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Cu_2ZnSnS_4 synthesized through a green and economic process

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ABSTRACT

Quaternary chalcogenide Cu_2SnZnS_4 (CZTS), a promising absorber material in solar cells, was demonstrated synthesizable through self-sustaining reactions by using an environmental friendly and cost-effective mechanochemical (ball milling) process from elemental Cu, Zn, Sn, and S, without using either polluting chemicals or expensive vacuum facilities. Transmission electron microscopy, X-ray diffraction, and Raman spectroscopy and X-ray photoelectron spectroscopy confirmed CZTS formation. CZTS could be formed after planetary ball milling the starting mixture of Cu, Zn, Sn, and S for 20 h. The grain size of CZTS decreased with a further increase in ball milling time.

1. Introduction

The quaternary semiconductor Cu_2ZnSnS_4 (CZTS) has recently attracted great attention and interest as a promising absorber material in thin film solar cells, due to its low cost, little toxicity, p-type conduction, suitable direct band gap and high photon absorption in visible light range. Various techniques have been developed in synthesizing CZTS, such as chemical solution synthesis, spray-deposition, electron-beam evaporation, RF-magnetron sputtering [1–5]. In these methods, either expensive vacuum technology or polluting chemicals are used in the processes. By considering small scale laboratory fabrication of CZTS, the employment of these methods does not appear to be a significant problem. However, in large scale industrial mass production, the use of expensive vacuum technology will increase the cost in addition to high energy consumption, and the usage of huge amount of chemical solutions and the generation of waste chemical solutions is detrimental to environment. Furthermore, the existing methods generally involve additional processing step of annealing the samples at a temperature of above 500 °C, with the flowing of toxic gas H_2S through the annealing chamber in order to achieve CZTS. In addition, environmental contamination of toxic H_2S and high energy consumption are introduced. It is great, if possible, to have a method without the involvement of using chemical solutions, toxic gas, high vacuum facilities, and high annealing temperature in the fabrication of CZTS. This paper will report the successful fabrication of CZTS nanoparticles by using mechanochemical process (MCP) or ball milling without the above short-comings. Although this paper will only focus on how to achieve CZTS nanoparticles, it is worth to mention that the formation of the desired nanoparticles is crucially important. A few leading thin film solar cell companies, such as Nanosolar Pte Ltd, have industrially and massively manufactured copper indium gallium selenide (CIGS) thin film solar cells and panels by utilizing an 'industrial' printing process to coat CIGS and other nanoparticle inks on low-cost aluminum foil followed by drying and other processes for cost-efficient solar cell products.

Ball milling is an old but efficient method for grinding materials into fine powders, used for selecting mine, fabricating building materials, etc. More interestingly to us is that it can induce chemical reactions in a variety of powder mixtures, offering direct reaction routes and be a solvent free, low temperature mechanochemical process (MCP) technology [6]. One great advantage, considering environmental issue, is that no chemical solutions are used, no chemical waste is generated, and no expensive vacuum facilities are employed in this process. Therefore, it is environmental friendly and cost-effective. Furthermore, as will be demonstrated later in this paper, it is also a one-step processing method in achieving CZTS without other processes such as post-annealing. Many materials including CdTe [7] and $CuInSe_2$ [8] have been obtained from mechanical process. However, first-principles calculations reveal that CZTS is a material that can only be formed in very small chemical potential domains [9]. It is not clear whether it is possible to synthesize CZTS by using the ball milling method. In this study, as will be demonstrated, CZTS can be synthesized from cheap elemental powders of Cu, Zn, Sn and S by means of planet ball milling. The effect of the milling time on microstructures of CZTS is investigated.

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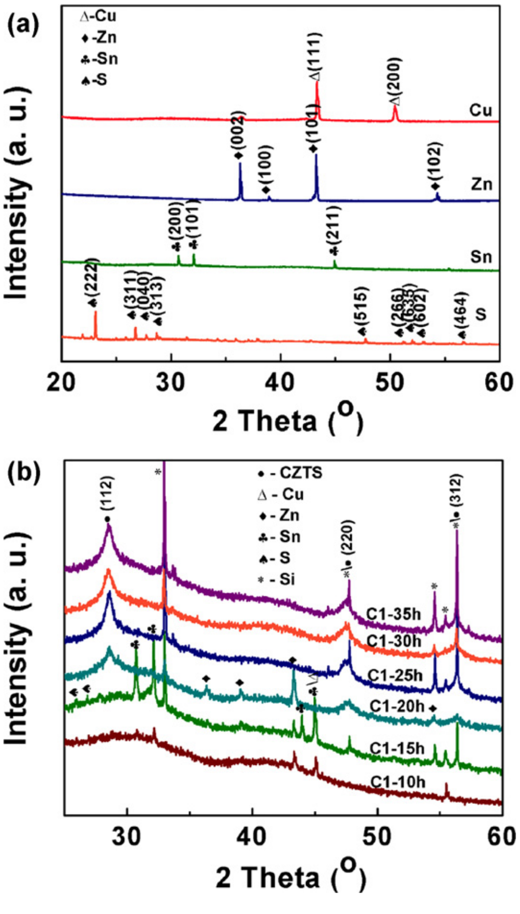

Fig. 1. (a) XRD pattern of the starting elemental materials, Cu, Zn, Sn, and S, (b) XRD pattern of mixture of Cu, Zn, Sn, and S in ratio of 2.0:1.0:1.0:4.0 after different ball milling time, 10, 15, 20, 25, 30, 35 h, respectively.

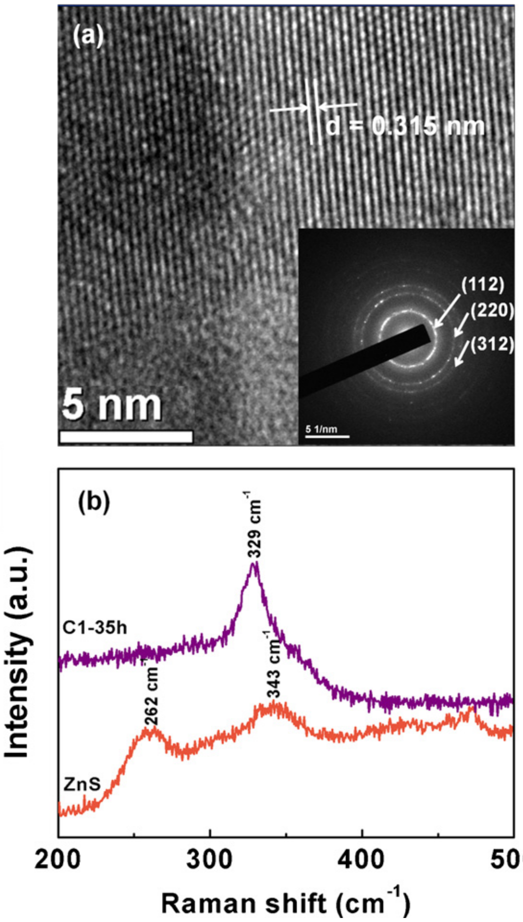

Fig. 2. (a) HRTEM image and the inset figure of the selected area electron diffraction pattern of sample C1-35 h, (b) Raman spectra for C1-35 h, and ZnS sample prepared from chemical bath deposition.

2. Experimental

The starting materials, elemental Cu (99.8 + %, 0.2–0.6 mm, Sigma), Zn (99.8 + %, 0.18–0.6 mm, Sigma), Sn (99.5 + %, <0.6 mm, Sigma), and S pieces (99.999%) were weighed and mixed in atomic ratios of 2.0:1.0:1.0:4.0 according to the stoichiometry of CZTS, and this sample will be denoted as sample C1 in the text later. The starting C1 mixture and ZrO_2 milling balls were loaded into ZrO_2 containers. The ball-to-powder weight ratio was maintained at 5:1. The mixtures were conducted in milling containers of a planetary ball mill operating at 50 Hz frequency, 300 rpm revolution speed and 600 rpm rotation speed. The milling time was set at 10, 15, 20, 25, 30, 35 h, respectively.

Crystal structure was characterized by using Bruker X-ray diffractometer (XRD) with Cukα radiation $\lambda_{k\alpha} = 0.15406$ nm, step size = 0.02°, and the time/step size = 0.6 s/step. High resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) patterns were recorded by using JEOL 2010F transmission electron microscope (TEM). Morphology of the samples was imaged by using Hitachi S-2300 scanning electron microscopy (SEM). A Kratos Axis Ultra DLD X-ray photoelectron spectroscopy (XPS) spectrometer with monochromatic Al Kα (1486.69 eV) was used to study the presence and the bonding states of CZTS. The High-resolution (HR) XPS spectra were collected in a concentric hemispherical analyzer in a constant energy mode with pass energy of 20 eV and a step of 0.05 eV for narrow scan. Raman spectra were obtained by LabRam HR800 with a green laser source ($\lambda = 532.15$ nm).

3. Results and discussion

The XRD patterns of the starting materials of Cu, Zn, Sn, and S elements before mixing and ball milling were shown in Fig. 1(a). These materials can be indexed to be Cu (JCPDS card no. #04-0836), Zn (JCPDS card no. #65-3358), Sn (JCPDS card no. #65-2631), and S (JCPDS card no. #08-0247), as expected. The XRD patterns of sample C1 after ball milling for different times, 10, 15, 20, 25, 30, and 35 h (C1-10 h, C1-15 h, C1-20 h, C1-25 h, C1-30, and C1-35 h, respectively) were shown in Fig. 1(b). The test sample powder was spread on a Si substrate, and XRD peak positions were calibrated with Si peaks as reference. After ball milling for 10 h and 15 h, peaks of the starting materials still existed, and the peaks could be assigned to Cu (JCPDS card no. #04-0836), Sn (JCPDS card no. #65-2631), Zn (JCPDS card no. #65-3358), and S (JCPDS card no. #08-0247). When the milling time increased to 20 h, peaks of Cu, Sn, and S disappeared, and three broad peaks appeared which can be assigned to CZTS (1 1 2), (2 2 0) and (3 1 2), with the coexistence of Zn peaks. This indicates that CZTS could be directly formed from Cu, Zn, Sn, and S elemental materials by the physical and chemical changes due to mechanical energy, pulverization, friction, and compression during the high revolution and rotation. The results suggest that the chemical reaction of $2Cu + Zn + Sn + 4S + \text{Sufficient Energy} \rightarrow Cu_2ZnSnS_4$ occurred after ball milling for 20 h. With an increase in milling time, the XRD patterns exhibited three peaks at $2\theta = 28.5°$, 47.3°, and 56.1°, which could be perfectly indexed to (1 1 2), (2 2 0), and (3 1 2) of kesterite CZTS with *I*-42*m* space group (JCPDS card no. #26-0575), without the presence of peaks of Cu, Zn, Sn, and S. From the XRD patterns of C1-25 h, C1-30 h, C1-35 h, it could be seen that positions and intensity of the three CZTS characteristic peaks did not change obviously. The full width half maximum (FHWD) of CZTS peaks increased with the ball milling time after 25 h of ball milling. The grain size was estimated by using the Scherrer's equation: $D = K\lambda/\beta\cos\theta$, where $K = 0.89$, D is the grain size (nm), $\lambda = 0.15406$ nm, β is FWHM (unit in radians), and θ is Bragg's angle (unit in degrees). The grain sizes of C1-25 h, C1-30 h, and C1-35 h were found to be 10.6, 9.2, and 8.9 nm, respectively, which suggests

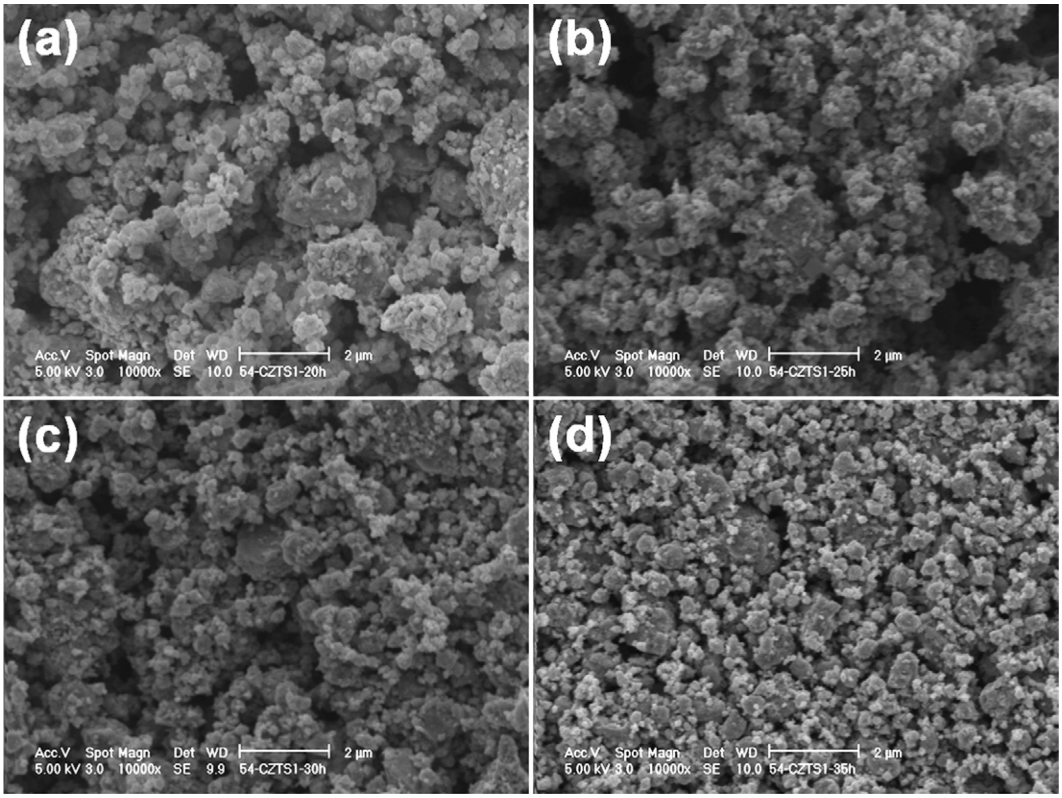

Fig. 3. Morphology of mixture of Cu, Zn, Sn, and S in ratio of 2.0:1.0:1.0:4.0 after different ball milling time, (a) 20 h, (b) 25 h, (c) 30 h, (4) 35 h.

that the CZTS grains formed were pulverized finer by this planetary ball milling. The ball milling process produced interactions caused by frictional and impact forces, which released high dynamic energies, resulting in the grain size reduction of the samples.

HRTEM image of sample C1-35 h was shown in Fig. 2(a). From the HRTEM image, the lattice spacing was found to be 0.315 nm that belongs to (1 1 2) plane of CZTS. The inset of Fig. 2 (a) showed the SEAD pattern of C1-35 h, which contained a series of diffraction rings corresponding to lattice spacings of 0.315, 0.194, and 0.166 nm, attributed to (1 1 2), (2 2 0), and (3 1 2) planes of kesterite CZTS. These results from HRTEM image and SEAD pattern were consistent with those from XRD. It should be noted that CZTS and ZnS

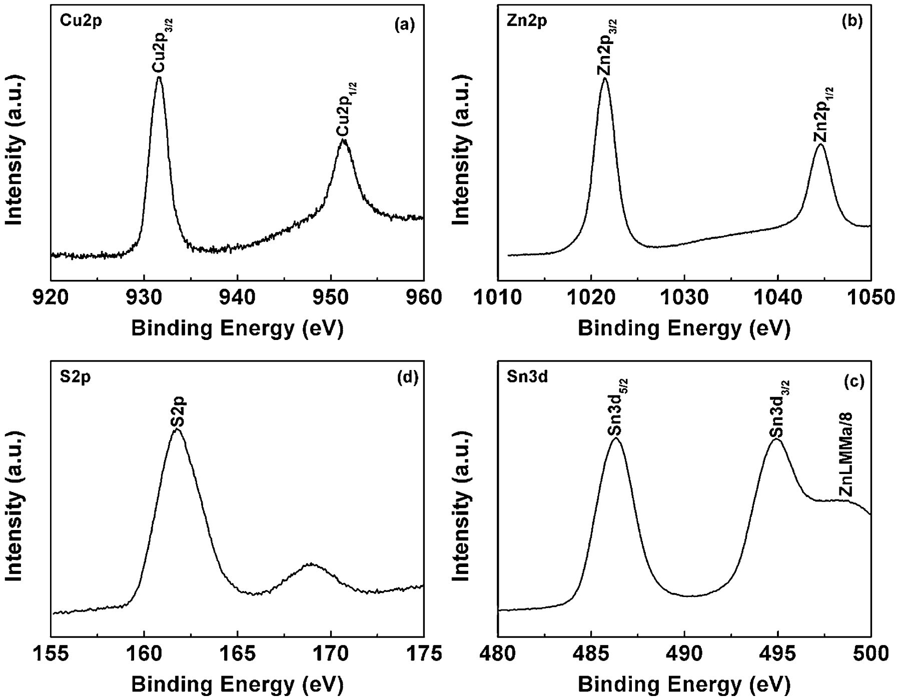

Fig. 4. The high resolution XPS spectrum of C1-35 h, (a) core level spectrum for Cu2p, (b) core level spectrum for Zn2p, (c) core level spectrum for Sn3d and (d) core level spectrum for S2p.

had similar XRD patterns. Hence, Raman scattering was used to further confirm the formation of CZTS by making use of the different vibration features of CZTS and ZnS. Raman shift peak 520 cm^{-1} of Si was used for calibration of Raman spectra. Fig. 2(b) showed Raman spectra for C1-35 h with the strongest peak at 329 cm^{-1}, similar to the result of 336 cm^{-1} reported by Himmrich et al. [10], confirming that our samples are CZTS. And the red-shift of Raman peak indicated that grain size of CZTS using our method was small. Raman scattering spectrum of ZnS sample prepared from chemical bath deposition was tested for comparison and shown in Fig. 2 (b), and two peaks of 262 and 343 cm^{-1} appeared, which were similar to 271 and 352 cm^{-1} attributed to the LO and TO phonon energies of ZnS reported by Nilsen [11]. The Raman scattering spectra of CZTS sample from MCP did not show ZnS peaks. The characteristic modes of SnS at 160 cm^{-1}, 190 cm^{-1}, 220 cm^{-1} and those of SnS_2 at 315 cm^{-1} were reported by Pakin et al. [12]. CuS and Cu_2S with characteristic strong peaks of 472 and 474 cm^{-1}, respectively, were reported by Minceva-Sukarova et al. [13]. In this study, this CZTS spectrum did not show any evidence of SnS, SnS_2, CuS, and Cu_2S.

The morphologies of sample C1-20, C1-25, C1-30, and C1-35 h were shown in Fig. 3, the particles sizes were measured to be in the ranges of 0.15–3.71, 0.10–1.93, 0.09–1.86 and 0.07–1.44 μm, respectively, based on the measurement of 30 particles in a randomly selected region for each sample. An increase in the milling time resulted in finer particles and more uniform size distribution.

XPS was employed to investigate the presence and chemical valence states of element constituents in the CZTS sample of C1-35 h. Calibration was made for each sample with respect to 284.5 eV of carbon C1 s. The core level spectra of Cu2p, Zn2p, Sn3d, and S2p regions were shown in Fig. 4(a)–(d). Fig. 4(a) showed the Cu2p HR-XPS, in which two narrow and symmetric peaks were observed at the binding energy (BE) values of 931.6 and 951.4 eV for $Cu2p_{3/2}$ and $Cu2p_{1/2}$ with a peak splitting of 19.8 eV, corresponding to Cu(I) state. Fig. 4(b) showed the Zn2p HR-XPS, in which the BE values of 1021.5 and 1045.6 eV for $Zn2p_{3/2}$ and $Zn2p_{1/2}$ with peak splitting of 23.1 eV are observed, suggesting Zn(II). Fig. 4(c) showed the BE peaks of 486.3 and 495.0 eV for $Sn3d_{5/2}$ and $Sn3d_{3/2}$ with a peak splitting of 8.7 eV, attributing to Sn(IV). Fig. 4(d) showed the BE values of 161.6 eV for $S2p_{3/2}$ from S(II) and 168.9 eV for $S2p_{3/2}$ from S(VI). The peaks are consistent with those of CZTS reported in literature [14–16].

4. Conclusion

Nano-crystalline Cu_2ZnSnS_4 were obtained through self-sustaining reactions by using an environmental friendly and cost-effective mechanochemical (ball milling) process from elemental Cu, Zn, Sn and S. CTZS formation was investigated. The results revealed that CZTS could be directly formed from its constituent elemental materials after planetary ball milling for 20 h. It was found from X-ray diffraction patterns that with increasing the ball milling time the grain size of mixture powders decreased. Transmission electron microscopy images, diffraction pattern, and Raman spectra confirmed CZTS formation.

Acknowledgements

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