm), 1:6 (6 nm), and 1:4 (8 nm), respectively.

2.3. Binder-free ink formulation and thin film deposition

One of the main challenges in nanocrystal-based solar cells is the making of fine, uniform ink. Usually, ink formulation requires organic surfactants or stabilizers, and binders to make fine ink, which are difficult to remove after film processing and result in impurities in the film [21]. Our primary goal was to develop a fine, uniform ink-formulation method with a binder-free single solvent. For ink formulation, the solvent needs to be so volatile that the films dry rapidly without leaving substantial residues; it also needs to have a functional group to stabilize the ink. This formulation method needs to be cost-effective and also be able to deposit uniform films over large areas. In this study, we used toluene as a solvent for ink formulation. The dried CZTS NPs were dispersed in toluene (150 mg/mL) to make nanoparticle ink. The dispersed nanoparticles were pot milled (used roller pot mill, rotation speed $\sim 20\text{ rpm}$) for 12 h with zirconium balls in order to form a uniform ink. Moreover, we found that the toluene-based ink was stable for many months without precipitation. These toluene-based inks were deposited onto several substrates such as fluorine-doped tin oxide (FTO) coated glass substrate, the soda-lime glass substrate, and molybdenum (Mo)-coated glass substrate by a simple doctor blading technique [22]. Typically, 250 μL of CZTS nanoparticle's ink is drop-casted on the one edge of a substrate; scotch adhesive tape is then used as a doctor-blading guide (Fig. S1). The thickness of the Scotch adhesive tape defines the initial thickness of the film. A smooth circular glass rod is used to deposit the films on the desired substrate. The similar process is repeated to get the required thickness of the absorber layer and these successive coatings will also help to fill the cracks in the previous layer. After each immediate coating, the substrate was covered with a narrow tube end funnel to avoid fast evaporation of the solvent. Fast evaporation of solvent could create a lot of cracks in the film, which is not desirable. Each layer of the nanoparticle films was found to be $\sim 0.4 \pm 0.1\text{ }\mu\text{m}$ in thickness when measured by the scanning electron microscope (SEM) cross-sectional analysis (Inset of Fig. 5a).

2.4. Surfactant removal and sulfurization process

After each CZTS layer coating, the as-deposited thin films were annealed at $400\text{ }^\circ\text{C}$ for 30 min with a continuous flow (50 sccm) of argon gas in a tubular furnace in order to remove the amine surfactant and to enhance the conductivity of the film. The post-annealing treatment also helps to densify the film and improves the film coverage. After annealing, the films were sulfurized using the sulfur powder that

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