Study of CZTS nano-powder synthesis by hot injection method by variation of Cu and Zn concentrations

Suresh Kumar*, Vikash Kumar, Valdek Mikli, Tiit Varema, Mare Altosaar, Maarja Grossberg

Tallinn University of Technology, Institute of Materials Science, Ehitajate tee 5, 19086, Tallinn, Estonia

Abstract

Copper Zinc Tin Sulphide (CZTS) nano-powders were synthesized by solution based method in oleylamine at 215°C, 225°C and 235°C using copper pentan2, 4-dionate, zinc acetate, tin (II) chloride and elemental sulphur as precursors. The influence of initial Cu/ (Zn + Sn) concentration ratio (from 0.82 to 0.33) on the morphology, phase composition and elemental composition of nano-powders was studied. It was found that the average size of colloidal nano-particles of CZTS nano-powders increased from 20 nm to 10 μm with decreasing initial Cu/ (Zn + Sn) concentration ratio at every used synthesis temperature. The elemental composition of the formed nano-powders was compatible to near-stoichiometric CZTS if initial Cu/ (Zn + Sn) concentration ratios were 0.82 and 0.74. Higher initial zinc concentration i.e. higher chemical potential at specific temperature reduces the final tin concentration component in the colloidal nano-powders.

1. Introduction

First prerequisite for solar energy conversion is a good absorber material composed from earth abundant elements with least toxicity, and having high absorption coefficient and direct band gap. Copper zinc tin sulphide (selenide)
CZTSSe is a material with all these properties [1]. Solution based methods were adopted to synthesise CZTS(Se) nano-powders and solar cells on their base have shown the highest power-conversion efficiencies (PCE) to date, with record efficiencies reaching 12.6% [2] compared to 9.7% for vacuum processed materials [3]. The fabrication of solar cells based on nano-crystal ink process starts from synthesis of nano-crystalline powders followed by sintering of the nano-crystal films in sulphur or selenium vapours [4, 5]. One of the most successful routes for the synthesis of CZTS nano-crystals is the hot-injection synthesis method that utilizes surfactant controlled growth of colloidal nano-crystals in a hot organic solvent [6]. Riha et al synthesised 12.8±1.8 nm mono-disperse nano-crystals using stoichiometric initial precursor concentration at the synthesis temperature of 300°C [6]. The synthesis of Cu₂ZnSnS₄ nano-crystals with off stoichiometric composition were demonstrated by Collard and Hillhouse [7]. Chernomordik et al described a method for rapid synthesis of 2-40 nm diameter CZTS nano-crystals by varying only synthesis temperature between 150°C to 340°C [8]. Coughlan and Ryan showed how changing of Cu and Zn precursors allowed the formation of polytypic acorn shaped nano-crystals or pencil shaped nano-crystals [9]. By tuning the solvent concentration different shapes of nano-crystals were formed: nanorods and ellipsoids, as well as atypical tadpole-shaped and P-shaped nanocrystals [9]. Karimi et al synthesized spherical platelet CZTS nanocrystallitites with particle size in the range of 20-25 nm [10]. In synthesis of nano-crystals the initial concentrations of metal precursors are always crucial in the formation of final composition of nano-powders [11] and shape of the formed colloidal nano-particles. The molar ratios of the metal ion precursors in synthesis may have an important effect on the chemical potential of each element and eventually on the phase composition of the obtained nanoparticles [11]. The synthesis temperature was selected from 215°C to 235°C because it is suitable for the synthesis of CZTS nano-powders in oleylamine as solvent. Oleylamine shows very high stabilising effect at this temperature range [4, 5, 6 and 11]. It has been shown that the electronic properties of CZTS in terms of band gap, work function and valence band edge position can be controlled by varying the precursor ratios [12]. It was reported that the CZTS sample with a Cu/(Zn+Sn) ratio of 0.86 and Zn/Sn ratio of 1.37 showed the highest photocurrent response [13]. Ping An [9] and co-workers and other groups have shown that high initial Zn concentration promotes the formation of quaternary CZTS, the results of these studies were based on variation of Cu/ (Zn + Sn) ratio from 1 to 0.90. So, it is useful to study the more wide variation of the initial Cu/ (Zn + Sn) concentration ratio. In the present work colloidal nano-powders were synthesised in oleylamine with variation of the initial Cu/ (Zn + Sn) concentration ratio in the range of 0.33-0.82 with the aim to study the effect of it on the elemental and phase compositions and morphology of synthesized CZTS colloidal nano-powder particles.

2. Experimental

2.1. Synthesis of CZTS colloidal nano-powders

Oleylamine was used as solvent, surfactant and capping ligand in the solution based synthesis of CZTS nano-powders [14]. The analytical grade chemicals from Sigma Aldrich copper 2,4pantenedionate, zinc acetate, tin (II) chloride and elemental sulphur were used as sources for Cu, Zn, Sn and S respectively. The precursors of metal elements were mixed in 12 ml of oleylamine in a three neck flask at 25°C. The initial concentration ratios of precursors varied as given in Table 1. Temperature of mixtures was increased to the required synthesis temperatures (215°C, 225°C and 235°C) and maintained at synthesis temperature for 30 minutes under inert gas (N₂) condition and then S component was added. For the preparation of S precursor, 0.32 g of sulphur (10 mmol) was added to 10 ml of oleylamine and sonicated for 30 min at 70°C. From this freshly prepared sulphur solution 4.5 ml was taken and added to the flask containing solution at required temperature. The solution mixtures were continuously stirred and maintained at each synthesis temperature for 30 minutes, as synthesis time has impact on the nucleation, growth and type of CZTS nano-crystal structure [6, 15]. The solution mixtures were cooled down naturally to room temperature in N₂ gas environment. CZTS nano-powders were separated from oleylamine solution and cleaned by repeated centrifugation with ethanol, hexane and isopropanol, while hexane was used for removing non-polar impurities and isopropanol for polar impurities [16].

<p>| Table 1 Experimental conditions i.e. synthesis temperature, precursor contents and concentration ratios in initial solutions. |
|---|---|---|---|
| Synthesis temperatures (°C) | Content of precursors in initial solutions (nmol) | Concentration ratios of precursors in initial solutions |</p>
<table>
<thead>
<tr>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>S</th>
<th>Cu/Zn</th>
<th>Cu/(Zn + Sn)</th>
<th>Zn/Sn</th>
</tr>
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</table>
ZEISS ULTRA 55 FE-SEM apparatus was used to investigate the morphological structure and to estimate the size of particles of nano-powders and to perform the energy dispersive x-ray spectroscopy (EDS) analysis to determine the elemental composition of nano-powder samples. The samples for the EDS analysis were prepared by pressing the nano-powders into pellets. Raman spectroscopy was performed using Horiba Jobin Yvon HR800 micro-Raman spectrometer.

3. Results and Discussion

3.1. SEM and EDS Analysis of Nano-powders

3.1.1. SEM analysis of nano-powders

SEM images of nano-powders are presented in Figures 1-3. The CZTS nano-powders synthesised at 215°C with varying the initial concentration ratio of precursors Cu/(Zn + Sn) (i.e. 0.82, 0.74, 0.60 and 0.48) show large variation in the size of nano-particles from 20 nm to 150 nm (Figure 1). Decreasing copper concentration with increasing zinc concentration causes the formation of colloidal nano-particles with sizes from 2 μm to 10 μm (Figure 1).

Figure 1. Colloidal nano-particles synthesised at 215°C with initial Cu/(Zn + Sn) ratio equal to 0.82, 0.74, 0.60, 0.48, 0.33 and 0.33 (10 μm scale) respectively.
For the CZTS nano-powders synthesised at 215°C with initial precursor Cu/(Zn + Sn) ratio equal to 0.33 the average size of agglomerated colloidal nano-particles is 10 μm. According to thermodynamics, as the synthesis temperature decreases then the chemical potentials of the elements increases. Therefore, at a particular synthesis temperature with high initial zinc concentration higher chemical potential of zinc in the solution is expected. The crystals in colloidal nano-powders synthesised at three different synthesis temperatures i.e. 215°C, 225°C and 235°C with initial precursor Cu/(Zn + Sn) ratio equal to 0.82 and 0.74 have size in the range 20 nm to 100 nm.
3.1.2. EDS analysis of nano-powders

The analysis of EDS results show that elemental composition of CZTS colloidal nano-powders synthesised at 215°C, 225°C and 235°C with initial precursor Cu/ (Zn + Sn) ratio equal to 0.82 and 0.74 are near-stoichiometric. The final concentration of copper varies with the initial copper concentration and as initial zinc concentration was increased, a respective increase in the final zinc concentration of colloidal nano-powders was detected.

Figure 4. Concentration ratios determined by EDS of components in colloidal nano-particles synthesised with different initial concentrations at 215°C, 225°C and 235°C respectively.

Following trends were observed in the colloidal nano-particles: with the increase in initial zinc concentration final concentration of tin decreases with initial precursor Cu/ (Zn + Sn) ratio equal to 0.82 and 0.74. This shows that the increase in initial zinc concentration not only increases the chemical potential of zinc but also decreases the chemical potential of tin state. The chemical potential of copper is unaffected by the increase in initial zinc concentration. The concentration of sulphur with respect to the sum of metal ions, S/ (Cu + Zn + Sn) remains stoichiometric at the all used initial precursor concentration ratios (Cu/ (Zn + Sn) = 0.82, 0.74, 0.6, 0.48 and 0.33) and at all used synthesis temperatures (215°C, 225°C and 235°C).

3.2. Raman analysis

3.2.1. Raman spectra analysis of nano-powders with near stoichiometric composition synthesised at different temperatures (215°C, 225°C and 235°C)

Raman spectra of CZTS colloidal nano-powders synthesised at 215°C, 225°C and 235°C with initial precursor ratios
Cu/(Zn + Sn) equal to 0.82 and 0.74 are shown in Figure 5.

![Diagram showing Raman spectra at different synthesis temperatures at initial precursor ratio Cu/(Zn+Sn) = 0.82 and 0.74]

The Raman peak positions were determined from the fittings of the spectra by using Lorentzian curves. Raman peaks observed in CZTS colloidal nano-powders synthesized at 215°C and 225°C are at 333 cm⁻¹, 292 cm⁻¹ and 355 cm⁻¹ which could correspond to Cu₂ZnSnS₄ or some other ternary sulphide [17, 18 and 19]. Dominating Raman peaks observed in CZTS nano-powders synthesized at 235°C are at 335 cm⁻¹ and 358 cm⁻¹ which could correspond to Cu₂ZnSnS₄ and at 299 cm⁻¹ which could correspond to Cu₃SnS₃ or other ternary sulphide [17, 18 and 19].

Katagari et al showed that Cu/(Zn+Sn) ratio equal to 0.69 or less results in binary phases of Sn and S (SnS and SnS₂) and ratio Cu/(Zn+Sn) above 1.09 results in binary compound of copper and sulphur (i.e. CuS) [20]. The highest photocurrent and solar cell efficiency was observed with Cu/(Zn+Sn) ratio equal to 0.85 [20]. The Cu/(Zn+Sn) ratio equal to 0.8 shows CZTS and CTS phase whereas Cu/(Zn+Sn) ratio equal to 1.19 shows CZTS phase with photocurrent and solar cell efficiency was observed with Cu/(Zn+Sn) ratio equal to 0.85 [20]. The Cu/(Zn+Sn) ratio above 1.09 results in binary compound of copper and sulphur (i.e. CuS).

3.2.2. Raman spectra analysis of nano-powders synthesised with big difference in Cu/(Zn + Sn) concentration ratios at particular temperatures (215°C, 225°C and 235°C)

The most intense Raman peaks of colloidal nano-particles shift from 333 cm⁻¹ to 335 cm⁻¹ as the synthesis temperature increases from 215°C to 235°C (Figure 5). Similar Raman shift of most intense peak from 333 cm⁻¹ to 337 cm⁻¹ is also observed when the Cu/(Zn + Sn) ratio decreases from 0.82 to 0.33 at synthesis temperature 215°C (Figure 6). The insertion of Zn ions into the CZTS is possible by two ways: first, with higher synthesis temperature, and second, by high initial zinc concentration by creating high chemical potential of zinc in the solution (EDS shows high zinc concentration in colloidal nano-powders). Raman spectra of CZTS nano-powders synthesised at 235°C with different Cu/(Zn + Sn) ratios (i.e. 0.82, 0.74, 0.60, 0.48 and 0.33) are presented in Fig. 6. Raman peaks observed in CZTS nano-powders at 235°C are for Cu/(Zn + Sn) ratios 0.82 and 0.74 are 335 cm⁻¹, 292-294 cm⁻¹ and 355 cm⁻¹ which could correspond to Cu₂ZnSnS₄ [15, 16 and 17]. Raman peaks observed in CZTS nano-powders at 235°C for Cu/(Zn + Sn) ratios 0.60, 0.48 and 0.33 are at 335 cm⁻¹ and 360 cm⁻¹ which could correspond to Cu₂ZnSnS₄ and Raman peak at 299-300 cm⁻¹ which could correspond to Cu₃SnS₃ or other ternary sulphide [15, 16 and 17].
The shift of the peaks towards higher wave number side is accompanied with the decrease in the peak half-width shows improved crystalline nature. The changing positions of the Raman peaks at the wave numbers corresponding to CZTS and Cu₂SnS₃ indicate that most probably the powders are a mixture of these two phases, CZTS prevailing at higher temperatures and at lower Cu/ (Zn + Sn) ratios.

4. Conclusions

The CZTS colloidal nano-powders were synthesised at 215°C, 225°C and 235°C by solution based hot injection method. The CZTS colloidal nano-powders synthesised with varying initial precursor concentration ratio Cu/ (Zn + Sn) (i.e. 0.82, 0.74, 0.60 0.48 and 0.33) at each synthesis temperature. It was found that the average size of colloidal nano-particles of CZTS nano-powders increased from 20 nm to 10 μm with decreasing initial Cu/ (Zn + Sn) concentration ratio at every used synthesis temperature. The most intense peak of Raman spectra shifted towards higher wave number probably because of high zinc component in the CZTS colloidal nano-powders with increase in the synthesis temperature from 215°C to 235°C. The changing positions of the Raman peaks at the wave numbers corresponding to CZTS and Cu₂SnS₃ indicate that most probably the powders are a mixture of these two phases, CZTS prevailing at higher temperatures and at lower Cu/ (Zn + Sn) ratios. At synthesis temperature 215°C, main Raman peak is shifted from 333 cm⁻¹ to 337 cm⁻¹ with variation of initial precursor Cu/ (Zn + Sn) concentration ratio from 0.82 to 0.33. Shoulder at the lower wave number side of this peak and also the shift of the second peak from 292 cm⁻¹ to 299 cm⁻¹ indicates that there is a coexistence of Cu₂ZnSnS₄ and Cu₂SnS₃ phases. The shift of the peaks is probably caused by the changing ratio of the two phases, CZTS prevailing at higher temperatures. Higher initial zinc concentration i.e. higher chemical potential at specific temperature reduces the final tin concentration in the colloidal nano-powders.

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