THE POST ANNEALED EFFECT ON THE OPTICAL PROPERTIES OF Cu2ZnSnS4 NANOMATERIALS

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Abstract
Cost effective photovoltaic Cu₂ZnSnS₄ (CZTS) nanomaterials with kesterite crystal phase were synthesized using a facile solvothermal method. Here ethylene glycol was the solvent and Polyvinylpyrrolidone (PVP) used as capping agent. The obtained CZTS nanoparticles were characterized by means of suitable analytical techniques such as X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Raman Spectroscopy, Ultraviolet- Visible (UV-Vis) Spectrometer and Photoluminescence (PL) respectively. The XRD results showed that the obtained sample presented as kesterite crystallinity with (112), (200), (220) and (312) planes of the CZTS nanoparticles and the average crystallite size was about 5.7 nm. The morphological investigation results given by the FESEM revealed that the average particle size of the sample was around 129 to 160 nm. In addition, the optical observation suggested by both the absorption of UV-Vis and emission spectra of PL showed that the CZTS nanoparticles produced by this solvothermal method has the direct band gap energy within the range of 1.49 to 1.53 eV, which is near the optimal value and it is a dynamic absorber material for the efficient photovoltaic application.

Keywords: Cu₂ZnSnS₄, Solvothermal, Nanomaterials, Semiconductors, Solar energy materials.

I. INTRODUCTION
In search of low cost photovoltaic materials, group I₂-II-IV-VI₄ quaternary Chalcogenides offers enormous opportunities as they are abundant in nature, environmentally safe and cost effective. Among the many important functions pursued, tailoring the optical band gap suitable for photovoltaic applications has gained considerable attention [1]. Cu₂ZnSnS₄ with an optimal direct band gap of 1.5 eV and a large absorption coefficient over 10⁴ cm⁻¹ [2, 3], is one of the most promising material for the absorber layers of thin film solar cells. However the preparation routes of CZTS thin films have been reported, such as sulfurization of sputtered [4] or evaporated [5] stacked films, the spray method [6], the sol-gel method [7] and electrode deposition [8,9], which leads to the current highest performing CZTS solar cells (>11% efficiency). In all these methods the relative complex devices, such as vacuum system [4] or an electro deposition apparatus are required [8, 9].

In this work we report a solution- based simple, low cost, large scale and high throughput solvothermal process. It is a non – vacuum based method and acquires nanostructures with controllable dimensions and aligned morphologies that can potentially provide more efficient charge generation, collection and transfer due to the large junction area and short collection distance to the interface [10]. In this process, the reaction between the process and the precursors and solvent is carried out in a closed system at a temperature higher than that of the boiling point of the temperature. The reaction temperature had given a great impact on the structure and morphology of the nanoparticles. Consequently, autogenous pressure parameter that involved in the process plays a major role to enhance the chemical reactivity [11]. The obtained CZTS nanoparticles could be used in the form of nanoparticles ink that were coated on a substrate and sintered into bulk material to prepare large –area uniform film with non toxic and low cost materials which acts as a promising p-type candidate for photovoltaic applications.

II. EXPERIMENTAL PROCEDURE
Materials and Synthesis
Copper (II) chloride dehydrate (CuCl₂ . 2H₂O), zinc (II) chloride (ZnCl₂) and tin (IV) chloride pentahydrate (SnCl₄ . 5H₂O) were all of analytical grade
and used as received. Thiourea (CH₄N₂S) was used as a source of sulfur, and Polyvinylpyrrolidone (PVP) was used as structure-directing ligands.

In a typical reaction, for the preparation of CZTS nanopowder, the precursor solution had the composition of atomic ratio Cu/Zn/Sn/S of 2:1:1:5. For the reaction, 5 mm copper (II) chloride dehydrate, 2.5 mm zinc (II) chloride, 2.5 mm tin (IV) chloride pentahydrate, 12.5 mm thiourea was dissolved in ethylene glycol under magnetic stirring for 30 min. Later 2 g of PVP were added to the above mixture in order to stabilize the growth and allow the formation of well defined structure without agglomeration. Then the mixed solution was transferred into a Teflon lined stainless steel autoclave with 80% of its capacity and maintained at 230 °C for 24 h. After solvothermal reaction, the autoclave was cooled down to room temperature under ambient air. The black precipitate was collected, washed many times with deionized water and ethanol by centrifugation at 4000 rpm for 15 min. The final product was dried overnight at 90 °C.

Characterization

The crystallinity and phase purity of the synthesized CZTS nanoparticles were investigated using X-ray Diffraction (XRD, Rigaku) equipped with Cu-Kβ (λ=1.39220 Å). The particle size and morphology of the synthesized product was analyzed using field emission scanning electron microscope (FE-SEM, ZEISS at accelerating voltage 5 KV). The optical absorption spectra were recorded on a Perkin–Elmer (Model Lambda 35) spectrophotometer. The room temperature Photoluminescence was recorded using Perkin–Elmer (Model Lambda 45) and the Raman analysis was performed using Bruker: RFS 27 respectively.

III. RESULTS AND DISCUSSION

The crystal phase of the CZTS nano particles are identified by X-ray diffraction shown in fig.1. Here the scanning range is from 10 ° to 90 °. The obtained pattern exhibit three broad peaks at 2θ =28.44°, 47.32° and 55.82°, that are attributed to the planes (112), (220), (312) respectively. These XRD pattern can be perfectly indexed as CZTS of kesterite structure and has a unit cell as tetragonal (JCPDS, card no. 26-0575) with the cell parameters a=b=5.434 Å and c=11.014Å.

According to the Debye–Scherrer formula, the average size of the nanoparticles was determined by

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where K is the Scherrer constant (K=0.9), λ denotes the wavelength of used radiation Cu-Kβ (λ=1.39220 Å), β is the full width at half maximum of the (112) diffraction peaks and θ is the Bragg angle. The average crystallite size of CZTS is calculated to be 5.7 nm. As the diffraction peaks that are observed in the pattern matches well simultaneously with that of ZnS (65-1691) and Cu₂SnS₃ (27-0198), making it difficult to distinguish. Hence Raman spectroscopy techniques are used to identify the secondary phase.

![Fig. 1. XRD pattern of the obtained CZTS nanoparticles.](image1)

![Fig. 2. Raman Spectra of the as-synthesized CZTS nanoparticles.](image2)
Fig. 2. give the Raman spectra of the CZTS nanoparticles. The existence of CZTS are confirmed by the Raman shift at 338 cm\(^{-1}\) and 293 cm\(^{-1}\) are in consistence of the CZTS Raman data reported by previous study[12], and most importantly the absence of shifts at 275 cm\(^{-1}\), 352 cm\(^{-1}\) and 267 cm\(^{-1}\), 303 cm\(^{-1}\),365 cm\(^{-1}\) suggests the absence of cubic ZnS and Cu\(_2\)SnS\(_3\), respectively. Therefore, the XRD data must correspond to CZTS [13].

The surface morphology of the synthesized CZTS nanoparticles is obtained from the FE-SEM images with low and high magnifications are shown in fig.3. From figure we can see that the CZTS nanoparticles are composed of a large number of uniform spheres like particles with average size of 129 nm to 160 nm.

The optical properties of the typical CZTS nano products are characterized by UV-Vis spectroscopy and Photoluminescence. Before doing annealing and post annealed CZTS nanoparticles at 110 °C for 2 hrs are taken for the optical analysis. Before doing the characterization the nano powder is completely dispersed in ethylene glycol by sonication. Fig.4.(a) shows the absorbance spectrum of the CZTS nanoparticles before annealing. Here we can see that the pre- annealed nano powder has obtained higher absorption in UV and near IR region and that weak absorption in the visible region. The band gap energy can be determined by extrapolating straight line of the plot \((\alpha h \nu)^2\) versus \((h \nu)\) as shown in the inset of fig.4.(a) \((\alpha = \text{absorbance}, h= \text{Plank's constant}, \text{and } \nu = \text{frequency})\). The band gap energy of the present sample is 1.38 eV. Fig. 4(b) gives the absorbance spectrum of the post annealed CZTS nanoparticles.

![Fig. 3. FESEM images of the obtained CZTS nanoparticles with (a) low and (b) high magnifications.](image)

![Fig.4. UV-Vis absorbance spectra of CZTS nano particles (a) before annealing (The inset image shows obtained band gap energy of 1.38 eV). (b)Post annealing (The inset image shows obtained band gap energy of 1.49 eV).](image)
broad absorption spectrum in the visible region. The direct optical band gap energy for this sample is 1.49 eV which is shown in the inset of the fig. 4(b). In both cases the optical absorption coefficient of the CZTS nano particles are around 10^6 cm⁻¹.

Fig.5 shows the PL spectra of CZTS nano particles. Post annealed CZTS nano particles exhibit emission in the range of 1.47 eV to 1.57 eV and the spectra is dominated by an intense exciton- related emission at 1.53 eV which is shown in fig. 5(a). Whereas the spectra that shown in fig 5. (b) has determined without heating obtains emission in the range of 1.504 eV to 1.56 eV with an intense exciton emission at 1.52 eV. The post annealing improves the optical properties of the CZTS nanoparticles by increasing the band gap energies of UV-Vis to 1.49 eV and PL emission to 1.53 eV which are consistent with the literature value of 1.45-1.6 eV [14-16].

IV. CONCLUSIONS

In conclusion, CZTS nanoparticles with kesterite structure were successfully synthesized via a facile solvothermal method. The structure, composition and morphology of the as- synthesized nano powder was confirmed by XRD, Raman scattering and FE-SEM characterizations. The post annealed effect on the optical properties of the CZTS nano materials improves the band gap energies in both UV-Vis absorption spectra and PL emission spectra. The direct band gap energy of the UV-Vis absorption was 1.49 eV and that of PL emission was 1.53 eV which were optimal for photovoltaic applications.

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