

Fabrication of compound semiconductor films for solar cells via supercritical fluid selenization and sulfuration

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ABSTRACT

In this study, we achieve the conversions of Cu-Zn-Sn oxide precursor films to $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films using solid selenium and sulfur sources. Selenization and sulfuration are essential reactions for the production of absorption layer in compound semiconductor thin-film solar cells containing metal chalcogenide absorption layer. Using supercritical ethanol having liquid-like high solubility as a reaction medium, solid selenium and sulfur sources with low vapor pressure, SeO_2 and S_8 , can be sufficiently supplied to the reaction field in selenization and sulfuration processes. Moreover, reductive assistance of supercritical ethanol facilitates the fabrication of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films having ideal band gap, even when both precursor film and selenium source contain oxygen. Such supercritical-alcohol-assisted selenization and sulfuration will contribute to the development of the cost-effective non-vacuum fabrication process for compound semiconductor solar cells.

INTRODUCTION

In the present circumstances, cost-effective production is a matter of top priority for solar cells. One of the most promising commercial devices is thin-film solar cells relying on direct band gap chalcogenide materials, such as CIGS ($\text{Cu}(\text{In,Ga})\text{Se}_2$). Due to its high absorption coefficient, material-cost for adsorption thin layer can be suppressed lower than crystalline Si solar cells. However, CIGS contains In and Ga, which are minor metal elements in the earth. Recently, CZTS ($\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$) solar cells, in which In and Ga of CIGS are replaced Zn and Sn, have attracted considerable attentions [1-4]. The progress in the conversion efficiency is very rapid and in 2013, IBM achieved over 12 % conversion efficiency for $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ [4].

Among the fabrication processes for the compound semiconductor solar cells, chalcogenization (selenization and sulfuration) process is essential for the industrial production of its absorption layer consisting of metal-chalcogenide. Selenium and sulfur sources in conventional vapor-phase selenization are the very toxic and hazardous gas, H_2Se and H_2S [2,3,5,6]. Usage of them results in high equipment cost for the exhaust system, which is absolutely needed for preventing H_2S and H_2Se gas leakage in the case of conventional selenization and sulfuration processes. To reduce the cost of absorption layer fabrication, the usage of less hazardous and cost-effective selenium and sulfur sources are desirable. Although alternative selenium and sulfur sources, e.g. pure selenium (sulfur) and organic-metal selenium (sulfur), are proposed, higher temperature, ~ 500 °C, is needed for the complete selenization and sulfuration of metal precursor films, because their lower vapor pressures cause the insufficient supply of the alternative sources.

Supercritical fluid (SCF) is the intermediate state between gas and liquid at high temperature and high pressure condition above the critical point. SCFs are advantageous reaction media because liquid-like high densities and high solubility are maintained with high diffusion coefficients. In previous reports, we applied supercritical ethanol as reaction medium for selenization process, and achieved the direct conversion of Cu–In precursor films to CuInSe₂ films at quite low temperature of 300 °C using the less hazardous metal–organic selenium source, diethylselenide [(C₂H₅)₂Se: DESe], which required high temperature, >490 °C, for conventional selenization in gaseous environment [7,8].

In this study, we developed selenization and sulfurization processes in supercritical ethanol. Low-vapor pressure, stable and low-cost selenium compounds, SeO₂, and elemental sulfur, S₈, which have not been regarded as appropriate selenium and sulfur sources for selenization and sulfurization processes, becomes usable by applying supercritical alcohol medium having liquid-like high solubility and high reduction power. As a result, the conversions of Cu-Zn-Sn oxide precursor films to Cu₂ZnSnSe₄ and Cu₂ZnSnS₄ films, having ideal band gap, using SeO₂ and S₈ as selenium and sulfur sources were achieved, even when both precursor film and selenium source contain oxygen.

MATERIALS AND METHODS

Mo-coated glass is employed as the substrate. Precursor films were deposited on the substrates using a spin-coating method. For the preparation of the precursor film, the spin coating solutions for CuO, ZnO and SnO₂ films (Kojundo Chemical Laboratory) were mixed together and spin coated on the substrates. After drying the substrate in an oven at 150 °C for 10 min, the dried solutions coated on the substrate were oxidized at 500 °C for 25 min in a furnace under air condition, then the oxide precursor thin films are formed. To obtain the precursor films with micrometer-order thickness, we repeated the spin coating and oxidation procedures.

For chalcogenization of Cu-Zn-Sn oxide precursor film, supercritical ethanol (scEtOH) [$T_c = 241$ °C, $P_c = 6.14$ MPa, $\rho_c = 0.276$ g/cm³ (6.0 mol/l)] was employed as the reaction medium. Selenization and sulfurization processes were carried out in a 10-ml batch-type Hastelloy reactor. Precursor films were placed in the reactor vessel containing S₈ and SeO₂ in ethanol. S₈, yellow solid, and SeO₂, colorless solid, have low vapor pressure (~0.1 Pa at 20 °C). S₈ is abundant and easier to get than other sulfides. On the other hand, the price SeO₂ is lower than elemental Se, because industrial production of pure selenium usually involves the extraction of SeO₂.

The ethanol density in the reactor is fixed to be constant at 0.24 g/cm³. The sealed reactor was kept at 400 °C in a specially designed tube furnace for 15 min. At this high-temperature condition, the ethanol becomes supercritical condition. Based on the previous report about the phase diagram of pure ethanol, the pressure inside the reactor is estimated as be around 22 MPa [9]. After heating, hot reactor was submerged into a water bath to terminate the reaction. The treated films were washed with deionized water and dried in vacuum.

For selenization, the concentration of SeO₂ in the reactor was 21.4 mmol/l. On the other hand, for sulfurization, we fixed the concentration of S at 50 mmol/l in the reactor.

The crystalline structures of the films were analyzed by θ – 2θ X-ray diffraction (XRD) using Cu-K α radiation and Raman spectroscopy. The chemical compositions of the films were determined by energy-dispersive X-ray spectroscopy (EDX) with scanning electron microscopy (SEM). The absorption spectra were obtained by using UV-vis absorption

spectrometer. In the measurement of absorption spectra, we used the $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films lifted off from Mo-coated glass by adhesive tape.

RESULTS

The SEM images of the surface of the Cu-Zn-Sn oxide precursor film before and after selenization and sulfurization in scEtOH are shown in Fig. 1. Before chalcogenization, the composition of Cu-Zn-Sn precursor film analyzed by EDX was $\text{Cu/Zn/Sn/O} = 13/9/7/71$. The precursor films in Fig. 1(a) shows smooth surfaces indicating nano-crystalline or amorphous structure.

On the other hand, after selenization and sulfurization, crystalline films (Fig. 1(b, c)) were synthesized. The crystalline size is around a few hundred nanometers. In the cases of selenization and sulfurization, the composition of the films were $\text{Cu/Zn/Sn/Se} = 25/14/10/51$ in $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu/Zn/Sn/S} = 29/16/10/45$ in $\text{Cu}_2\text{ZnSnS}_4$, respectively. The Cu/Zn/Sn ratios were almost ideal before and after selenization and sulfurization. From these results, we confirmed the selenization and sulfurization, respectively.

The XRD patterns of the films after chalcogenization are shown in Fig. 2. Except for the XRD peak derived from Mo substrate, the films after chalcogenization shows only the peaks corresponding to $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ kesterite structure, i.e., (112), (220)/(204), and (312)/(116) at $27.2\text{--}28.6^\circ$, $45.1\text{--}47.3^\circ$ and $53.8\text{--}56.1^\circ$, respectively.

It is known that in the case of direct band gap semiconductor, such as CIGS and CZTS, the band gap can be estimated by plotting $(Ah\nu)^2$ (A : absorbance, h : Planck's constant, and ν : frequency) against photon energy. The energy, at

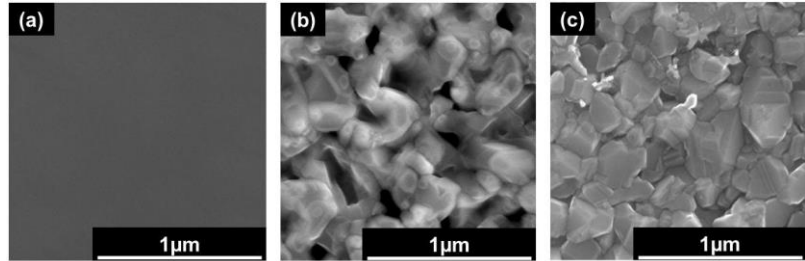


Figure 1. SEM images of (a) Cu-Zn-Sn oxide precursor film, (b) $\text{Cu}_2\text{ZnSnSe}_4$ film, (c) $\text{Cu}_2\text{ZnSnS}_4$ film.

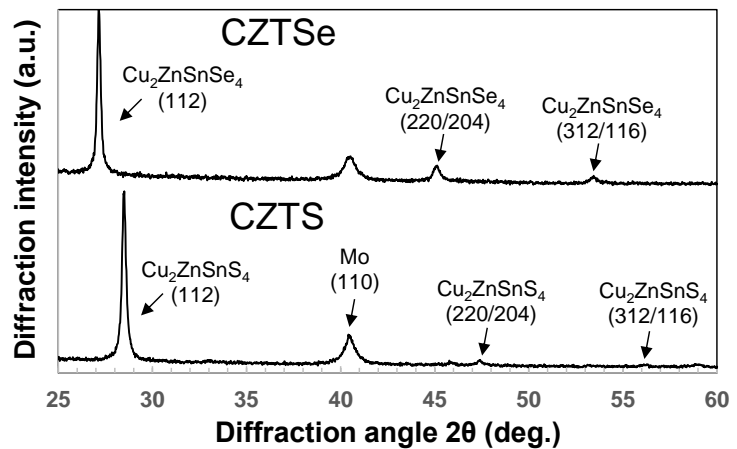


Figure 2. XRD patterns of the $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films fabricated by selenization and sulfurization in supercritical ethanol.

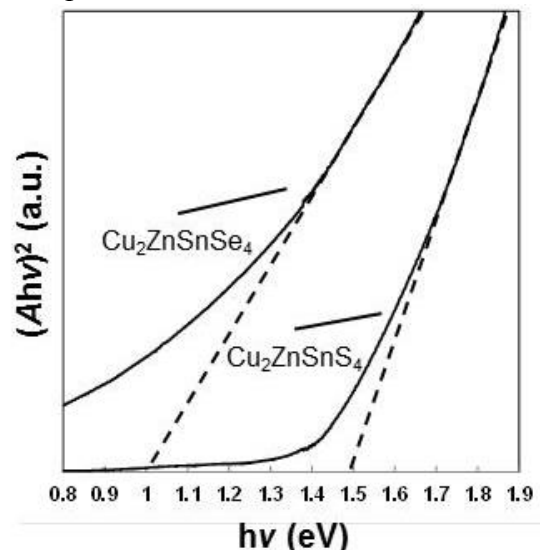


Figure 3. The plot of the $(Ah\nu)^2$ as a function of $h\nu$ (A : absorbance, h : Planck's constant, and ν : frequency) for $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$.

which the extrapolated the straight line of $(Ah\nu)^2$ versus $h\nu$ reaches $(Ah\nu)^2=0$, can be regarded as the band gap. Fig. 3 shows the plot of the $(Ah\nu)^2$ as a function of $h\nu$ based on the absorption spectra of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films. The estimated values of band gap energies are indicated in Table 1. The band gap energies of the films determined from the plots are consistent with the reported energies of $\text{Cu}_2\text{ZnSnSe}_4$ around 1 eV and $\text{Cu}_2\text{ZnSnS}_4$ around 1.5 eV. The solid solutions of kesterite-structured $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ show the band gap energy between them in the range of 1 and 1.5eV, respectively.

CONCLUSION

In summary, chalcogenization processes, such as selenization, sulfurization and simultaneous selenization/sulfurization, for the preparation of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ film were demonstrated using low-cost selenium and sulfur sources, SeO_2 and S_8 , in scEtOH. From EDX, XRD and Raman spectroscopy analyses, it was found that by the selenization and sulfurization of Cu-Zn-Sn oxide precursor film, the fabrication of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ films with kesterite structure can be achieved. It is supposed that the high reduction and high dissolving powers of EtOH facilitate the usage of low-cost solid selenium and sulfur sources, and result in the fast and low-temperature selenization and process. Moreover, the measurements of the absorption spectra revealed that the films have ideal band gap energies, and the band gap energy is tunable by varying the ratio of selenium and sulfur sources. The chalcogenization process in EtOH, which developed in this study, will be the promising technique for low-cost fabrication of compound semiconductor solar cell device, but also contribute to the fabrication of other chalcogenide-based optical materials.

REFERENCES

- [1] Ito, K., Nakazawa, T., *Jpn. J. Appl. Phys.*, Vol. 27, **1988**, p. 2094.
- [2] Katagiri, H., *Tech. Dig. Photovoltaic Science and Engineering Conf.*, Vol. 9, **1996**, p.745.
- [3] Katagiri, H., Jimbo, K., Yamada, S., Kamimura, T., Maw, W. S., Fukano, T., Ito, T., Motoyoshi, T., *Appl. Phys. Express*, Vol. 1, **2008**, 041201.
- [4] Wang, W., Winkler, M. T., Gunawan, O., Gokmen, T., Todorov, T. K., Zhu, Y., Mitzi, D. B., *Adv. Energy Mater.*, **2013**, DOI: 10.1002/aenm.201301465.
- [5] Ganchev, M., Kaupmees, L., Iliyana, J., Raudoja, j., Volobujeva, O., Dikov, H., Altosaar, M., Mellikov, E., Varema, T., *Proc. Inorg. and Nanostructured Photovoltaics*, Vol. 2, **2010**, p. 65
- [6] Tanaka, K., Moritake, N., Uchiki, H., *Sol. Energy Mater.*, Vol. 91, **2007**, p. 1199
- [7] Tomai, T., Rangappa, D., Honma, I., *ACS Appl. Mater. Interfaces*, Vol. 3, **2011**, p. 3268.
- [8] Tomai, T., Yanaka, M., Honma, I., *The J. Supercritical Fluids*, Vol. 83, **2013**, p. 41.
- [9] Bazaev, A. R., Abdulagatov, I. M., Bazaev, E. A., Abdurashidova, A., *Int. J. Thermophys.*, Vol. 28, **2007**, DOI: 10.1007/s10765-007-0158-2