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Short communication

Preparation of $Cu(In,Ga)Se_2$ films via direct heating the selenium-containing precursors without selenization

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Abstract

$Cu(In,Ga)Se_2$ films were successfully prepared using synthesized precursors that contained selenide compounds. A chemical reduction route with $NaBH_4$ as the reducing agent was adopted to produce the precursor powders in an ambient atmosphere with a nanometer size around 50–100 nm. Since the species have various redox potentials, copper indium selenide compounds were formed and coexisted with gallium metal. Heating at 400 °C in a reducing atmosphere without H_2Se or Se vapor caused a $Cu(In,Ga)Se_2$ phase to start to form, and the desired pure phase was obtained after heating to 550 °C for 0.5 h. The presence of selenide species in the precursors enlarged the grains upon heating, and densified the prepared $Cu(In,Ga)Se_2$ films. The root-mean-square (RMS) roughness of the prepared films was measured using AFM to be 75 nm. The developed process is a superior method for preparing selenide compounds, since no toxic gas (H_2Se or Se vapor) is used during calcination, and it can also be applied to prepare other materials for forming absorber layers in solar cells

Keywords: $Cu(In,Ga)Se_2$; Thin films; $NaBH_4$

1. Introduction

Thin-film solar cells have been extensively investigated with a view to their potential application to renewable energy production. Copper indium gallium diselenide ($Cu(In,Ga)Se_2$), which has the chalcopyrite structure, is a promising material for use as an absorber layer materials due to its excellent properties, such as a high absorption coefficient and a direct band gap [1,2]. Accordingly, numerous vacuum-based approaches, such as co-evaporation [3,4] and sputtering routes, [5,6] have been developed. To reduce the manufacturing cost and simplify the process of manufacture, several groups also have prepared $Cu(In,Ga)Se_2$ films by coating with the pastes [7]. The properties of precursors that used in the pastes greatly affect the characteristics of the films thus formed including the grain size and morphology [8]. Heating at high temperature in a controlled atmosphere (H_2Se or Se vapor) is essential as the pastes containing oxygen precursors [9]. However, it is difficult to control the amount of selenium species in $Cu(In,Ga)Se_2$ films in the above process [10]. Additionally, the use of oxygen-free precursors containing chalcogenide compounds in the pastes is reportedly found to promote the synthesis of $Cu(In,Ga)Se_2$ films with large grains [11].

In this study, precursors containing selenide compounds with nanometer-sized particles and a controlled composition were obtained via a chemical reduction route using $NaBH_4$ as a reducing agent. These precursors were used in the pastes to prepare $Cu(In,Ga)Se_2$ films. The amount of selenium species is controlled and the need to use toxic gas is eliminated for forming $Cu(In,Ga)Se_2$ films. The phases of the obtained precursors were investigated for use in coating $Cu(In,Ga)Se_2$ films. The reluctant compounds and the microstructures of the heated films were examined. The electrical properties of the fabricated solar cell device were elucidated.

2. Experiment

Copper (II) chloride ($CuCl_2$), indium chloride ($InCl_3$), gallium nitrate ($Ga(NO_3)_3$) and selenium dioxide (SeO_2) were used as starting materials for preparing the precursors of $Cu(In,Ga)Se_2$ films. The staring materials were dissolved in ethylene glycol (EG). The reducing agent (sodium borohydride,

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$NaBH_4$) and a particle stabilizer (triethylamine, TEA) were then added into the above solution with continuous stirring. The molar ratio of $NaBH_4$ to the cations (Cu^{2+}, In^{3+}, Ga^{3+}, and Se^{4+} ions) was set to be 1:10, and the molar ratio of $NaBH_4$ to TEA was fixed at 1:1. After stirring, the nanoparticles were formed. The formed precipitates were centrifuged and washed with methanol to remove the residual organic species presented in the system. The precipitates were then dried at 80 °C to get the precursor powder. The obtained powders were mixed with the surfactant and ethanol for preparing the pastes. $Cu(In,Ga)Se_2$ films were coated on Mo-coated soda lime glass substrates via the doctor-blade route employing the pastes. Subsequently, the coated films were heated in a reducing atmosphere (5 vol% H_2 and 95 vol% N_2) at various temperatures ranging from 400 to 550 °C for 0.5 h.

The precursors and the heated specimens were characterized via X-ray powder diffraction (XRD, Philips X'Pert/MPD) analysis operated at 40 kV and 30 mA using CuK radiation. The particle size and morphology of the precursors and the heated films were examined using scanning electron microscopy (SEM, Hitachi S-800) and a transmission electron microscopy (TEM, Hitachi H-7100). The surface morphology of the heated films was investigated via atomic force microscopy (AFM, Seiko E-sweep System). Raman spectra were measured employing a micro-Raman spectrometer (Raman, Jobin Yvon T64000) using as Ar ion laser (λ = 514.5 nm) as an excitation source. The optical properties of the prepared films were investigated via a UV–vis-NIR spectrometer (Jasco V-570) at room temperature.

3. Results and discussion

Fig. 1(a) shows the representative XRD patterns of specimens obtained after a chemical reduction. The XRD results indicate that copper indium selenide and gallium metal were formed via the chemical reduction using $CuCl_2$, $InCl_3$, $Ga(NO_3)_3$, and SeO_2 as the precursors, and $NaBH_4$ as the reducing agent. According to the literature [12,13], metal atoms can easily be formed using $NaBH_4$ as the reducing agent, resulting in a subsequent transfer of electrons from the reducing agent to the metal ions. The standard potentials (E°) of Cu^{2+}/Cu, In^{3+}/In, Ga^{3+}/Ga, and Se^{4+}/Se are 0.34, 0.34, 0.53, and 0.75 V, respectively [1,14]. The redox potentials of copper, indium, and selenium exceed that of gallium. Correspondingly, the rates of reduction of copper, indium, and selenium ions exceed that of gallium ions. Therefore, copper, indium, and selenium species were reduced and then produces copper indium selenide compounds (the unidentified phase) before gallium species was reduced. Similar results were observed for nanoparticles of another alloy that were formed using $NaBH_4$ as the reducing agent [15]. The composition of the nanopowders was Cu: 24.75%, In: 18.03%, Ga: 7.64%, and Se: 49.58%, as determine using EDS analysis.

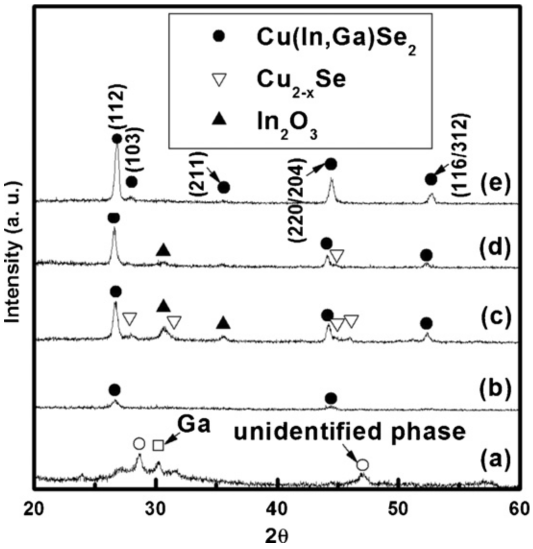

Fig. 1. X-ray diffraction patterns of (a) the obtained nanopowders via the chemical reduction and the obtained films heated at (b) 400 °C, (c) 450 °C, (d) 500 °C, and (e) 550 °C in a reducing atmosphere.

The prepared nanopowders via the chemical reduction were used in the pastes for coating the film. The as-coated films were heated at various temperatures for 0.5 h in a reducing atmosphere to synthesize $Cu(In,Ga)Se_2$ films. Fig. 1(b)–(e) display the XRD patterns of the films after heating. After heating at 400 °C, only small amounts of $Cu(In,Ga)Se_2$ were identified, but when the temperature was raised to 450 °C, $Cu(In,Ga)Se_2$ was found to coexist with In_2O_3 and $Cu_{2-x}Se$. It is suggested that some indium and copper species were not completely reduced and remained as amorphous phases in the precursors. The reaction of the remaining indium species with the organic species from the surfactant and the solvent used was responsible for the formation of In_2O_3 [16]. Therefore, increasing the heating temperatures causes amorphous copper species and indium species to form $Cu_{2-x}Se$ and In_2O_3. Additionally, gallium metal would become amorphous as raising the heating temperatures. Upon heating to 500 °C, the amounts of $Cu(In,Ga)Se_2$ further increased, and the amounts of In_2O_3 and $Cu_{2-x}Se$ corresponding decreased. It is due to the fact that amorphous gallium species are reacted with $Cu_{2-x}Se$ and In_2O_3 to yield $Cu(In,Ga)Se_2$. Upon further heating at 550 °C, all impurities disappeared, and only $Cu(In,Ga)Se_2$ was found in the product. Pure $Cu(In,Ga)Se_2$ films were successfully obtained via the precursors containing selenide compounds upon direct heating in a reducing atmosphere that did not include H_2Se or Se vapors.

Fig. 2(a) presents the microstructural evolution of the nanopowders via the chemical reduction. The average particle size of the obtained powders was 50–100 nm. The microstructures of the prepared films after heating at various temperatures in a reducing atmosphere are depicted in Fig. 2(b)–(e). The as-heated films that were heated at 400 °C and 450 °C exhibited a porous morphology with nanometer-sized grains in a range of 80–200 nm (Fig. 2(b) and (c)). As the heating temperature was raised to 500 °C (Fig. 2(d)), the particles of the prepared films became enlarge and the grain size was around 0.3 μm owing to the existence of $Cu_{2-x}Se$ in the prepared films. According to the literature [7], $Cu_{2-x}Se$ serves as the fluxing agent and promotes the grain growth of the

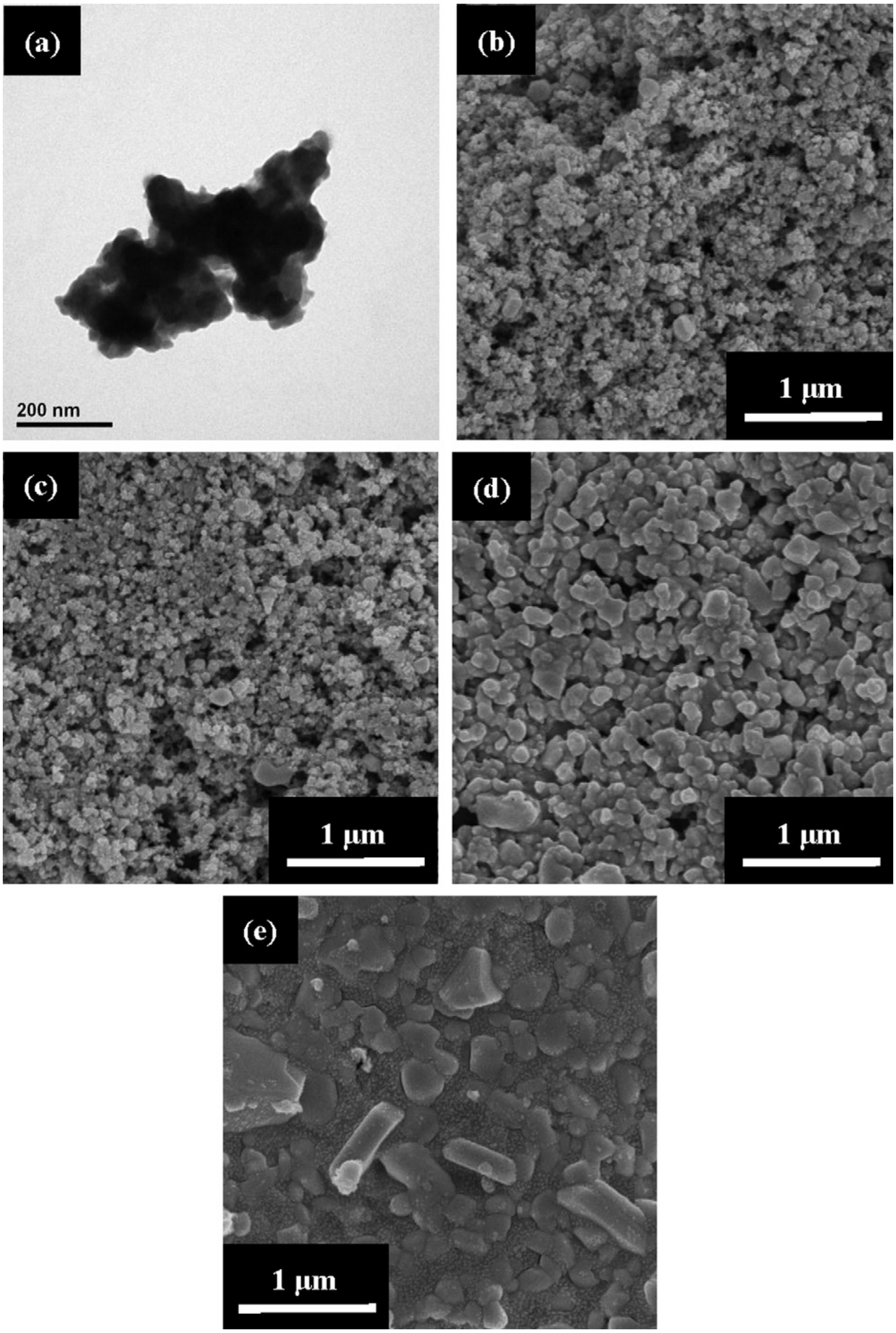

Fig. 2. (a) Transmission electron micrograph of the nanopowders via the chemical reduction, scanning electron micrographs of the obtained films heated at (a) 400 °C, (b) 450 °C, (c) 500 °C, and (d) 550 °C in a reducing atmosphere.

obtained films. When the calcination temperature was increased to 550 °C, the grain size of the prepared Cu(In,Ga)Se_2 films was increased to 0.5–1 μm. The densified and smooth morphology of the obtained film result from the increased amount of the melted flux agent-$Cu_{2-x}Se$ at high temperatures (Fig. 2(e)).

An atomic force micrographs of the Cu(In,Ga)Se_2 films are shown in Fig. 3. The root-mean-square (RMS) roughnesses were decreased from 203 to 75 nm for the prepared films after heating at temperature that was raised from 400 °C to 550 °C. It reveals that the 550 °C-heated films had a uniform surface morphology and a low RMS roughness when the precursor films that contained selenide compounds. The use of Cu(In,Ga)Se_2 absorber films with a low RMS roughness (<300 nm) is reportedly crucial to ensure the high efficiency of solar cell devices [17].

Rietveld refinement was also utilized to confirm the crystal system of Cu(In,Ga)Se_2 films heated at 550 °C for 0.5 h, as seen in Fig. 4. The ‘‘×’’ marks denote experimental diffraction data,

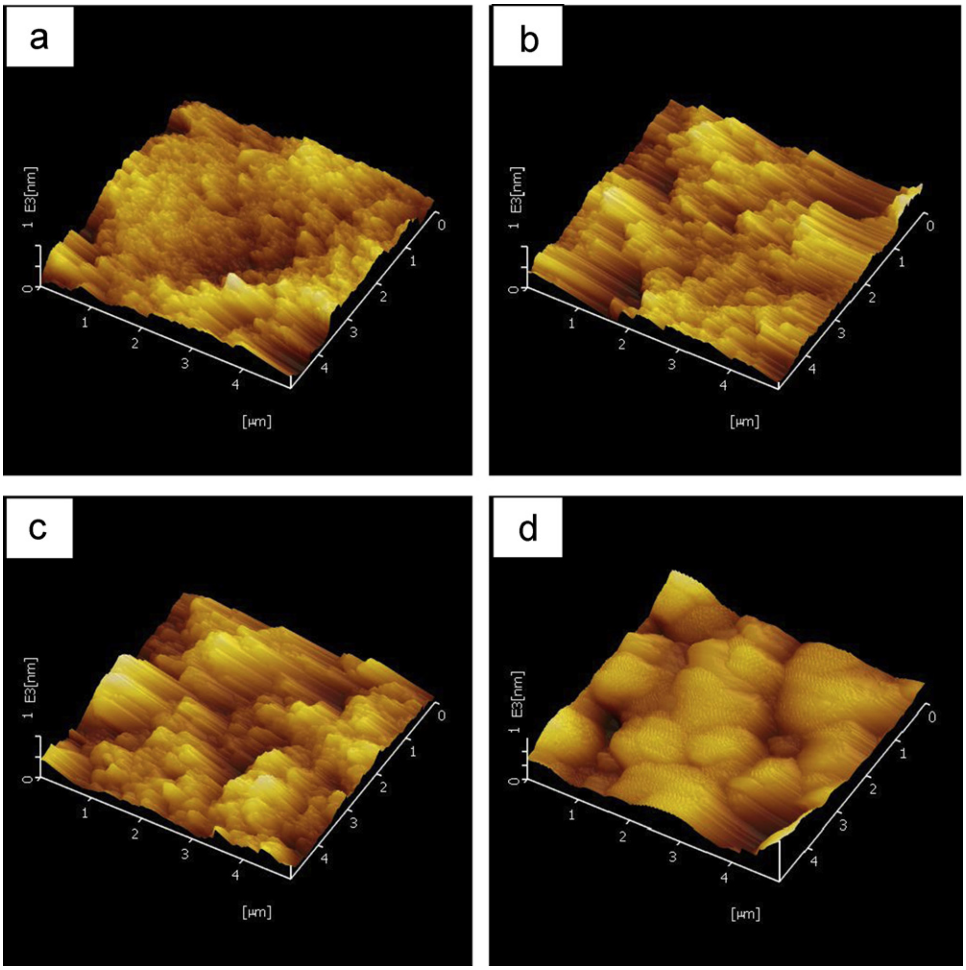

Fig. 3. Atomic force micrographs for the obtained film after heating at (a) 400 °C, (b) 450 °C, (c) 500 °C, and (d) 550 °C in a reducing atmosphere.

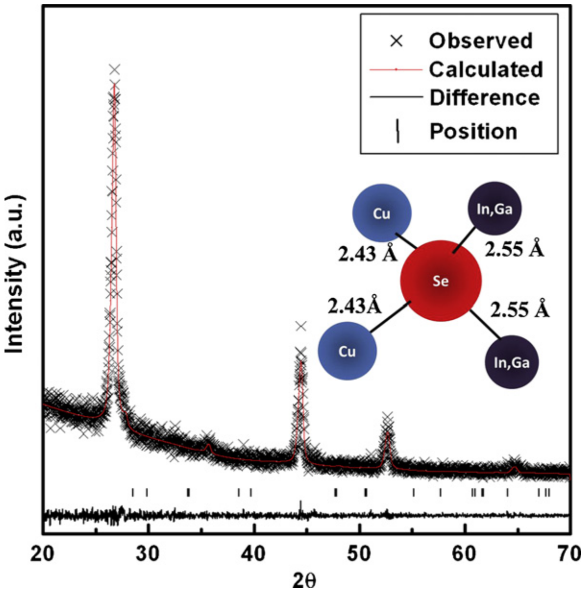

Fig. 4. Observed (×) and calculated (solid line) X-ray diffraction pattern of the 550 °C-heated $Cu(In,Ga)Se_2$ films. The inset refers coordination environment of the Se atoms in $Cu(In,Ga)Se_2$.

the solid curves represent simulated diffraction data, the straight bars indicate the positions of the simulated diffraction patterns, and the dotted lines show the deviation between the simulated and experimental values. The obtained reliability factors wR_p and R_p were 12.49% and 8.71%, respectively. The lattice constants of $Cu(In,Ga)Se_2$ were listed in Table 1. The bond lengths of Cu–Se and (In,Ga)-Se were evaluated to be 2.43 Å and 2.55 Å, respectively [18]. These values are given in the inset in Fig. 4.

The band gap of the prepared $Cu(In,Ga)Se_2$ films was calculated from the data of optical absorbance according to the following equation [19]:

$$\alpha h\nu = k(h\nu - E_g)^{1/2} \qquad (1)$$

where α is the absorption coefficient, k is a constant, $h\nu$ is the photon energy, and E_g is the energy of band gap. The value of the band gap was estimated from the extrapolation of the straight data line in the plot to $(\alpha h\nu)^2 = 0$. The value of the band gap for the 500 °C-heated films was around 1.1 eV. Upon heating at 550 °C, the optical band gap of the $Cu(In,Ga)Se_2$ films was 1.18 eV. Because of the existence of the impurities (as shown in Fig. 1(d)) and the incomplete reaction, the value of the band gap for the 500 °C-heated films is less than that of the 550 °C-heated films.

Table 1
Crystal structural data and lattice parameters of Cu(In,Ga)Se_2 films.

Formula	Cu(In,Ga)Se_2
Crystal system	Tetragonal
Space group	I-42d
Lattice constants	
a/Å	5.75(1)
c/Å	11.5(3)
η=c/2a	1.0024
x(Se)	0.222
Cell volume (V/Å^3)	381.34
R values	wR_p = 12.49%
	R_p = 8.71%

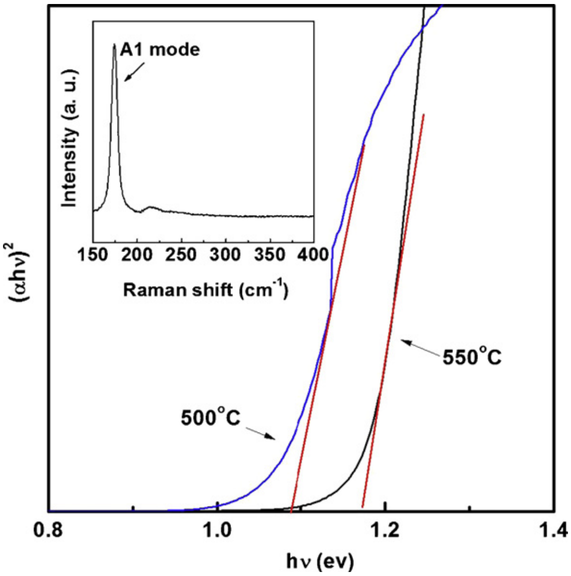

Fig. 5. Absorbance spectra of the prepared films heated at 500 °C and 550 °C. The inset plots Raman spectrum of the 550 °C-heated Cu(In,Ga)Se_2 films.

The inset in Fig. 5 plots the Raman spectrum of the 550 °C-heated Cu(In,Ga)Se_2 films. Two major peaks at 174 cm^{-1} and 214 cm^{-1} were observed. The peak at 174 cm^{-1} was assigned to A1 mode of Cu(In,Ga)Se_2. The A1 mode phonon results from the interaction of Se atoms in motion with cation atoms at rest [20]. The other peak appearing at 214 cm^{-1} is attributed to the E mode of Cu(In,Ga)Se_2. It indicated that single-phase chalcopyrite Cu(In,Ga)Se_2 was successfully synthesized.

4. Conclusions

Copper indium gallium diselenide films were successfully obtained after direct heating precursor films at 550 °C for 0.5 h in a reducing atmosphere. In a chemical reduction process, $NaBH_4$, acting as a reducing agent, reduced the constituent cations containing copper, indium, gallium, and selenium ions, leading to the formation of selenide compounds for coating Cu(In,Ga)Se_2 films. Heating at high temperature markedly densified the synthesized films because of the improved distribution of selenide compounds in the precursor powders via chemical reduction and the presence of the second phase, $Cu_{2-x}Se$, during the heating process. The band gap of the prepared Cu(In,Ga)Se_2 films was measured to be 1.18 eV via the UV–vis-NIR spectroscopy. The Raman spectroscopy and the Rietveld refinement method confirmed that monophasic Cu(In,Ga)Se_2 films were synthesized without using toxic gas (H_2Se or Se vapor).

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