Na-doped $\text{Cu}_2\text{ZnSnS}_4$ single crystal grown by traveling-heater method

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Abstract

We investigate high-quality Na-doped $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) single crystals grown by using the traveling-heater method and the effect of Na doping on the fundamental properties of these crystals. Na-doped CZTS single crystals were obtained from Sn solution at growth temperatures of 850–900 °C and at speeds of 4 mm/day. The crystals have a kesterite structure, as determined by powder X-ray diffraction and Raman measurements. The Hall effect properties such as hole concentration, conductivity, and hole mobility are enhanced with increasing Na concentration. These results reveal that Na improves the electrical properties of CZTS.

Keywords : B1. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), B2. Quarternary alloys, A2. Growth from solutions

1. Introduction

The development of sustainable energy sources has become one of the most important issues in modern science because of the need to alleviate the current stress on the environment. Thus, efficient power conversion, low cost, and more eco-friendly technologies are required. Recently, solar cells fabricated from I₂–II–IV–VI₄-group kesterite compounds Cu₂ZnSn(S_xSe_{1-x})₄ (CZTSSe) have become attractive for use as the absorbing layer in photovoltaic technology because these materials are made from abundant, nontoxic elements and achieve 12.6% power conversion efficiency when using the hydrazine-assisted-deposition approach [1]. However, this technology has limitations such as obtaining high-quality absorbing layers and interfaces between p–n layers. The open-circuit-voltage (V_{OC}) deficit $E_g/q - V_{OC}$, where E_g and q are the bandgap energy and the elemental charge, remains one of the most significant problems faced by CZTSSe- compound solar-cell technology. For example, the 11.6% efficiency of pure Cu₂ZnSnSe₄ (CZTSe) has a V_{OC} deficit of 577 mV [2], and the 8.4% efficiency of pure Cu₂ZnSnS₄ (CZTS) has a V_{OC} deficit of 789 mV [3].

One way to improve the device properties of a CZTSSe absorbing layer is sodium (Na) doping, which is used with solar cells made from the related compound Cu(In, Ga)Se₂ (CIGS), which has a high power conversion efficiency of over 20% [4]. Incorporating Na into the CIGS absorbing layer has positive effects that lead to enhanced CIGS thin-film solar-cell efficiency. The same positive influences of Na in CIGS thin films have been claimed in previous reports. Na passivates or removes grain-boundary defects such as In antisites on Cu and Se vacancies [5, 6]. The oxygen model suggests that the hole density increases owing to the neutralization of donor V_{Se} defects through an enhanced chemisorption of atomic oxygen in the presence of Na [6]. Na replacing a Cu site results in the formation of a stable compound NaInSe₂, which exhibits a larger bandgap and leads to a larger V_{OC} [5]. In addition, Na affects the orientation of the (112) texture, grain size, and the morphology [7, 8]. The research on CZTSSe solar cells is less developed than that on CIGS, and

the topic of Na incorporation in CZTSSe is fairly undeveloped. However, to obtain higher efficiency, we must understand how Na affects CZTSSe. Several reports claim that Na affects the physical properties of CZTSSe. Li *et al.* reported that Na doping improved the hole concentration and increased the built-in potential of the p–n junction; consequently, it also affected V_{OC} and the fill factor of the solar cell for co-evaporated CZTSe thin film [9]. By using a spray pyrolysis technique, Prabhakar *et al.* found that Na diffusion in CZTS thin films enhanced the grain size, the (112) texture of films, and the hole concentration [10]. Enhanced grain size was also confirmed by Oo *et al.* and Bras *et al.* [11, 12], who concluded that the presence of Na in CZTSSe increased the grain size, the preferred (112) texturing, and the carrier concentration, which is similar to that found in CIGS. However, the effect of Na on CZTSSe is not yet well understood and must be elucidated to obtain higher-efficiency CZTSSe solar cells.

We focus on CZTSSe single crystals and cite some papers that discuss the growth of single crystals and their fundamental properties [13–16]. In our previous studies of crystal growth [17], we obtained high-quality CZTSSe single crystals by using the traveling-heater method (THM), which is a solution-growth process. It is generally difficult to grow high-quality single crystals from a melt with compounds of the $I_2-II-IV-VI_4$ group because most of the compounds grow through a peritectic reaction or by a solid-state transition during cooling [18, 19]. CZTSSe compounds form according to the peritectic reaction (liquid phase + ZnS or ZnSe), so growth by the THM, which can proceed below the melting point, is well suited to the growth of high-quality CZTSSe single crystals. CZTSSe single crystals can be obtained below the peritectic point by using the THM with Sn as solvent, based on the CZTSSe-solute–Sn-solvent pseudobinary system.

High-quality single crystals constitute an excellent tool for investigating the fundamental properties of materials. Growing high-quality CZTSSe single crystals is thus important for investigating how Na doping affects these materials. To the best of our knowledge, no reports exist of the growth of Na-doped CZTS single crystals. Thus, we report herein the growth of high-quality

Na-doped CZTS single crystals with the THM and with Sn as solvent. In addition, we investigate the structural and electrical properties of Na-doped CZTS single crystals.

2. Experimental procedure

First, feed polycrystallines of CZTS were prepared by using a melting reaction. Cu (99.999%), Zn (99.9999%), Sn (99.9999%), and S (99.9999%) shots and Na₂S (99%) powder were used as starting materials. Prior to growth, Cu, Zn, and Sn were chemically etched by HCl solution for 60 s and then rinsed in ultrapure water. The prescribed amounts of elements were loaded into a carbon-coated quartz ampoule (9 mm × 12 mm) under high vacuum (5.0×10^{-6} Torr) and then sealed off. In a vertical furnace, the sealed ampoule was heated at 100 °C/h to 1100 °C and held at this temperature for 24 h to obtain a complete reaction and to ensure homogenization. The ampoule was then removed from the vertical furnace and allowed to cool rapidly in air. A feed polycrystalline Na-doped CZTS ingot and Sn solvent were loaded into a carbon-coated quartz ampoule (10 mm × 13 mm). The ampoule was sealed under high vacuum (10^{-6} Torr), then inserted into the THM furnace. The detailed composition of the crystals thus grown was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) from the growth tip portion at 5 mm intervals. Samples were dissolved into a mixed acid containing 1.2 mol L⁻¹ HNO₃ and 0.3 mol L⁻¹ HCl.

The structural properties were measured by powder X-ray diffraction (XRD), the X-ray rocking curve (XRC) method (XRD and XRC; Panalytical X'Pert PRO), and Raman spectroscopy (T64000; HORIBA). The tube voltage, tube current, and step width were 40 kV, 40 mA, and 0.01° for XRD, and 45 kV, 40 mA, and 0.002° for XRC. Cu-K_α radiation was used in the XRD and XRC measurements. A 514 nm Ar⁺ laser was used in the Raman measurements and focused on the sample by an objective lens with a numerical aperture of 0.55. The laser power on the sample was 100 mW. The spectra were calibrated based on the position of the 520 cm⁻¹ Si peak. The electrical

properties of all samples were obtained by Hall effect measurements, which were done at room temperature under a 0.54 T magnetic field in the Van der Pauw geometry. The sample dimensions were 5 mm × 5 mm × 0.5 mm and the sample was mechanically polished with 0.01 μm Al₂O₃ powder. Multiple Au contacts of diameter 1 mm were deposited by evaporation onto the corners of each CZTS bulk single crystal to a thickness of 200–300 nm. The wafers cut off at 5–10 mm from tip position were used for powder XRD, XRC, Raman spectroscopy and Hall effect measurements.

3. Results and discussion

For the THM growth, excess Sn was added to the Na-doped CZTS feed polycrystalline, which had a mole fraction of

$$X [\text{mol}\%] = \frac{\text{CZTS} [\text{mol}]}{\text{CZTS} [\text{mol}] + \text{Sn} [\text{mol}]} \times 100\%. \quad (1)$$

The polycrystalline Na-doped solute ingots weighed approximately 15 g, and the desired weight of the Sn solvent was calculated from Eq. (1). Based on our previous studies of the CZTS–Sn pseudobinary system [13], the CZTS single crystal was grown from a single-phase Sn solution (CZTS + Sn liquid) with $X = 60\text{--}90$ mol% and at 680–980 °C. For $X < 60$ mol%, the Sn-rich liquid phase located at the bottom of the ampoules and SnS_x secondary phases were observed, because Sn is denser than CZTS and a large amount of Sn creates Sn–S compounds. Na-doped CZTS single crystals were grown from the single-phase liquid Sn solution by pulling the ampoule through the THM furnace. The THM furnace has three coil heaters (upper, main, and bottom), and the temperature profile on the axis measured without the growth ampoule is shown in Fig. 1. The upper heater was used to prevent a sulfur deficiency in the grown CZTS crystal. The sulfur species evaporated from the liquid zone condensed on the cold wall of the ampoule without heating the upper part, thereby reducing the sulfur mole fraction in the crystal. For the THM growth, the main heater temperature (growth temperature) was 850–900 °C which is ~ 50 °C higher than liquidus temperature, and the temperature gradient between the main and bottom heaters (i.e., in the

supersaturation region for single-crystal growth) was about 45 °C/cm. This temperature gradient can control length of solution zone ~1 cm. The lowering speed was 4 mm/day for 10 days. Figure 2 (a) - (c) show the examples of the resulting Na-doped single crystals. The dimensions of ingot are 10 mm in diameter and 40 mm in length. Large size ~ 5mm of single grains could be clearly observed in Fig. 2 (a). Fig. 2 (b) - (c) show the polished single crystal slices for each measurements, which there are no grain boundaries. A longitudinal slice of one of single crystal ingot is shown in Fig. 3. From the longitudinal cross section of the single crystal, the solid–liquid interface is confirmed to be slightly convex. Controlling the shape of the interface has long been desired for melt- and solution-growth processes. In general, a convex interface in the crystal is expected to minimize the potential for crystal defects such as dislocations, grains, and twins that may arise from deleterious ampoule–wall interactions to propagate toward the bulk crystal [20]. The convex interface is thus favorable for growing single crystals. Table I shows the composition of various Na-doped samples as determined by ICP-AES measurements. All samples have metallic ratios of $[Cu]/([Zn] + [Sn]) = 0.92\text{--}0.98$, $[Cu]/[Zn] = 1.73\text{--}1.86$, and $[Zn]/[Sn] = 1.06\text{--}1.15$, which are slightly Cu-poor, Zn-rich conditions. It can also be clearly seen that the compositions of all samples are homogeneous along the growth direction at 5 mm intervals. A Na concentration of 0.04 and 0.13 atm% in CZTS is also observed, which is important for this study.

Figure 4 shows the powder XRD patterns from each composition of Na-doped CZTS single crystals. CZTS crystallizes in the tetragonal structure known as the kesterite type. The XRD pattern of all samples exhibit major peaks corresponding to diffraction lines of the kesterite structure of CZTS (ICDD data #01-075-4122 CZTS). No other peaks of secondary phases are observed in the XRD pattern. Kesterite-type phases also exhibit a different distribution of Cu/Zn, which is termed the disordered kesterite structure [21]. The peak at around $2\theta = 18.3^\circ$ is a useful tool for distinguishing between the ordered and disordered kesterite structures. This peak appears in all samples, which indicates that they have the ordered kesterite structure. Figure 5 summarizes the

lattice parameters such as lattice constants and unit cell volume extracted from the XRD peaks corresponding to the main (112), (220/204) and (312) diffraction peaks, which shifts to lower 2θ with increasing Na concentration, indicating an increase in the lattice spacing owing to the Na radius being larger than that of the cations in CZTS. The peak positions were calibrated by using Si powder (NIST SRM 640d) as an internal reference. A significant observation revealed by the XRD pattern is that the unit-cell size is apparently enhanced upon increasing the Na concentration, where the undoped unit cell is $318.9 \text{ \AA}^3$ and the 0.13 atm% doped unit cell is $324.5 \text{ \AA}^3$. This result assumes that Na is the substitutional impurity in CZTS because the Na radius is greater than that of the cations in CZTS. Figure 6 shows the XRC for the (112) orientation for an exemplary sample of Na 0.13 atm% CZTS single crystal. The CZTS crystallinity obtained is very good because the full-width at half-maximum (FWHM) is 125–152 arcsec. Furthermore, we performed Raman spectroscopy by using the 514 nm line of the Ar^+ -ion laser to evaluate the secondary phases. Raman spectroscopy is a useful tool to evaluate secondary phases because the distinct XRD peaks of CZTS overlap well with those of $\text{Cu}_2(\text{S, Se})$ and $\text{Zn}(\text{S, Se})$. We observe no differences by Raman spectroscopy, as shown in Fig. 7. The spectra show clearly the CZTS peaks at 287, 337, and 371 cm^{-1} [13]. No main peaks of the secondary phases were observed in the spectra, such as for Cu_2SnS_3 with tetragonal or cubic structures that have lattice constants very similar to those of CZTS. The peaks of tetragonal Cu_2SnS_3 appear at $336\text{--}337 \text{ cm}^{-1}$, which corresponds to the CZTS A_1 -mode peak; however, no distinct peaks appear at $303, 355 \text{ cm}^{-1}$ (cubic) and 351 cm^{-1} (tetragonal) [22]. The major ZnS peaks, which would appear at 218, 295, 386, 422, and 448 cm^{-1} , are not observed [23]. In addition, other possible secondary phases, for example, Cu–S- and Sn–S-related compounds, are also not observed [24]. No secondary phases are detected by XRD and Raman measurements.

The electrical properties of the Na-doped CZTS single crystal were analyzed using Hall effect measurements at room temperature; see Table II. The electrical properties, such as the hole concentration p , conductivity σ , and hole mobility μ , are enhanced with increasing Na concentration.

We focus on how p depends on the Na concentration, which the Na 0.13 atm% sample indicates is ten times higher than for the undoped sample. From first-principles calculations [25], Zn on antisite Cu (Zn_{Cu}) is the dominant donor defect in CZTS. We believe that the formation of the Zn_{Cu} donor defects is inhibited by a finite Na substitution for the Zn_{Cu} antisites ($= \text{Na}_{\text{Cu}}$). In addition, the neutral Na_{Cu} defects indicate that defect scattering decreases. However, the lattice crystallinity decreases with increasing Na concentration. This could be understood from the increasing FWHM of the (112) XRD peaks and the A_1 -mode Raman peaks with increasing Na concentration. We assume that intrinsic point-defect scattering is more dominant than lattice scattering in CZTS. Indeed, Li *et al.* reported experimental results from the CZTSSe group that indicated the concentration of certain deep-level defects in CZTSe thin film with increasing Na concentration, and the hole mobility was enhanced [9]. It is difficult to conclude that Na replaces intrinsic acceptor Cu vacancies (V_{Cu}) or Cu on antisite Zn (Cu_{Zn}) or donor (Zn_{Cu}), even though the unit-cell size in CZTS increases with increasing Na concentration. However, this result reveals that Na doping improves the electrical properties of CZTS. These results indicate that the efficiency of CZTS solar cells may be improved.

4. Conclusion

By using the traveling-heater method, high-quality Na-doped CZTS single crystals were grown from Sn solution to investigate how Na doping affects CZTS. For THM growth, the growth temperature and the temperature gradient were 850–900 °C and 45 °C/cm, respectively. The lowering speed was 4 mm/day for 10 days. The XRD patterns of all samples exhibit major peaks corresponding to diffraction lines of the kesterite structure. No other peaks of secondary phases appear in the XRD patterns or in Raman scattering. Powder XRD measurements reveal the expansion of the unit cell in Na-doped CZTS, which is evidence of Na on antisite cations in CZTS. We also find that the hole concentration, conductivity, and hole mobility all increase with increasing Na concentration in the high-quality single-crystal samples. Na is thus an important dopant for

controlling the electrical properties of CZTS single crystals.

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Figures captions

Figure 1 Temperature profile on the axis measured without growth ampoule in THM furnace.

Figure 2 Example of the resulting Na-doped single-crystal ingot. (a) radial slice (b)-(c) polished slice for each measurements.

Figure 3 A longitudinal slice of one of Na-doped CZTS single crystal ingot.

Figure 4 Powder XRD patterns of each composition of Na-doped CZTS single crystals.

Figure 5 Lattice parameters of each composition of Na-doped CZTS single crystals.

Figure 6 XRC of (112)-oriented exemplary sample of Na 0.13 atm% CZTS single crystal.

Figure 7 Raman spectra of each composition of Na-doped CZTS single crystal.

Tables

Table I Composition of various Na-doped samples obtained by ICP-AES measurements.

Table II Results of room-temperature Hall effect measurements.

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Table I

Na [atm%]	Cu [atm%]	Zn [atm%]	Sn [atm%]	S [atm%]	Cu/(Zn+Sn)	Zn/Sn
0	23.94	13.87	12.05	50.14	0.92	1.15
0.04	23.33	12.56	11.87	52.20	0.95	1.06
0.13	23.68	12.72	11.52	51.95	0.98	1.10

Table II

Na [atm%]	Carrier concentration [cm^{-3}]	Conductivity [$\Omega^{-1}\text{cm}^{-1}$]	Mobility [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]
0	8.80×10^{16}	2.22×10^{-2}	8.35
0.04	2.03×10^{17}	1.46×10^{-2}	13.9
0.13	7.42×10^{17}	1.07×10^{-1}	15.4

Table I

Na [atm%]	Cu [atm%]	Zn [atm%]	Sn [atm%]	S [atm%]	Cu/(Zn+Sn)	Zn/Sn
0	23.94	13.87	12.05	50.14	0.92	1.15
0.04	23.33	12.56	11.87	52.20	0.95	1.06
0.13	23.68	12.72	11.52	51.95	0.98	1.10

Table II

Na [atm%]	Carrier concentration [cm ⁻³]	Conductivity [$\Omega^{-1}\text{cm}^{-1}$]	Mobility [cm ² V ⁻¹ s ⁻¹]
0	8.80×10 ¹⁶	2.22×10 ⁻²	8.35
0.04	2.03×10 ¹⁷	1.46×10 ⁻²	13.9
0.13	7.42×10 ¹⁷	1.07×10 ⁻¹	15.4