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Effect of Thiourea Concentration on Structural, Optical and Electrical Properties of Spray-pyrolysed Copper-Zinc-Tin-Sulphide Films

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Abstract

Copper-zinc-tin-sulphide (CZTS) thin films were prepared by spray pyrolysis technique using copper chloride, zinc chloride, tin (IV) chloride and thiourea as copper, zinc, tin and sulphur source respectively. In this work, the effect of thiourea (sulphur source) concentration on the structural, optical and electrical properties of *CZTS* films was investigated by X-ray diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy and van der pauw four point probing. Higher optical absorption, lower optical band gap energy and increased electrical conductivity were achieved with higher sulphur source (thiourea) concentration in CZTS.

Key words: *CZTS*, thiourea concentration, optical band gap, electrical conductivity

Introduction

Copper zinc tin sulphide (*CZTS*) is one of the promising materials for an absorber layer in thin film solar cells. *CZTS* has a direct band gap of ~1.5 eV, which is near the optimum band gaps of single-junction photovoltaic devices, and a large absorption coefficient on the order of 10^4 cm^{-1}. Moreover, *CZTS* is composed of abundant and nontoxic elements. It can alleviate the material bottlenecks present in copper indium gallium selenide *CIGS* (scarcity of indium). In 1988, Ito and Nakazawa reported, for the first time, the fabrication of *CZTS* thin films and the photovoltaic effect in *CZTS* solar cells. To date, there have been many reports on the fabrication of *CZTS* films and solar cells using physical vapor methods. Katagiri *et al*.

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reported the highest efficiency of 6.77% in *CZTS* solar cells. Their absorber layer was prepared using an RF co-sputtering system followed by a solid-state reaction in H_2S atmosphere [1].

Several preparation methods have been reported in literature for preparation of *CZTS* solar cells [2-5]. Spray pyrolysis is a versatile as well as a low-cost technique that has been used to deposit semiconductor films. In this process, a thin film is deposited by spraying a solution on a hot surface. The constituents react to form a chemical compound. The chemical reactants should be properly selected such that the products other than the desired compound are volatile at the temperature of deposition.

Experiment

The Cu_2ZnSnS_4 (*CZTS*) thin films on glass substrates were prepared by the spray pyrolysis. Before the films deposition, the glass substrates were cleaned with standard cleansing process. The mixture solution was prepared by mixing 0.04 M of Copper Chloride, 0.01 M of Zinc Chloride, 0.01 M of Tin IV Chloride and different molar concentrations of thiourea (0.08 M, 0.16 M, 0.24 M and 0.32 M). All the chemicals were dissolved in ethanol. These mixture solutions were stirred at 50 °C for 1 hr. After stirring, the precursor *CZTS* solution was formed. After that, this solution was sprayed onto the 250 °C heating glass substrate using home-made spray pyrolysis setup to form *CZTS* thin films.

The structural property of the films was determined using X-ray diffraction (RIGAKU Multiflex (Japan). The absorption spectra of the samples were acquired by using UV-vis spectrophotometer (GENESIS 10S UV-Vis) and the thickness of thin films were determined by Tencor Alpha-Step IQ surface profiler. The electrical conductivity of the *CZTS* films were measured using der pauw four point probing.

Results and Discussion

We have studied the effect of thiourea concentration on structural, optical and electrical properties of *CZTS* films. The X-ray diffraction (XRD) analysis has been employed to examine the phase and structure of *CZTS*. Major diffraction peaks in our observed XRD patterns were examined using Joint Committee on Powder Diffraction Standard (JCPDS) reference data of *CZTS*. To improve the solubility of $CuCl_2$ in *CZTS* solution, excess amount of thiourea ($(NH_2)_2CS$) beyond the stoichiometric ratio is needed. The optimum thiourea concentration is 0.08 M. By increasing the thiourea concentration by multiple times, the structural and optical properties of *CZTS* films were investigated. The phase and structure of *CZTS* changed upon the thiourea concentration were examined using XRD. Fig. 1 shows the XRD pattern of *CZTS* with different thiourea concentrations. The major diffraction peaks in XRD pattern indicates that the films are composed of *CZTS*. As observed, the peaks at 2θ = 28.283°, 1.9086° and 1.6418° were be indexed to the (112), (220) and (312) planes of the *CZTS*, which are characteristic of the kesterite structure. *CZTS* possesses tetragonal structure with average lattice constants (a = 5.4119 nm and c = 11.0971 nm) for thiourea (0.08 M), (a = 5.4244 nm and c = 10.9190 nm) for thiourea (0.16 M), (a = 5.3791 and c = 10.9249 nm) for thiourea (0.24 M) and (a = 5.4355 and c = 10.5639 nm) for thiourea (0.32 M). Upon varying thiourea concentration, the lattice constant of *CZTS* were almost unchanged. By increasing thiourea concentration, the peak intensity of all observed peaks increased, indicating the better crystallinity of *CZTS*.

The average nanocrystalline size was calculated using Debye-Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D = crystalline size, K = shape factor (taken as 0.9), λ = wavelength of CuK_α radiation, θ = Bragg angle and β = full width at half maximum height (FWHM). The calculated nanocrystalline sizes are 30.4 nm for thiourea (0.08 M), 19.3 nm for thiourea (0.16 M), 17.8 nm for thiourea (0.24 M) and 20.4 nm for thiourea (0.32 M). It is generally observed that increased thiourea concentration enabled to change the crystalline size.

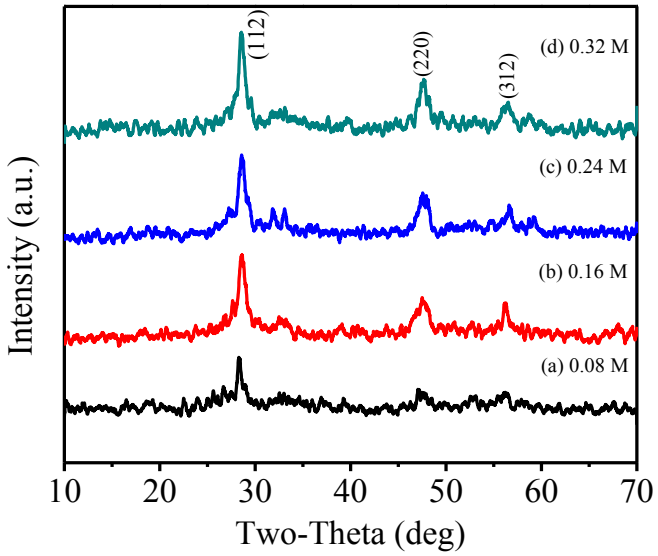

Fig. 1 The XRD pattern of *CZTS* samples prepared from the *CZTS* (*Cu* –0.04 M) precursor solutions with different thiourea concentrations (a) 0.08 M, (b) 0.16 M, (c) 0.24 M and (d) 0.32 M

We also studied the optical properties of *CZTS* films with fixed *Cu* (0.04 M) but different thiourea concentration by using UV-vis Spectrophotometry. The absorption spectrum of *CZTS* films with varying thiourea concentration is shown in Fig. 2 (a). Upon increasing thiourea concentration, the optical absorption increased over the spectral region below 600 nm. The optical band-gap energy of *CZTS* films (*Cu* (0.04 M)) with different thiourea concentration were calculated on the basis of the optical absorption spectra using the equation,

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon}$$

where α is absorption coefficient, hν is the incident photon energy, A is the proportionality constant, E_g is the band-gap energy and n is either 2 for indirect band gap semiconductor or 1/2 for direct band-gap semiconductor. Since *CZTS* is a direct band-gap semiconductor [1], the optical band-gap of *CZTS* was attained by plotting $(\alpha h\upsilon)^2$ versus incident photon energy (hυ).

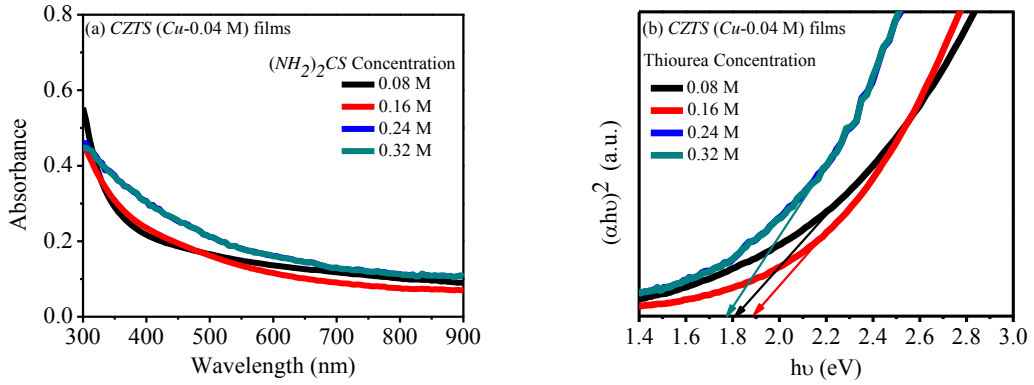

Fig. 2 (a) Absorption spectra and (b) Plot of $(\alpha h\upsilon)^2$ Vs. hυ for *CZTS* (*Cu*-0.04 M) films: varying thiourea concentrations (0.08 – 0.32 M)

Table 1 The optical band-gap energies of *CZTS* films (*Cu* – 0.04 M) using different thiourea concentrations (0.08 – 0.32 M)

CZTS Films *Cu* (0.04 M)	Optical Band-gap Energy (eV)
Thiourea 0.08 M	1.81
Thiourea 0.16 M	1.89
Thiourea 0.24 M	1.79
Thiourea 0.32 M	1.79

Fig. 2 (b) shows the plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ for the *CZTS* films with different thiourea concentrations. The calculated band-gap energies are listed in Table 1. The band-gap energy varied between 1.79 and 1.89 eV. Low band-gap energy is requisite for cell application since it can absorb the low energy photons.

In addition to the structural and optical properties, the electrical conductivity/ mobility also plays a key role in determining the efficiency of *CZTS* solar cells. Thus we have determined the electrical conductivity of *CZTS* films with different thiourea concentrations using Van der Pauw four point probe method. In order to promote the solubility of $CuCl_2$ in *CZTS* solution, at least three fold molar amount of thiourea is required as compared to $CuCl_2$ [6]. We investigated the electrical conductivity of *CZTS* films by varying thiourea (0.08 M, 0.16 M, 0.24 M and 0.32 M) concentrations. Fig. 3 shows the electrical conductivity of *CZTS* films against the thiourea concentration (M). It is found that the electrical conductivities of *CZTS* films dramatically increase with increasing thiourea concentrations. Electrical conductivity of *CZTS* film with thiourea (0.32 M) is as high as 3.36 S/m. This may be due to the sufficient amount of copper chloride dissolve in *CZTS* precursor solution.

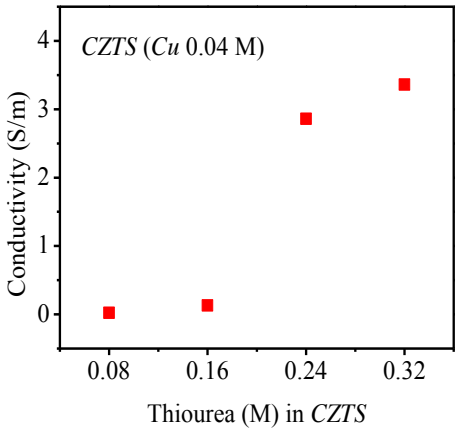

Fig. 3 Plots of the electrical conductivity of *CZTS* films against the thiourea concentration (0.08 – 0.32 M)

Conclusion

Copper zinc tin sulphide (CZTS) thin films have been successfully deposited by spray pyrolysis technique. XRD analysis indicates that the deposited films have tetragonal kesterite structure with crystalline size of 17–30 nm. The crystallinity of the films was improved with increasing thiourea concentrations. The optical band gap energies of the films fell within 1.79 – 1.89 eV and the electrical conductivity was as high as 3.36 S/m for the films with highest thiourea concentration of 0.32 M. High crystallinity, low band gap energy and high electrical conductivity are basic requisites for light absorber layer in solar cells.

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