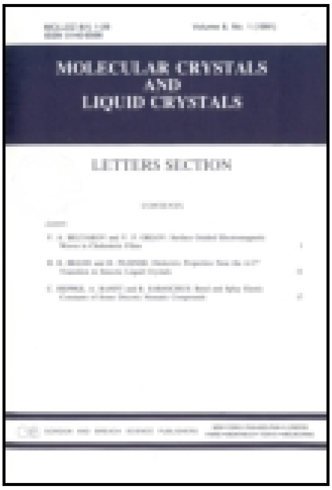

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Effect of Sodium Chloride (NaCl) as Crystallization Catalyst on Cu_2ZnSnS_4 (CZTS) Films Deposited by Wet-solution Coating Method

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The CZTS ink was prepared by a sonochemical method and properties of the CZTS thin films deposited by a spraying method were investigated. We used $CuCl_2$, $ZnCl_2$, $SnCl_2$ and thiourea as precursor materials, 2-methoxyethanol as solvent, monoethanolamine as stabilizer, and NaCl as catalyst. X-ray diffraction (XRD) patterns from the CZTS films mainly exhibited the (112), (200), (220), and (312) planes of the kesterite structure. The grain size of CZTS films increased with increasing NaCl concentration. The optical band-gap of CZTS films decreased from 1.27 eV to 1.08 eV, and the absorption coefficient was increased, when the concentration of NaCl was increased. The elemental ratio of Cu:Zn:Sn:S in CZTS films was approximately 2:1:1:3.6, and the ratio of the films seldom changed at different synthesis conditions. These results demonstrate that the major role of NaCl is the enhancement of crystallinity and light absorption in CZTS films. The CZTS ink developed in this study has a promising potential for the formation of high quality CZTS thin films for photovoltaic devices.

Keywords Absorption; CZTS; NaCl; sonochemical; spray; XRD

Introduction

$CuInGaSe_2$ (CIGS) materials have been used as a light absorber in thin film solar cells due to their suitable energy band-gap ($\sim$1.4 eV) and a high absorption coefficient ($\sim 10^4$ cm^{-1}) [1–3]. However, the indium and selenium used in CIGS material are rare in the earth, and this means there are some restrictions in near future, when the energy production systems are built in large scale [1, 3]. Thus, it is necessary to develop alternative materials from earth-abundant resources, and this issue has stimulated researches to develop alternative absorption layers composed of earth-abundant elements. Currently, Cu_2ZnSnS_4 (CZTS) materials have become interested as promising light absorption materials for low-cost

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photovoltaic devices, because CZTS materials are made of earth-abundant elements, and contain environment-friendly, stable compounds. In addition, CZTS materials are suitable for photovoltaic devices due to its suitable optical band-gap ($\sim$1.4 eV) and large absorption coefficient ($\sim 10^4$ cm^{-1}) [2–6].

Deposition methods of CZTS thin films can be largely classified into a vacuum method and a non-vacuum method. The vacuum-based methods have many advantages such as high reproducibility with high quality and ease of control in composition [1–3]. However, vacuum-based methods have suffered from low deposition rate, high production cost, and limitation of precursor materials. On the other hand, non-vacuum methods have advantages in relatively easy processing sequence, high growth rate, and low production cost [1–6], although they suffer from relatively lower device performance. Especially, it is important to prepare suitable precursor ink in non-vacuum methods and the deposition process is determined by properties of precursor ink.

In this study, the CZTS inks were prepared at room temperature using chlorine based precursors ($CuCl_2$, $ZnCl_2$, and $SnCl_2$) and sodium chloride (NaCl) as a crystallization catalyst was added to investigate the effect of NaCl during annealing process. The chemical reaction for the synthesis of CZTS inks was activated by a sonochemical method and CZTS film depositions were carried out by spray method. Furthermore, we proposed the mechanism for crystallization enhancement due to NaCl addition.

Experimental Details

$CuCl_2$ (97%, Aldrich), $ZnCl_2$ (98%, Aldrich), $SnCl_2$ (98%, Aldrich) and thiourea (99%, Aldrich) are used as precursor materials to prepare crystallized CZTS inks. 2-methoxyethanol (99.3%, Aldrich) is used as solvent, monoethanolamine (99%, TCI) is used as stabilizer to prevent premature formation of precipitates, and NaCl is added as catalyst. The atomic ratio of Cu, Zn, Sn, and S precursor used in the synthesis is 2:1:1:4, and the concentration of NaCl (99.9%, Aldrich) is varied from 0 to 0.04 mmol to study the effect of NaCl addition. First, $CuCl_2$, $ZnCl_2$, $SnCl_2$ and NaCl are dissolved into the mixture of 2-methoxyethanol and monoethanolamine (MEA), and then thiourea is added into the prepared solution. As-prepared solutions are sonochemically treated for 30 min at room temperature, and the ultrasonic power of 30 W is continuously applied using an ultrasonic machine operated at 20 kHz (Sonics & Materials, VCX 750). After the sonochemical reaction, a dark grey colored solution is acquired, and this CZTS ink is sprayed onto Mo-coated glass substrates, keeping the substrate temperature at 150°C to remove the solvent and stabilizer during the spray-coating process. The spray-coating is carried out for 2 min at the spraying rate of 1 mL/min. As-deposited CZTS films are finally sintered in vacuum for 1 h.

The structural properties of CZTS films are investigated by X-ray diffractometer (XRD, Philips X'Pert-APD), and the optical properties of the films are studied by UV-Vis NIR spectrometer (Varian, Cary 5000). The morphologies of CZTS films are characterized by scanning electron microscope (SEM, Hitachi S-4200) operated at 25 kV, and elemental analyses of the films are carried out using an energy dispersive X-ray spectroscopy (EDS and EMAX).

Results and Discussion

Figure 1(a) and 1(b) show X-ray diffraction (XRD) patterns of CZTS films formed using a normal and CZTS ink containing NaCl, respectively. All the CZTS films show clear diffraction peaks from the (112), (220), and (312) crystal planes irrespectively of annealing

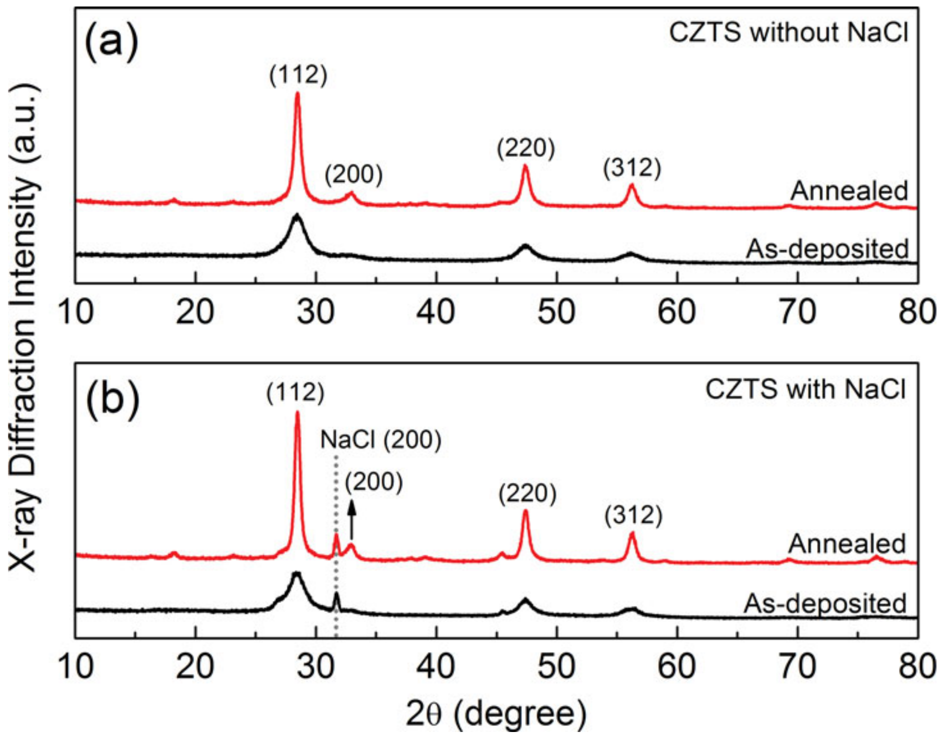

Figure 1. X-ray diffraction (XRD) patterns of as-deposited and annealed CZTS films: (a) CZTS films deposited using normal ink and (b) CZTS films formed using CZTS ink containing NaCl.

process and NaCl, in which the peaks correspond to kesterite phase (JCPDS card 26-0575). The kesterite phase has a tetragonal unit cell including sulfur atoms positioned in a face centered cubic (fcc) sublattice and other atoms (Cu, Zn, and Sn) occupying half of the tetrahedral interstitial sites within the S sublattice [5, 7, 8]. The XRD patterns of CZTS films formed from the normal CZTS inks and inks containing NaCl exhibit slight difference in full-width at half maximum (FWHM) value, but the presence of NaCl does not change the crystalline phases of CZTS films, whether the films are annealed or not. In addition, the NaCl diffraction peak is observed independently in XRD spectra, as shown in Fig. 1. This implies that the NaCl is not incorporated into the CZTS materials and just acts as a catalyst material to play important roles in enhancing the crystallinity of CZTS films. The variation of FWHM value and the grain size of CZTS films as a function of NaCl concentration are shown in Fig. 2. The grain size of CZTS is calculated using the Scherrer's equation, and the equation is given by [9]:

$$D = \frac{0.9\lambda}{(B - b)\cos\theta} \tag{1}$$

where, D is the grain size, λ is the wavelength of CuKα X-ray source, B is the FWHM value of a diffraction peak, b is the instrumental line broadening, and θ is the diffraction angle. The grain size of CZTS films increases with the rise of NaCl concentration and the existence of NaCl as a catalyst plays an interesting role to determine the crystallinity. Thus, the increase of grain size is closely related to the electron transfer during the crystallization

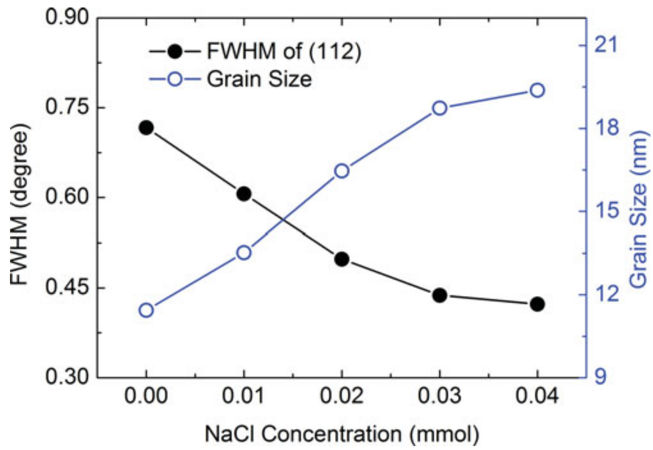

Figure 2. The variation of full-width at half maximum (FWHM) for XRD peak of (112) (solid circle) and the grain size of CZTS films (open circle) as a function of NaCl concentration.

process. Usually, the effects of Na ions in CZTS materials have been suggested that Na can be incorporated into the CZTS film, and mobile Na atom with low melting point can enhance the grain growth by vapor-liquid-solid (VLS) mechanism [10, 11]. In this study, NaCl salt does not dissolve in the mixture of 2-methoxyethanol and monoethanolamine, and NaCl is just well-dispersed in as-synthesized CZTS inks due to the sufficient viscosity of the inks. For this reason, effect of NaCl for the crystallinity enhancement of CZTS films does not consider along the same lines as the effects of Na ions. Thus, we propose the mechanisms for the crystallinity enhancement of CZTS films as follows: The NaCl has an ionic bond with little covalence and this causes the weak adsorption of CZTS components on NaCl materials. This adsorption causes the localized charge distribution on CZTS atoms near NaCl materials and there is an electron transfer process due to localized charge distribution inside CZTS films. Consequently, the charge transfer plays a crucial role to grow the grain size of CZTS atoms.

The difference in grain size is also confirmed from the SEM images of CZTS films with or without NaCl. The SEM images of CZTS films formed from CZTS inks with different NaCl concentration is shown in Fig. 3. In CZTS films formed from the inks without NaCl material, it was observed that small-size CZTS particles are physically aggregated together.

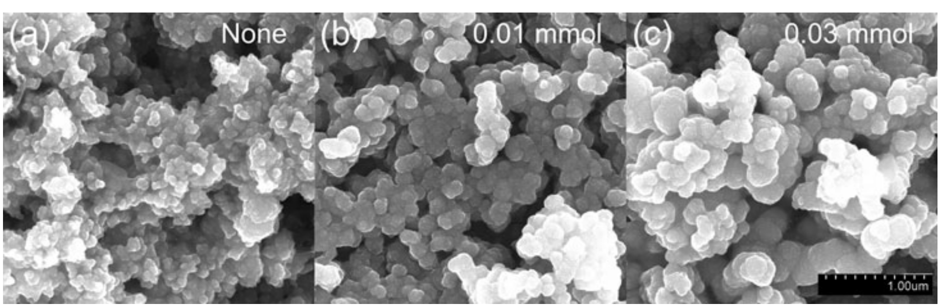

Figure 3. Scanning electron microscopic (SEM) images of CZTS films at different NaCl concentration: (a) none, (b) 0.01 mmol, and (c) 0.03 mmol of NaCl.

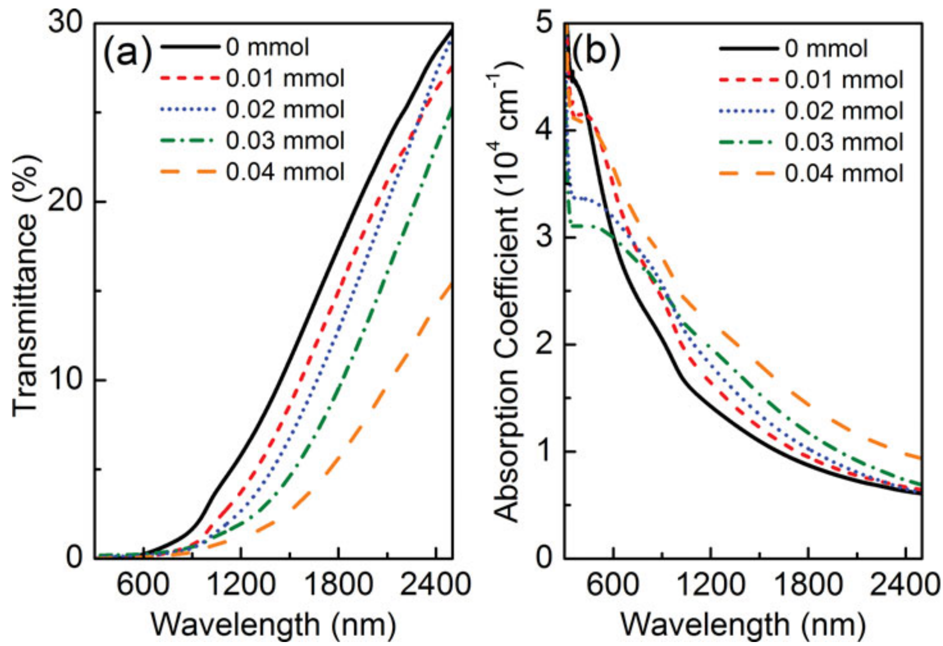

Figure 4. Optical properties of CZTS films according to NaCl concentration: (a) transmittance spectra and (b) absorption coefficient of CZTS films.

However, the size of lumps gradually grows due to a necking process between adjacent lumps in CZTS films containing NaCl, and the grain size of CZTS crystals increases with the increase of NaCl concentration. This result is consistent with the XRD results discussed above. From these results, it is conjectured that sonochemically synthesized inks already have crystallized particles at low temperatures, and the sonochemical method can be a promising technique to produce crystallized inks for non-vacuum methods. Furthermore, NaCl acts as an effective catalyst to enhance the crystallinity of CZTS films.

Figure 4(a) and 4(b) show the transmittance and absorption coefficient of CZTS films according to the NaCl concentration, respectively. As the concentration of NaCl is increased, the transmittance of CZTS films is decreased, and thus the absorption coefficient of the films is increased. In addition, the optical band-gap of CZTS films, which are evaluated using Tauc's method [12, 13], shows a red-shift to lower energy with an increase of NaCl concentration and this can be explained as the band-gap shift of semiconducting nanoparticles due to effects of quantum confinement [14]. The morphology of the as-deposited films is similar to the network structure of CZTS nano-particles and the value of grain size is below 20 nm. This value is small enough to cause the quantum confinement effects. Thus, the reason for the band-gap shift can be considered as the quantum confinement effects due to the change of the grain size however, more studies should be required to verify the definite reason for the band-gap shift. Fig. 5 shows the shift of optical band-gap with varying NaCl concentration.

The elemental ratio of CZTS films at different NaCl concentrations is nearly constant, and the ratio of Cu:Zn:Sn:S in CZTS films is approximately 2:1:1:3.6. This elemental ratio of Cu, Zn, and Sn in CZTS films is similar to the ratio of Cu, Zn, Sn in precursor ratio including NaCl concentration. This result shows that the precursors of Cu, Zn, and

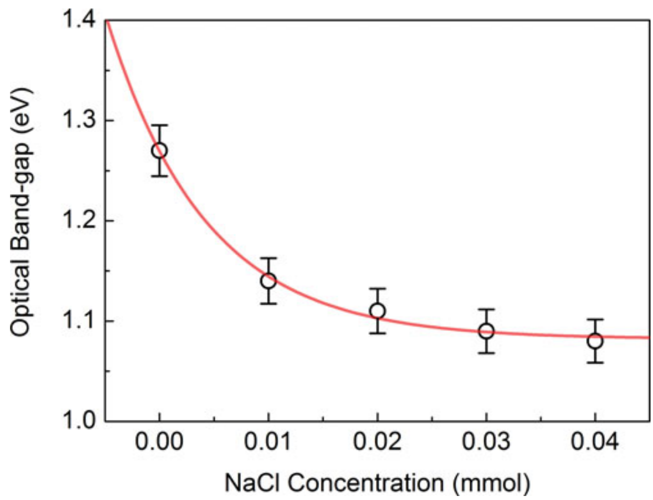

Figure 5. The optical band-gap of CZTS films as a function of NaCl concentration.

Sn are equivalently reacted with S element via S-redox process. Usually, the CZTS solar cells exhibit high power conversion efficiency at Cu-poor and Zn-rich growth conditions in the elemental ratio [2, 15]. Thus, controlling the atomic elemental composition of CZTS absorption layer is important to fabricate high-efficiency photovoltaic devices, and the method developed in this study can be a very effective method to control the elemental composition.

Conclusions

In this study, the CZTS-containing inks were prepared by a sonochemical method, and the effects of NaCl addition were studied in depth. As-synthesized inks were deposited on Mo-coated glasses by a spray-coating method. The CZTS films exhibited a single phase CZTS without annealing process, and phase transitions did not occur even after the annealing process, which implied that the CZTS-containing inks already contained CZTS crystallites which were formed during the sonochemical synthesis. The crystallinity of CZTS was improved by adding NaCl materials, and XRD peaks from the CZTS films corresponded to the (112), (200), (220), and (312) planes, indicating that the kesterite structure is formed. The optical properties of CZTS films also changed at different NaCl concentrations. The optical band-gap was varied from 1.27 to 1.08 with the increase of NaCl concentration, and the absorption coefficient of the films also increased. The reason is thought to be the increase of the grain size and the quantum confinement effects due to the change of grain size. From all these results, we confirmed that the role of NaCl as a catalyst material to cause the enhancement of crystallinity in CZTS films, and also the sonochemically derived CZTS ink is very suitable for depositing the CZTS thin films for photovoltaic devices, because the ink can be easily spray-coated on substrates and reproduced as thin films of well-controlled elemental composition, with good crystallinity and optical properties, in a fairly controllable way.

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