

Sonochemical synthesis of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ nanoparticles for thin film photo absorber application



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ABSTRACT

CuInGaSe_2 (CIGS) has been considered as promising solar absorber material for thin film solar cells leading to efficiencies exceeding 22% on lab scale. CIGS thin film solar cells fabricated from CIGS nanoparticles (NPs) inks by nonvacuum techniques is essential for cost effective cell fabrication process and for upscaling. In this regard, one step sonochemical synthesis of CIGS NPs employing relatively non-toxic precursors of metallic salts and selenourea in an aqueous medium under ambient conditions is being presented. Precursor ratios and sonication time were optimized to realize high-quality chalcopyrite crystal phases of CIGS NPs obtained by sonochemical route. X ray diffraction, UV–vis–NIR, Raman, Energy dispersive spectroscopy and Transmission electron microscopy confirmed the formation of tetragonal chalcopyrite CIGS NPs with a band gap of 1.42 eV and NPs size of about 20 nm.

1. Introduction

CuInGaSe_2 (CIGS) based solar cells with efficiencies [1] exceeding 22% (lab scale), and 15–16% (module scale) is leading among thin film solar technologies. CIGS is key semiconductor absorber material with tunable band gap exhibiting a high absorption coefficient of the order of 10^5 cm^{-1} , with high thermal and chemical stability [2]. Optical and electrical properties of CIGS can be controlled using appropriate doping of Gallium and Sulphur [3]. Vacuum based co-evaporation, sputtering-selenization are existing popular routes but are slow, expensive and comprised of toxic selenization and KCN etching steps [4]. Therefore alternative non-vacuum route employing precursor deposition of CIGS nanoparticles (NPs) coated on the Molybdenum coated substrate using spin coating, spray coating or doctor blading followed by rapid selenization [5–8], laser [9], Intense pulsed light post-treatment [10,11] are reported to obtain CIGS thin film absorber layer. The above mentioned nanoparticle based route provides a high degree of phase uniformity and better material utilization suitable for scale-up. Apart from thin film solar cells, CIGS NPs were successfully employed in dye sensitized [12], quantum dot based solar cells [13–15] photodetectors, solar water splitting [16] and as fluorescence material in biological imaging [17].

Various chemical routes were reported for the synthesis of CIGS NPs such as hot injection [18,19], solvothermal [20,21], microwave [22–24] for the mentioned applications. Most of the conventional

chemical routes engage amine based solvents like oleyamine, ethylene diamine as complexing and reducing agents. These techniques often require a controlled/ inert atmosphere, high reaction temperatures of the order of 200–300 °C, and longer durations, therefore have limitations to scale up. Mechanochemical synthesis [25] of submicron CIGS NPs using controlled ball milling of metallic precursors was reported but have poor control over CIGS composition specifically $0.80 < \text{Cu}/(\text{In} + \text{Ga}) < 0.95$ which is essential [26,27] for avoiding secondary phases of Cu-Se. Sonochemical synthesis is a very attractive and simple route for the controlled synthesis of various metal chalcogenide nanoparticles with the desired composition and is widely reported for binary materials [28–31]. However, there are only a few reports for the sonochemical synthesis of ternary [30,32–34] and quaternary materials [35,36]. Cha et al. [37] reported the synthesis of CIGS NPs using the sonochemical route in controlled conditions using toxic hydrazine based solvents. Therefore simple and cost-effective large scale production of high-quality CIGS NPs in ambient conditions using non-toxic chemicals is still challenging and desired. In present work, we are reporting simple route for the synthesis of CIGS NPs by sonochemical reaction of aqueous metal salts precursors with selenourea in ambient conditions. The ultrasonication parameters and precursor composition were optimized to achieve high quality and stable CIGS NPs.

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2. Experimental

Analytical grade Copper nitrate hydrate, Indium nitrate hydrate, Gallium nitrate hydrate, Selenourea, Triethanolamine (TEA), Ethanol were purchased from Alfa Aesar and used as received without further purification. Initially, appropriate quantities of aqueous solutions of Copper nitrate (0.008 M), Indium nitrate (0.007 M) and Gallium nitrate (0.003 M) were prepared and mixed followed by stirring for 10 min resulting in a weak blue colored solution. Appropriate quantities of TEA (0.020 M) were added to previous solution resulting in dark blue solution indicating the formation of the metal complex. TEA increases the viscosity of the solution. Therefore, DI water emerges suitable solvent for ultrasonication at high power density for longer durations without considerable evaporation. Aqueous Selenourea (0.02 M) was added to previous solution resulting black-brown color solution indicating the formation of amorphous Cu-Se and In-Se nanoparticles. Ultrasonication treatment (Q500 sonicator, Qsonica LLC) was carried out using titanium horn (taper tip thickness 0.5") for variable time periods of 30–150 min at 20 kHz frequency and power of 300 W. After ultrasonication dark black colored precipitated were centrifuged and washed with DI water and Ethanol respectively followed by drying in hot air oven at 80 °C for 2 h. The yield of obtained CIGS nano powder is observed to be about 80%. As prepared CIGS NPs (10 wt%) were again dispersed in ethanol and spray casted on CdS/Al:ZnO/SLG substrate at 120 °C to obtain 1.5–2 μm thin film. 200 nm thick Molybdenum thin films were coated over to produce superstrate device structure. Here 900 nm Al:ZnO thin films were sputtered on Soda lime glass substrate (SLG) followed by chemical bath deposition of 100 nm CdS thin films. Deposition parameters of Mo thin film contacts [38] are discussed elsewhere.

The phase Constitution of CIGS NPs was determined using X-ray diffraction (XRD) analysis (XRD; CuK α radiation, D8 Advance, Bruker, Germany) and Transmission electron microscope (FEI TECNAI 20G2). Micro Raman Spectrometer (Horiba Jobin Yvon, Labram) was used for further phase analysis. The elemental composition was measured using X-ray fluorescence spectroscopy (XRF; XDVSD, Fischer Switzerland). Optical properties were studied using a UV-visible-NIR spectrophotometer (Varian, Cary 5000). Scanning electron microscope (SU1510, Hitachi) was employed for morphological and compositional studies, and Current Voltage characteristics were measured using a solar simulator (94123A; Oriol Instruments) with 1.5 AM spectrum corresponding to 100 mW/cm².

3. Results and discussions

Sonochemical synthesis of metal chalcogenides NPs being presented here typically involves metal salt precursors and selenourea as selenium source in an aqueous medium. Hydrolysis of selenourea under ultrasonication typically forms H₂Se which reacts with metal cations (e.g., Cu⁺, In³⁺, Ga³⁺) to form corresponding metal selenide [39].

The formation rate of various metal selenide phase during the sonochemical reaction is expected to be different as Cu⁺ is more reactive towards Se than In³⁺ or Ga³⁺ thereby promoting the formation of excess Cu-Se binary phase. To control the rate of formation of Cu-Se phase TEA as complexing agent plays a major role also as stabilizer thereby reducing the release rate of Cu⁺ cation during synthesis. As Cu poor CIGS is highly desired to get p-type conductivity, to obtain slightly Cu poor CIGS NPs, initial precursors of Cu metal salt was adjusted accordingly. The color of the metal complex solution changes to black brown by adding selenourea, indicating the formation of binary amorphous phases of Cu-Se, In-Se, and Ga-Se. Further, sonication is expected to promote ions diffusion [14] to yield CIGS phase. Given this, the sonication time was varied to realize the optimal time for CIGS phase formation, discussed in detail henceforth.

XRD analysis was carried out to understand the evolution of various phases with ultrasonication time as seen from Fig. 1. For 30 min of

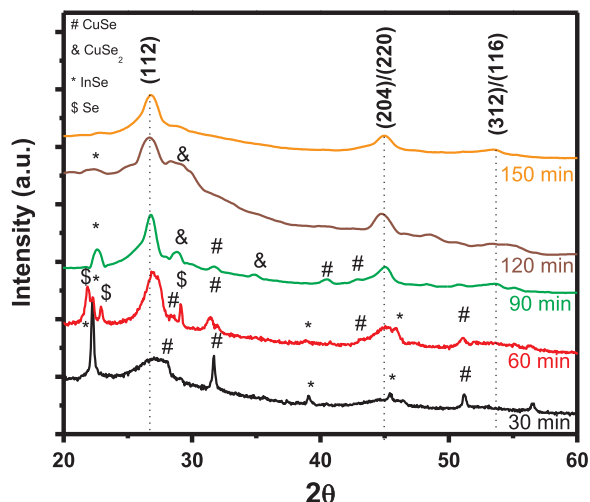


Fig. 1. X ray diffraction pattern for CIGS NPs obtained for various ultrasonication durations.

sonication time, obtained NPs were comprised of a mixture of CuSe (JCPDS Data 00-049-1456) and InSe (JCPDS Data 04-003-2450) phases. With the further increase in sonication time, tetragonal chalcopyrite CIGS phase (JCPDS Data 35-1102) found to evolve as major phase indicating diffusion of various binary phases. After sonication time of 150 min, single phase CIGS with chalcopyrite structure without any secondary phases were observed. Crystallite size calculated using Debye Scherer formula [40] for CIGS NPs obtained by sonication is found to be 6 nm. Apart from XRD, Raman spectroscopy was used to analyze and reconfirm phase evolution of CIGS NPs obtained for various sonication times as seen from Fig. 2. Raman shift observed at 172 cm⁻¹ corresponding to the A₁ vibration mode of CIGS [41] found to improve with sonication time while shifts at 120 cm⁻¹ and 260 cm⁻¹ corresponding to InSe and CuSe phases respectively diminished. No peaks corresponding to oxides of Cu, In, Ga and Se were detected. Raman A₁ mode of vibration for CIGS at 172 cm⁻¹ is also an indicator of elemental composition corresponding (Ga/(Ga + In)) ≈ 0.3 which is an ideal composition for CIGS thin film solar cells [26], reconfirms the initial elemental precursors taken were in an appropriate concentration. EDS spectrum with quantitative compositional analysis as seen from Fig. 3, confirmed slightly copper poor composition with near ideal (Ga/(Ga + In)) [26]. Morphology and crystal phase analysis of as synthesized CIGS NPs obtained by ultrasonication for 150 min were further studied using TEM and Selected area electron diffraction pattern (SAED) which is

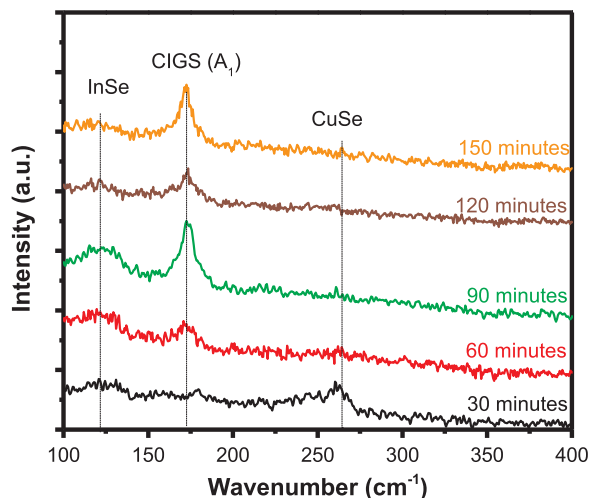


Fig. 2. Raman spectrum for CIGS NPs obtained for various ultrasonication durations.

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