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CHARACTERISTICS OF Cu_2ZnSnS_4 THIN FILM PREPARED BY CALCINATION AND SULFURIZING OF METAL (Cu,Zn,Sn)-ETHANOLAMINE PRECURSOR COMPLEXED FROM METAL (Cu,Zn,Sn)-HYDRATE

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Ethanolamine was used to complex a metal (Cu,Zn,Sn)-ethanolamine from copper (II) acetate monohydrate, zinc acetate dehydrate and tin (II) chloride dehydrate. Calcination and sulfurization of the spin coated metal (Cu,Zn,Sn)-ethanolamine precursor were conducted to form kesterite Cu_2ZnSnS_4 (CZTS) thin films adhesive to the substrate. The optical-electrical properties of the films exhibited p-type semiconductivity with a mobility and resistivity of 7.64 cm^2/Vs and 3.78 Ωcm, respectively, and a band gap of 1.52 eV with an absorption coefficient > 10^5 cm^{-1} at a copper-poor,zinc-rich composition of Cu/(Zn+Sn) = 0.83, Zn/Sn =1.76 and S/metal = 1.08. Using metal (Cu,Zn,Sn) ethanolamine at the chemical bath deposition process, a CZTS thin film suitable for solar absorber layer applications was fabricated.

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Keyword: Cu_2ZnSnS_4, Metal-Ethanolamine, Calcination, Sulfurization, Metal-hydrate.

1. Introduction

The chemical bath deposition process is used as a low cost and simple process for the preparation of Cu_2ZnSnS_4 (CZTS) solar absorber layers. Metal (Cu,Zn,Sn) hydrates are normally used as a cost raw materials for CZTS solar absorber layer preparation in the chemical bath deposition process [1-5]. During the chemical bath deposition process, zinc ions in an aqueous solution oxidize easily, such as $Zn(OH)_2$ particulates from a reaction between Zn^{2+} and OH^- ions due to the low solubility product (K_{sp}) of $Zn(OH)_2$ (~ 3 x 10^{-17}) [6,7]. Zinc oxide in the film suppresses the formation of a CZTS compound and adheres to substrate. To avoid these problems, colloidal-based zinc organic matter (i.e. ethylene glycol, 2-methoxyethanol) is often applied [1,8,9]. On the other hand, the effects on suppressing zinc ion oxidation are limited using water or alcohol as a diluent to reduce the viscosity of the colloid.

This study focused on modifying the process to suppress zinc ion oxidation during chemical bath deposition using metal (Cu,Zn,Sn)-ethanolamine complexed from the metal (Cu,Zn,Sn)-hydrate. In addition, this process is a simple process that uses low cost and non-toxic source materials [5,10]. The compositions, structures, morphologies and optical-electrical properties of the films prepared were assessed for solar absorber layer applications.

2. Experiment

Copper (II) acetate monohydrate (0.0176 moles), zinc acetate dehydrate (0.0120 moles) and tin (II) chloride dehydrate (0.0100 moles) were dissolved separately in 20 ml of ethanolamine under ultrasonication and then combined. The composition ratios were set to a copper-poor, zinc-rich composition of Cu/(Zn+Sn) = 0.80 and Zn/Sn = 1.20 from CZTS compound stoichiometry, which is a well-known composition for solar absorber layer applications with high conversion

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efficiencies [11]. To reduce the surface tension of ethanolamine (81.61 dyne/cm), a metal ethanolamine solution was diluted with ethanol to a solution volume of 100 ml. The solution exhibited a dark blue color that was transparent in appearance. Subsequently, 0.05 ml of the metal (Cu,Zn,Sn)-ethanolamine solution was spin coated on the soda lime glass (1.25 cm × 1.25 cm), and then calcined at 200 °C for 10 min under an Ar atmosphere. The calcined precursors were sulfurized under an Ar + H_2S (5%) atmosphere at 550 °C for 120 min and cooled in a furnace.

The chemical composition of the films was analyzed by energy dispersive X-ray spectrometry (EDS, Horiba, Japan). The crystal structures were determined by X-ray diffraction (XRD, PANalytical MPD, Netherlands). Fourier transform infrared spectroscopy (FTIR, 8410S, Switzerland) was used to examine the bonding of the organic ligand. The morphology was observed by scanning electron microscopy (SEM, Hitachi S4800, Japan). The absorption spectra were recorded using a UV-Vis-NIR spectrophotometer (Varian Carry 5000, U.S.A). The electrical properties were examined by Hall-Effect measurements using a Van der Paw apparatus (HMS-3000, Ecopia U.S.A.).

3. Result and discussion

3.1 Composition

Table 1 lists the compositions of the metal (Cu,Zn,Sn)-ethanolamine solution, metal (CZT) precursor calcined at 200 °C for 10 min and CZTS films sulfurized at 550 °C for 120 min.

Table 1. Chemical composition of the metal (Cu,Zn,Sn)-ethanolamine solution, metal (CZT) precursor calcined at 200 °C for 10 min and CZTS film sulfurized at 550 °C for 120 min.

Sample	Elements	Atomic Percent (%)	Zn/Sn	Cu/(Zn+Sn)	S/metal
Metal (Cu,Zn,Sn)-ethanolamine Solution	S	-	1.20	0.80	-
	Cu	44.31			
	Zn	30.15			
	Sn	25.54			
Metal (CZT) precursor (After Calcination)	S	-	1.25	0.78	-
	Cu	43.98			
	Zn	31.10			
	Sn	24.92			
CZTS Film (After Sulfurization)	S	(51.81)	1.76	0.83	1.08
	Cu	(21.80), 45.25*			
	Zn	(16.83) 34.93*			
	Sn	(9.55) 19.82*			

*Calculated by excluding the sulfur atom

The metal (Cu,Zn,Sn)-ethanolamine solution consisted of composition ratios set to Cu/(Zn+Sn) = 0.80 and Zn/Sn = 1.20.

The composition ratios of the calcined metal(CZT) precursor was Cu/(Zn+Sn) = 0.78 and Zn/Sn = 1.25, which is close to the composition ratio with the metal (Cu,Zn,Sn)-ethanolamine solution.

The organic ligand and zinc oxidation of the calcined metal (CZT) precursor were examined by FTIR spectroscopy, as shown in Fig.1.

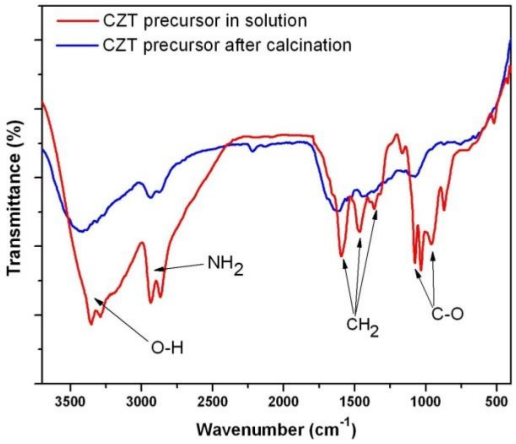

Fig. 1. FTIR spectrum of a metal (Cu,Zn,Sn)-ethanolamine solution and metal (CZT) precursor calcined at 200 °C for 10 min.

The calcined metal (CZT) precursor has a residues of the organic and a slight O-H ligand, which suggests that the metal (CZT) precursor was not oxidized by the CO_2, H_2O, NH_3, and Cl gases released by the decomposition of ethanolamine during calcination.

The composition of the sulfurized CZTS film changed to composition ratios of Cu/(Zn+Sn) = 0.83 and Zn/Sn = 1.76 with a slightly higher copper content and an increasing tin composition from the CZT precursor. This was attributed to tin evaporation during sulfurization at 550 °C for 120 min. To compensate for tin evaporation, supplementary tin addition was performed during sulfurization [12,13].

Zinc oxidation of the metal (CZT) precursor was suppressed during the formation of zinc sulfide and CZTS, which formed a non-uniform CZTS phase with zinc oxide or other sulfides with poor adhesion to the substrate. A higher temperature and additional sulfurizing time was needed for the formation of a homogeneous CZTS compound than with no oxide.

3.2 Structure

The structure of the metal (CZT) precursor and CZTS film were identified by XRD, as shown in Fig. 2.

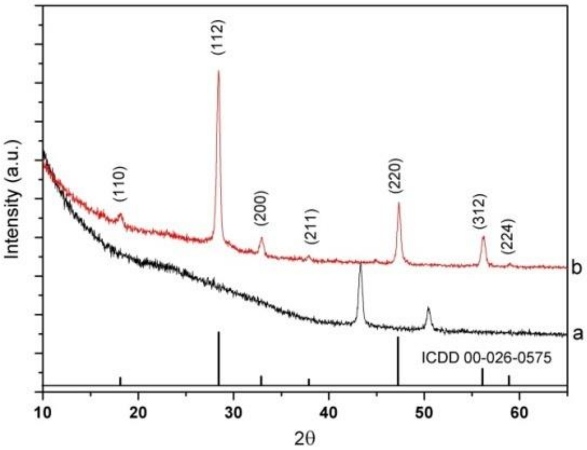

Fig. 2. XRD patterns of the CZT precursor (a) calcined at 200 °C for 10 min and the CZTS film (b) sulfurized under an Ar + H_2S (5%) atmosphere at 550 °C for 120 min

The XRD pattern of the calcined CZT precursor (Fig.2a) consisted of two XRD peaks at 43.33° and 50.41° 2θ, which were assigned to intermetallic binary compounds, Cu_5Zn_8 (ICDD: 00-025-1228) and Cu_5Sn_6 (ICDD: 00-045-1488) [14-17]. The metal (Cu,Zn,Sn) ethanolamine was assumed to decompose and transform to a Cu-Zn, Cu-Sn intermetallic compound precursor first during calcination according to the following reaction:

$$[(Cu,Zn,Sn)(ETA)_x]^y \rightarrow Cu\text{-}Zn\text{-}Sn(Cu_xZn_y,Cu_xSn_y) + a\,CO_2 + b\,H_2O + c\,NH_3 + d\,Cl$$

In Fig.2b, the CZTS thin films sulfurized under an Ar + H_2S (5%) atmosphere at 550 °C for 120 min, were identified. The XRD peaks were indexed to the (110), (112), (200), (211), (220), (312), and (224) planes of the kesterite structure CZTS (ICDD: 00-026-0575). Although the tin contents in the film decreased after sulfurizing, as shown in Table 1, the kesterite structure in the CZTS in the film remained.

Fig. 3 shows the EDS spectra of the CZTS film. No impurities, such as C, O and Cl, were observed. The presence of Cu, Zn, Sn, and S was attributed to the decomposition of ethanolamine. A kesterite structure CZTS with no other phases or impurities was identified from the structure of the CZTS film in Fig. 2b and the ED spectra in Fig. 3.

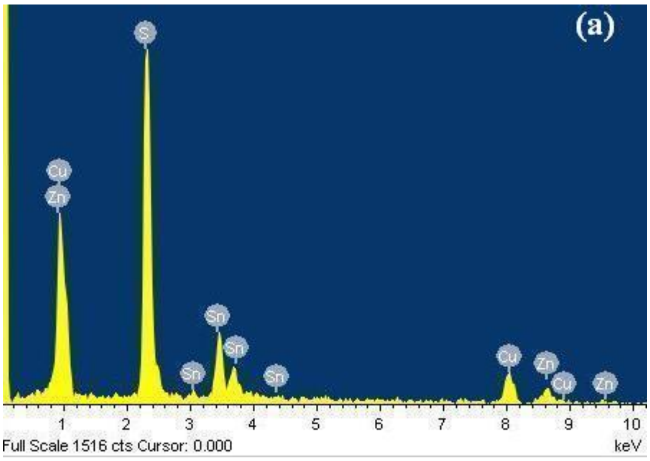

Fig. 3. ED spectra of the CZTS films sulfurized under Ar + H_2S (5%) at 550 °C for 120 min.

3.3 Morphology

Fig. 4 shows SEM images of the metal (CZT) precursor and CZTS film, which are surface view (Fig.4a), cross-section (Fig.4c) images of the metal (CZT) precursor, and the surface view (Fig.4b), cross-section (Fig.4d) images of the CZTS film. The image of the metal (CZT) precursor (Fig.4(a)) showed a surface with a uniform grain and cross-section with good adhesion (Fig.4(c)) to the substrate. The CZTS film showed larger grains (Fig. 4(b)) than the metal (CZT) precursor and adhered well to the substrate (Fig. 4(d)).

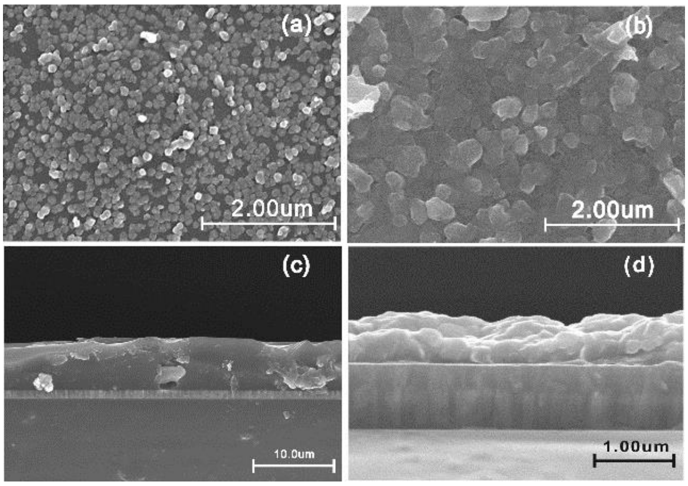

Fig. 4. SEM images of metal (CZT) precursor (a), CZTS film (b) and cross-section of metal (CZT) precursor (c), CZTS film (d).

During the sulfurizing process, the film became thinner due to tin evaporation (as shown in table 1); however, increasing the Cu/(Zn+Sn) ratio in the CZTS film enhanced grain growth as a grain growth flux [13]. As shown in Fig. 4d, a dense and adhesive film to the substrate and an approximately 800 nm thick CZTS film were observed.

3.4 Properties

The optical properties (i.e., transmittance and optical band gap) of the CZTS films were examined by UV-Vis-NIR spectrophotometry, as shown in Fig. 5.

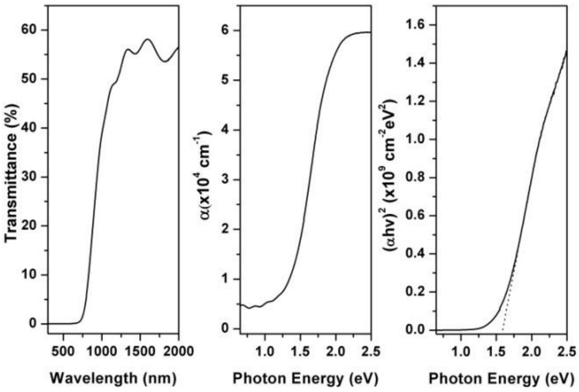

Fig 5. Optical properties of the CZTS film sulfurized at 550 °C for 120 min under Ar + H_2S (5%) transmittance (a), absorption coefficient (b) and optical band gap (c)

The CZTS films showed low transmittance in visible light (< 800 nm) and transmitted more than 50 % in the infrared light range (1200 nm to 2000 nm) (Fig.5a). The CZTS thin film showed a high absorption coefficient (> 10^5 cm^{-1} in visible light) (Fig.5b) with a direct band gap of 1.52 eV (Fig.5c). The band gap and absorption coefficient were similar to those reported elsewhere [1,5,9].

Table 2 lists the electrical properties, such as the semiconductor type, mobility and resistivity of the CZTS thin film.

Table 2. Electrical properties of the CZTS film sulfurized at 550 °C for 120 min

Semiconductor type	Mobility (cm^2/Vs)	Resistivity (Ωcm)
p-type	7.64	3.78

The mobility and resistivity of the films were 7.64 cm^2/Vs and 3.78 Ωcm, respectively, as shown in Table 2. The electrical properties were similar to values reported elsewhere [16-18]. The results using metal(Cu,Zn,Sn)-ethanolamine for CZTS solar absorber layer preparation by a chemical bath deposition process are promising.

4. Conclusions

To suppress zinc ion oxidation in an aqueous solution for CZTS solar absorber layer preparation from copper (II) acetate monohydrate, zinc acetate dehydrate and tin (II) chloride dehydrate, ethanolamine was employed as a complexing agent to form metal (Cu,Zn,Sn)-ethanolamine. Subsequent calcination and sulfurization of a metal (Cu,Zn,Sn)-ethanolamine was conducted under an Ar + H_2S (5%) atmosphere at 550 °C for 120 min to form a uniform CZTS film with a single kesterite structure that was adhesive to the substrate. The opto-electrical properties of the films with a copper-poor, zinc-rich composition of Cu/(Zn+Sn) = 0.83, Zn/Sn =1.76 and S/metal = 1.08 exhibited a direct band gap energy of 1.52 eV with an absorption coefficient > 10^5 cm^{-1}, and p-type semiconductivity with a mobility and resistivity of 7.64 cm^2/Vs and 3.78 Ωcm, respectively. By employing metal(Cu,Zn,Sn) ethanolamine to suppress zinc ion oxidation from the zinc hydrate solution, single kesterite CZTS thin films adhesive to the substrate could be prepared easily for solar absorber layer applications.

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