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Optical characterization of $Cu_2ZnSnSe_{4-x}S_x$ nanocrystals thin film

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ABSTRACT

$Cu_2ZnSnSe_{4-x}S_x$ (CZTSeS) nanocrystals have been shown to be a potential application for sustainable thin-film solar cell devices. In this paper, we have presented the growth of nanocrystals CZTSeS and their thin films applications successfully prepared on soda-lime glass substrates by using spin coating techniques. The CZTSeS nanocrystals have been synthesized by hot-injection method. In-depth characterization has indicated that pure stoichiometric CZTSeS nanocrystals with an average particle size mostly distributed between 15 and 20 nm have been formed. We have analyzed the optical transmission and reflection spectra of nanocrystal CZTSeS thin film. Optical band gap E_g and absorption coefficient (α) of thin film have been determined by standard optical analysis and also several optical parameters such as refractive index (n), extinction coefficient (k), the Urbach energy (E_U) and real and imaginary parts of dielectric constant (ε) have been calculated. Detailed characterization data including X-ray diffraction, surface morphology, cross section analysis, optical transmittance and reflectance spectroscopy have been presented in order to use in the performance of single-junction solar devices. Optical measurements have showed a band gap of 1.51 eV, which is optimal for a single-junction solar device.

1. Introduction

$CuZnSnSe_{4-x}S_x$ (CZTSeS), Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) nanocrystals have already gained remarkable relevance due to their potential application for sustainable thin-film solar cell devices. They have advantages such as significant consistency of earth abundant elements, extremely low toxicity and high radiation stability. In addition to these, CZTSe have a high absorption coefficient ($>10^4$ cm^{-1}) and a low band gap (1.0–1.5 eV) [1–4]. These materials also have an optimal direct band gap for solar energy conversion [5–8]. Comparatively, the composition of naturally abundant and low-cost element Zn and Sn makes $Cu_2ZnSn(Se,S)_4$ (CZTSeS) a particularly attractive candidate for large-scale commercial applications. CZTSe and CZTS thin film solar cells have shown efficiencies of 9.15% [9] and 8.4% [10], respectively. Among these materials, the thin film CZTSeS solar cells show the highest power conversion efficiency of 12.6% [5–8]. To further meet the requirement for practical applications and improve the efficiency of the cells, it still remains challenging to improve production techniques that can offer control over the uniformity, morphology and composition of CZTSeS thin films [8].

Many experimental methods have been employed for preparing CZTSeS thin films: sputtering methods [11,12], vacuum evaporation [13], pulsed laser deposition [14], and electron beam evaporation [15]. However, these methods involving high vacuums have brought a high cost. CZTSeS nanocrystals have been prepared based on the hot-injection solution synthesis in our work. This method involves injecting a cold solution of precursors into a hot surfactant solution, leading to the immediate nucleation and growth of nanocrystals and eliminates the need of high vacuum and high temperature, which is promising for the large scale fabrication of cost-effective solar cell absorber. Guo et al. [16] have reported that annealing CZTSeS nanocrystals have resulted in a PV device with 7.2% conversion efficiency using the hot-injection solution synthesis. Todorov et al. [17] have reported the highest power conversion efficiency of 9.66% for CZTSeS thin film solar cell using the hydrazine-based solution processing.

For high efficiency in thin film solar cells, the band gap of the absorber layer is one of the important parameters. The band-gap of

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the $Cu_2ZnSn(S,Se)_4$ can be controlled by varying the selenium/sulfur (Se/S) ratio in the material. Several groups have reported that E_g can be tuned by changing the ratio of Se and S in CZTSeS solid solutions [18–21]. The band gap of CZTSeS can be tuned from about 0.96 eV of CZTSe to 1.5 eV of CZTS by changing the molar ratio of S/Se [18]. Li et al. [19] have synthesized $Cu_2ZnSn(S_xSe_{1-x})_4$ nanocrystals by using solvo thermal method. They have found that the optical band gap value after sulfurization of 90 min and the average size of the CZTSeS nanocrystals vary as around 20 nm and 1.30 eV, respectively. He et al. [20] have fabricated $Cu_2ZnSn(S,Se)_4$ (CZTSSe) thin films on heated quartz substrates using pulsed laser deposition (PLD) method. Their research results have revealed that the atomic Se and S are highly miscible and the band gaps of CZTSSe can be tuned almost linearly between 0.96 and 1.5 eV with a small bowing constant. Gurav et al. [21] have prepared $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) thin films by selenizing a single-step electrodeposited Cu–Zn–Sn–S precursor. They have reported that the band gap energy of CZTSSe thin films is tuned in the range of 1.40–1.08 eV by varying the Se vaporization temperature. The similar near-linear dependence of band gap of the CZTSSe with a small bowing parameter has also been predicted by Chen et al. [18] by using first-principles calculations.

Some physical properties of CZTSeS crystals are still unknown and also the optical dielectric and dispersion parameters have not been studied in detail, yet. The main purpose of this work is to achieve CZTSeS crystals growth by hot injection. This paper reports that the morphology, composition, and optical properties of CZTSeS thin film prepared by hot injection solution synthesis. The second aim of this work is to determine the optical dispersion and dielectric parameters of the film. For this purpose, CZTSeS nanocrystals have been chosen as precursor and CZTSeS nanocrystals have been prepared by spin coating on Corning-1737 glass substrate. Furthermore, the absorption spectra have been measured in the wavelength range 200–2500 nm and the energy gap of the CZTSeS nanocrystal have also been estimated. Based on the experimental results, self-compensation in CZTSeS thin film and the temperature dependence of the PL spectra have been discussed.

2. Experimental details

In this study, we have analyzed the optical transmission and reflection spectra of nanocrystal CZTSeS thin film prepared by spin coating method. Synthesis of CZTSeS nanocrystals have been carried out based on previously published procedure [22–24]. 1 mmol copper(II) acetate monohydrate, 0.5 mmol Zinc(II) acetate dihydrate, 0.5 mmol Tin(II)Acetate dihydrate and 20 mL OLA (>70%) have been added to a 25 mL two-neck flask and heated to 280 °C under N2 flow. When a reddish brown solution has been observed, a solution of 2 mmol sulfur (99.99%) and 2 mmol selenium (99.99%) powder in oleylamine have been added to above solution at ~180 °C. Then, the temperature has been increased to 280 °C and kept for 30 min by stirring. After 30 min with continuous stirring, the reaction mixture has been cooled to room temperature. Finally, CZTSeS nanocrystals have been participated by adding toluene-2-propanol (4:1) mixtures and centrifuging. CZTSeS nanocrystals have been washed several times with ethanol and dried at 70 °C for 2 h.

We have prepared a solution from CZTSeS nanocrystals dispersed in toluene-propanol mixtures. The prepared solution has been stirred for 30 min and coated on Corning-1737 glass substrate by spin coating at room temperature. Prior to coating, glass has been ultrasonically cleaned in acetone and propanol for 25 min, respectively, and then left in UV-Ozone cleaner for 30 min and finally dried in nitrogen.

The thickness measurement of the coated CZTSeS thin film has been performed by stylus profilometer Veeco Dektak 150 and the thickness has been determined approximately as 135 nm.

X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) patterns of colloidal nanoparticles have been recorded with a Bruker Advance D8 XRD (Cu α source with 1.5406 Å wavelength), in powder mode. Raman spectra of nanocrystals in room temperature have been recorded by Renishaw in via confocal-raman spectrometer. ZeissEvo model scanning electron microscope has been used to analyze atomic percentage of elements. JEOL JEM-2100F 200 kV model transmission electron microscope (TEM) has been used to collect microscopic images and selected area electron diffraction pattern (SAED) of CZTSeS nanocrystals. The optical transmittance and reflectance spectrum of thin film have been measured in a wide spectral range from 200 to 2500 nm by UV-VIS-NIR photospectrometer (Jasco V-670 photospectrometer).

3. Results and discussion

X-ray diffraction (XRD) pattern of colloidal CZTSeS nanocrystals is given in Fig. 1. Characteristic peaks for nanocrystals are clearly observed on XRD patterns. We have to emphasize that, XRD peaks indicate two main crystalline structures as kesterite and stannite. Both structures are described by a tetragonal unit cell. Since their similar crystal structure, it is difficult to separate these structures from diffraction peaks. However, kesterite phase is more stable than stannite phase as it has been reported many times in literature [25,26]. The as-synthesized CZTSeS nanocrystals show three intensive XRD peaks centered at $2\Theta = 27.48°$, $45.52°$ and $54.28°$ corresponding planes to (112), (220) and (312), respectively. The diffraction values of 2Θ for CZTSeS nanocrystals appear between CZTSe (JCPDS 70-8930) and CZTS (JCPDS 26-0575) values, due to the coexistence of larger Se (1.98 Å) and smaller S (1.84 Å) atoms in sample [24,25]. As well known, XRD peaks are broadened by decreasing the particle size (Fig. 1). The sample of nanocrystals shows broad diffraction peaks and this broad peaks are due to small size of the CZTSeS nanocrystals. The average particle size of nanocrystals is found to be around 19 ± 1 nm using the Sherrer method. Moreover; the average particle size distribution of nanocrystals has been calculated to be 18 nm by using SAXS method (Fig. 2).

The structure and phase purity of the CZTSeS nanocrystals have been investigated by using Raman analysis. The Raman spectra of CZTSeS nanocrystals are presented in Fig. 3. The characteristic peaks of $CZTSe_{4-x}S_x$ are clearly observed on spectra. Two Raman

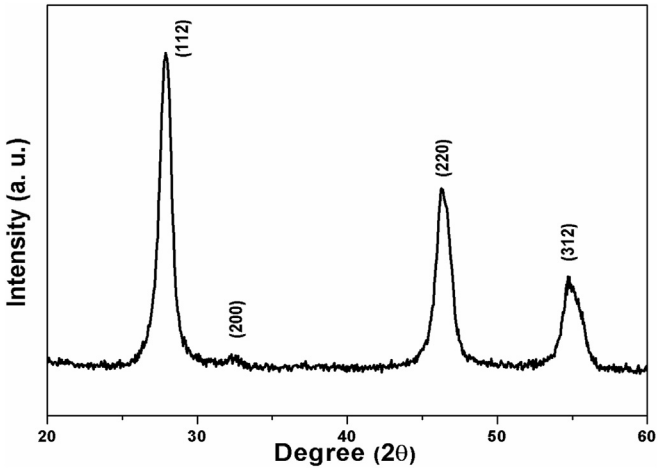

Fig. 1. XRD Patterns of CZTSeS nanocrystals.