Facile One Pot Synthesis of Single Phase Kesterite Cu_2ZnSnS_4 Nanocrystals

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***Abstract*— Cu_2ZnSnS_4 (CZTS) nanocrystals were synthesized by employing facile one pot thermal decomposition method. In this study, the influence of reaction time (30 min, 1,2,4 and 8 h) on the structural, morphological and compositional properties of CZTS nanocrystal was investigated. Structural analysis showed presence of $Cu_{2-x}S$ phase in the CZTS nanocrystals synthesized for lesser than 2 h. As the reaction time proceeds, Zn^{2+} and Sn^{4+} cations diffuse into $Cu_{2-x}S$ lattice and lead to the formation of single phase CZTS. Morphological analysis showed CZTS nanocrystals with irregular shape as well as inhomogeneous size distribution with respect to various reaction time. The composition of CZTS nanocrystals was found to be approaching the targeted value (Cu: Zn: Sn: S = 2:1:1:4) as the reaction time increases.**

Keywords*— CZTS, Kesterite, Reaction time, Single phase

I. INTRODUCTION

In recent years, CZTS semiconductor has attracted tremendous research interest due to its excellent electronic, optical and optoelectronic properties. And it has been considered as an alternative absorber layer to $CuInGaSe_2$ because of shortage and high material cost of indium and gallium [1]. CZTS is composed of earth abundant elements with direct bandgap of 1.5 eV and high optical absorption coefficient (~10^4 cm^{-1}). CZTS thin films can be deposited by vacuum and non-vacuum methods. Particularly, non-vacuum based thin film deposition methods have gained much attention owing to low cost and high throughput [2].Moreover, the reported high efficient CZTS solar cell uses non -vacuum method to deposit CZTS films. So far, the reported highest efficiency of CZTS based solar cell is 12.6% [3]. Non-vacuum based thin films are deposited using nanocrystals ink followed by annealing. To date, various methods have been reported to synthesize CZTS nanocrystals such as hot injection [4], heating up method [5], solvothermal [6], hydrothermal [7] and one pot method [8]. Among them, one-pot method is a facile, economical, non-injection process. It is a high temperature synthesis process which requires less reaction time and easy purification process.

Here, we have successfully synthesized single phase kesterite CZTS nanocrystals by one-pot method. Influence of reaction time on the structural, morphological and compositional properties have been investigated. Thus, the synthesized single phase CZTS nanocrystals can be used as an absorber layer in low-cost thin film solar cells.

II. EXPERIMENTAL PROCEDURE

The chemical reagents used for the synthesis of CZTS nanocrystal were copper (II) chloride ($CuCl_2$) (99.999%), zinc acetate ($Zn(Ac)_2$) (99.99%), tin (II) chloride ($SnCl_2$) (99.99%), sulfur powder (99.99%), oleylamine (OLA) (technical grade, 70%), chloroform (99.80%) and ethanol (99.90%). All the reagents were used without further purification.

In a typical reaction, 2 mmol of $CuCl_2$, 1 mmol of $Zn(Ac)_2$, 1mmol of $SnCl_2$ and 4 mmol of sulfur powder were added into 10 mL of OLA. The reaction mixture was heated to 260°C under inert atmosphere. Aliquots were withdrawn from the reaction mixture at regular intervals (30 mins to 8 h). Once the reaction finished, the mixture was cooled down to 100ºC. Then, the reaction mixture was washed with chloroform and ethanol followed by centrifugation process for several times to remove unreacted particles and by-products. The final product was dried at 100°C for 2 h in an oven and then used for various characterization.

XRD patterns of CZTS samples were recorded in X-ray powder diffractometer (PANanalytical) which was operated at 40kV and 200mA using Cu-Kα radiation (λ =1.5418Å). Micro-Raman measurements were performed using HORIBA Jobin Yvon spectrometer with He-Ne laser (632.8nm) at room temperature. The morphologies of the samples were observed using Transmission electron microscopy (TEM) (JEM-

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ARM200F) and the chemical composition was measured by energy disservice analysis (EDS) (XFlash Detector 5010).

III. RESULTS AND DISCUSIION

A. Structural analysis

XRD patterns of CZTS nanocrystals synthesized at different reaction times were shown in fig (1). The (112), (200), (220) and (312) planes correspond to kesterite crystal structure [9] of CZTS (JCPDS 01-075-4122) were observed in all the samples. $Cu_{2-x}S$ phase was detected at lesser reaction times (30 mins to 2 h) due to incomplete reaction. As the reaction time progress, $Cu_{2-x}S$ phase intensity decreases and finally single phase of CZTS was obtained at 4 h. Further increasing reaction time to 8 h, significant difference was not observed which suggests that 4 h is enough to form single phase CZTS.

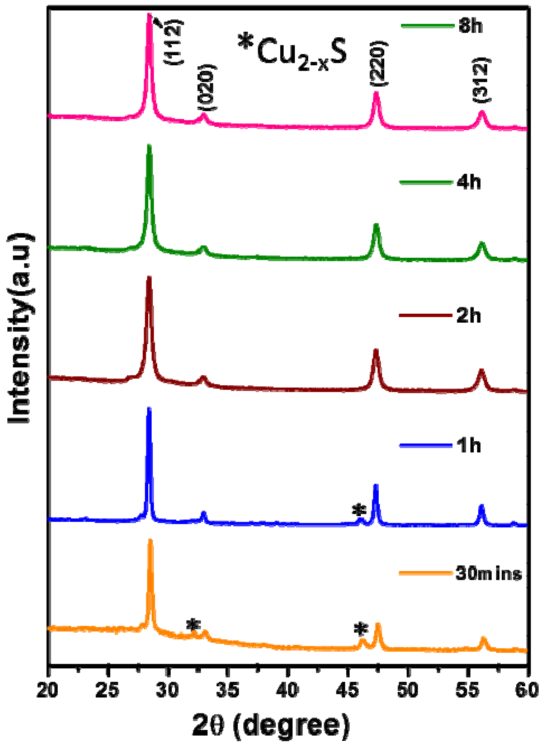

Fig. 1 XRD patterns of CZTS nanocrystals synthesized at 260°C for different reaction times.

XRD is unable to accurately distinguish the presence of CTS (Cu_2SnS_3) and CZTS phases due to overlapping diffraction peaks. So, Raman measurements were carried out for further confirmation of phase purity of synthesized CZTS nanocrystals. Raman spectra (fig.2) showed prominent peak at around 334 cm-1 in all the samples. It correspond to A1 optical phonon vibrational mode of kesterite crystal structure. This peak was originated from pure anionic (S) mode vibration regardless of static neighboring cations (Cu, Zn, and Sn) [10]. We could observe two shoulder peaks at around 286 and 373 cm^{-1} which were also ascribed to the kesterite phase of CZTS. Peaks corresponding to $Cu_{2-x}S$ and CTS were observed in the samples synthesized for 30 mins and 1 h.

According to hard–soft acid–base theory [11], soft Lewis acid of Cu^{+} react with soft Lewis base of S^{2-} leading to the formation of $Cu_{2-x}S$ at lesser reaction times. As the reaction time proceeds, Sn^{4+} ions diffuse into $Cu_{2-x}S$ crystal lattice to form CTS phase. Finally, the diffusion of Zn^{2+} ions into CTS crystal lattice led to form pure CZTS.

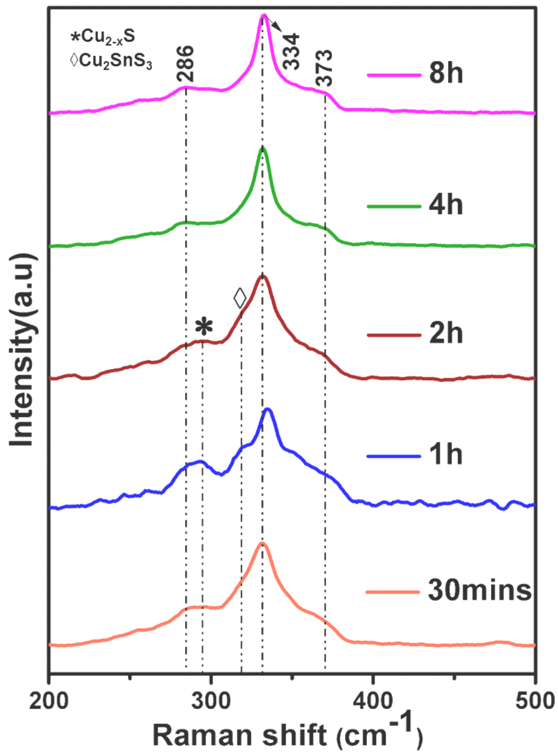

Fig.2 Raman spectra of the CZTS nanocrystals synthesized at 260°C for different reaction times.

B. Morphological and compositional analysis

TEM images of CZTS nanocrystals synthesized at different reaction times were shown in fig.3. TEM micrographs depicted irregular morphology of the nanocrystals for all the samples. As the reaction time increases, the size of the crystals were increased from 60 to 85 nm. The inhomogeneous size distribution and irregular shape of nanocrystals are due to "digestive ripening" which causes rearrangement of particles at higher temperature for longer reaction time [12,13]. EDS analysis was used to study the elemental compositions of CZTS nanocrystals and the results were shown in table 1. As the reaction time increases, Cu/(Zn + Sn) ratio decreased from 1.38 to 1.02, while the Zn/Sn ratio increased from 0.94 to 1.23. The samples prepared at reaction time of 30 mins, 1 and 2 h showed Cu and Sn-rich composition which led to the formation

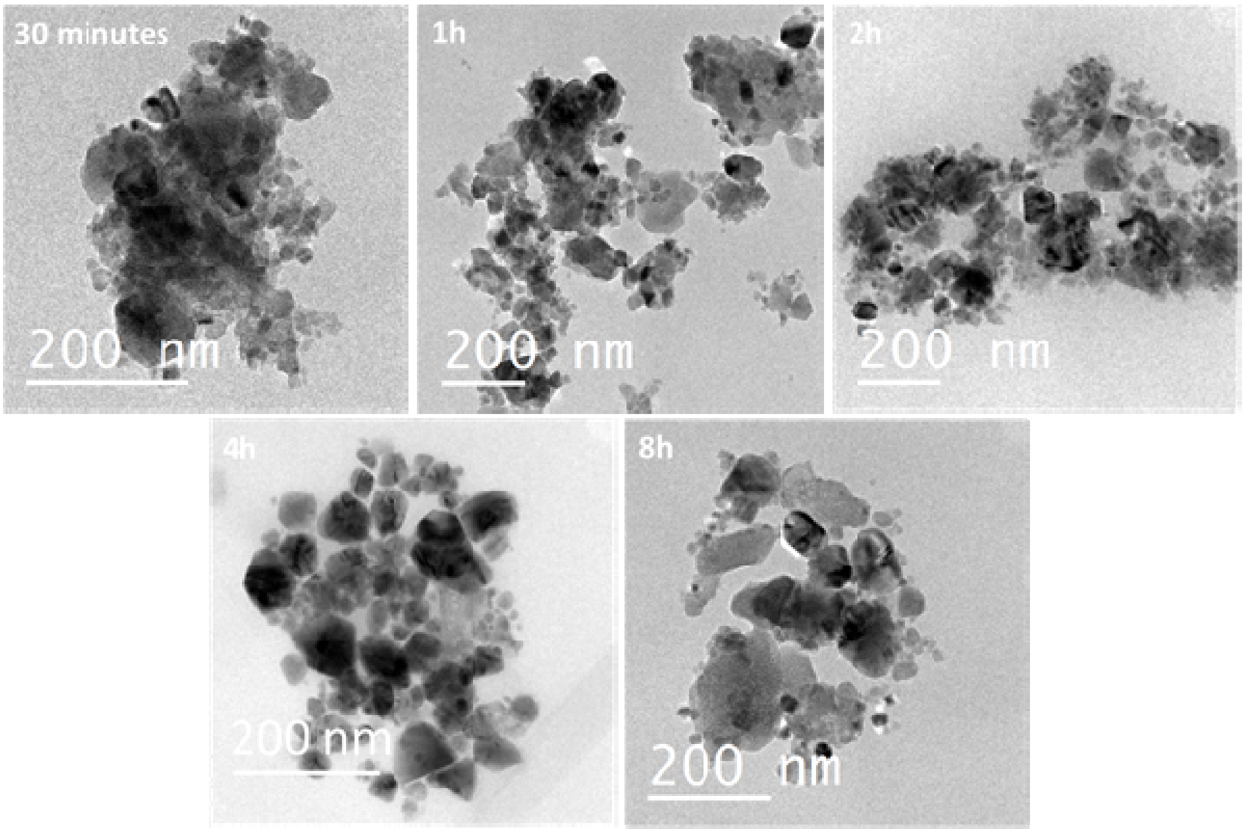

Fig.3 TEM images of CZTS nanocrystals synthesized at 260°C for different reaction times.

of $Cu_{2-x}S$ and CTS phases as detected from structural analyses. The obtained composition of CZTS at 4 h was very close to the calculated values.

TABLE 1 EDS ANALYSIS OF CZTS NANOCRYSTALS SYNTHESIZED AT 260°C FOR DIFFERENT REACTION TIMES.

Reaction time	Cu	Zn	Sn	S	Cu/ (Zn+Sn)	Zn/Sn
30minutes	30.00	10.50	11.12	48.38	1.38	0.94
1h	28.40	10.24	12.40	48.96	1.25	0.82
2h	27.02	11.05	12.50	49.43	1.14	0.88
4h	25.12	13.52	11.20	50.16	1.01	1.20
8h	25.43	13.72	11.14	49.71	1.02	1.23

IV. CONCLUSION

Single phase CZTS nanocrystals were successfully synthesized by facile thermal decomposition method with reaction time of 4 h. The results obtained for CZTS nanocrystals synthesized at different reaction time suggest that $Cu_{2-x}S$ is the initial phase form during thermal decomposition of $CuCl_2$, $Zn(Ac)_2$), $SnCl_2$, S in OLA. The rapid diffusion of cations Sn^{4+} and Zn^{2+} to the crystal framework of $Cu_{2-x}S$ lead to the formation of CZTS nanocrystals. Morphological analysis showed an increment in the size of nanocrystals with increase in reaction time. Composition of CZTS nanocrystals was greatly affected with increment in the reaction time. The CZTS nanocrystals synthesized for 4 h possess composition very close to the targeted value.

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