Preparation of narrow band-gap Cu₂SnS₃ and Cu₂Sn(S,Se)₃ and fabrication of their films by Printing/High-pressure Sintering process

Takeshi Nomura, Tsuyoshi Maeda, and Takahiro Wada

Department of Materials Chemistry, Ryukoku University 1-5, Yokotani, Oe-cho, Seta, Otsu, Shiga, 520-2194, Japan Phone: +81-77-543-7468 E-mail: t12m084@mail.ryukoku.ac.jp

1. Introduction

Cu(In,Ga)Se₂ (CIGS) has attracted attention as the most promising absorber material for thin-film compound semiconductor solar cells. The efficiency of CIGS thin-film solar cells has reached 20.3% [1]. However, mass production of CIGS solar cells is limited by availability of the rare metals In and Ga. Cu₂ZnSnS₄ (CZTS) is a well-known indium-free photovoltaic material. Recently, new kinds of In-free Cu chalcogenides, Cu₂SnS₃ (CTS) and Cu₂SnSe₃ (CTSe), have been studied. Katagiri's group fabricated CTS solar cells with an efficiency of 2.54% by a combination of electrodeposition of the precursor layer and postsulfurization methods [2]. CTS was a secondary impurity compound in the preparation of CZTS thin films [3]. Various kinds of crystal structures with different band gap energies were reported for the CTS. The cubic and tetragonal CTS films were obtained by a sputtering/sulfurization method. The reported band gaps of cubic and tetragonal CTS were 1.35 and 0.96 eV, respectively [4]. The band gap of the CTS film prepared by solution method was 0.95 eV [5]. Recently, we theoretically evaluated the electronic structures of CTS and CTSe [6]. The calculated band gap of CTSe is narrower than those of CIS and CZTSe. Basic research is necessary to study the crystal structure and band gap energy of CTS and CTSe films.

In this study, we synthesized Cu_2SnS_3 and $Cu_2Sn(S,Se)_3$ (CTSSe) and fabricated their films. The crystallographic structures and optical properties were characterized.

2. Experimental Procedures

2.1 Fabrication of Cu₂Sn(S,Se)₃ powder

Elemental powders such as Cu, Sn, S, and Se were weighed to give a molar ratio of Cu:Sn:S:Se = 2:1:3(1-x):3x. The milling was conducted in a planetary ball mill (Fritsch premium line P-7) under a rotational speed of 800 rpm and a milling period of 20 min. CTSSe powders were synthesized by post-annealing at 400-600°C for 30 min after the milling.

2.2 Fabrication of Cu₂Sn(S,Se)₃ films

The $CuSn(S,Se)_3$ films were fabricated by the Printing/High-pressure Sintering (PHS) process [7]. Particulate precursor ink was prepared by mixing the obtained CTSSe powder with an organic solvent such as ethylene glycol monophenyl ether by planetary ball milling. The precursor CTSSe layer was deposited on a soda-lime glass substrate by a screen-printing technique. The organic solvent was removed from the screen-printed films. The porous precursor layer was sintered into a dense polycrystalline film by high-pressure sintering.

2.3 Characterization of Cu₂Sn(S,Se)₃ powders and films

The phases in the obtained powders and films were identified by X-ray diffraction. Optical properties of the CTSSe powders were characterized by UV-Vis-NIR spectroscopy (JASCO; V-670). The band gaps of CTSSe powders were determined by a diffuse reflectance spectrum of the powder. The transmittance spectra of the CTSSe films were characterized by UV-Vis-NIR spectroscopy. The band gaps of the films were determined from the transmittance spectrum.

3. Results and discussion

$3.1 Cu_2Sn(S,Se)_3$ powder

Figure 1 shows X-ray diffraction patterns of Cu_2SnS_3 without additional heating and post-heating at 400-600°C.



Fig. 1 X-ray diffraction patterns of Cu₂SnS₃ powder without additional heating and after post-annealing at 400-600°C.

	Cu ₂ SnSe ₃ ICSD#97966	
Intensity/arb. units	X=1.0 ·	
	X=0.8	l
	X=0.6	l
	X=0.4	l
	X=0.2	l
	X=0.0	ļ
	Cu ₂ SnS ₃ ICSD#91762	
	10 20	30 40 50 60 2θ/degrees



In the case of Cu(In,Ga)Se₂, the CIGS powder could be synthesized from the elemental powders by planetary ball milling in an N₂ gas atmosphere without any additional heating [8]. However, we could not synthesize CTSSe only by a mechanochemical process without additional heating. The CTS (x=0.0) powder was successfully synthesized from elemental powders by planetary ball milling and post-heating at 600°C for 30 min.

Figure 2 shows X-ray diffraction patterns of CTSSe powders with x=0.0-1.0 synthesized by post-annealing at 600° C for 30 min after the milling. The diffraction pattern of Cu₂SnS₃ (x=0) is identical to that of monoclinic CTS (ICSD #91762). The diffraction pattern of Cu₂SnSe₃ (x=1.0) is identical to that of monoclinic CTSe (ICSD #97966). The diffraction peaks of CTSSe solid solution are shifted to the lower angle side with increasing Se content.

Figure 3 shows the typical diffuse reflectance spectra (a) and $(F(R)hv)^2$ vs. hv plot (b) of CTSSe powders with



Fig. 3 Diffuse reflectance spectra (a) and $(F(R)hv)^2$ vs. hv plot (b) of CTSSe powders. The reflectance edges are shown by arrows.



Fig. 4 Band gap of $Cu_2Sn(S_{1-x} Se_x)_3$ solid solution determined by diffuse reflectance spectrum.

x=0.0-1.0. The reflectance edges of the CTSSe powders shifted to longer wavelength with increasing Se content.

Figure 4 shows the band gap (E_g) of $Cu_2Sn(S_{1-x}Se_x)_3$ solid solution determined by a diffuse reflectance spectrum. The band gap of Cu_2SnS_3 is 0.87 eV, which is in good agreement with reported E_g (0.96 eV) of tetragonal CTS [4]. The E_g of the CTSSe solid solution linearly decreases with increasing Se content. The E_g of $Cu_2Sn(S_{0.8}Se_{0.2})_3$ (x=0.2) was 0.82 eV; therefore, it has potential as a narrow band-gap absorber for thin-film full spectrum solar cells.

3.2 Cu₂Sn(S,Se)₃ films

Then, we fabricated the Cu_{1.9}Sn(S_{0.8}Se_{0.2})₃ film by the Printing/High-pressure Sintering (PHS) process [7]. The thickness of the Cu_{1.9}Sn(S_{0.8}Se_{0.2})₃ film fabricated by PHS process was about 1 μ m. The Cu_{1.9}Sn(S_{0.8}Se_{0.2})₃ grains were well-sintered without large pores. The size of the grains was less than 1 μ m, which is smaller than that in CIS films. In the case of CIS, CIS grains grew by adding CuSe as a sintering additive. The band gap of Cu_{1.9}Sn(S_{0.8}Se_{0.2})₃ film determined from the transmittance spectrum was 0.82 eV. This value agreed with the band gap of the powder determined by a diffuse reflectance spectrum.



Fig. 5 Band gap of $Cu_{1,9}Sn(S_{0,8}Se_{0,2})_3$ film determined from transmittance spectrum.

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