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Preparation of Thin $CuInSe_2$ Films Using Cu–In Alloy Nanoparticles

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Thin $CuInSe_2$ films were synthesized via selenizing Cu–In alloy-containing precursors. The alloy nanoparticles with CuIn and Cu_2In were obtained via chemical reduction in ethylene glycol. Nanoparticles with a size around 40–60 nm were formed. The thin monophasic chalcopyrite $CuInSe_2$ film with large grains was formed at 450 °C. Using the alloy nanoparticles for the coating process was demonstrated to be a potential way for preparing thin $CuInSe_2$ films.

Thin-film solar cells have been intensively investigated as second-generation solar cells because of the increasing demand for renewable energy. Among various types of thin-film solar cells, Cu(In, Ga)Se_2 has become a promising solar cell for large-scale production.[1] Because chalcopyrite copper indium diselenide (α-$CuInSe_2$) has a high absorption coefficient (ca. $10^5\,cm^{-1}$),[2] this material is suitable for use in the absorber layers of thin-film solar cells.

Thin Cu(In, Ga)Se_2 films are usually prepared via vacuum methods such as the coevaporation and sputtering.[3,4] The complicated processes in these vacuum methods restrict the development of Cu(In, Ga)Se_2 solar cells. For simplifying the preparation processes, various nonvacuum methods have been developed to prepare Cu(In, Ga)Se_2. These processes include the synthesis of submicron-sized alloys and the preparation of oxides or nitrides.[5–8] In these methods, high temperatures above 900 °C, a particular atmosphere, and reduction of the thin films at high temperatures prior to selenization are necessary.

To simplify the above nonvacuum processes, chemical reduction was utilized to synthesize nanosized Cu–In alloys in this study. Cu–In alloy nanoparticles were prepared in ethylene glycol using $NaBH_4$ as the reducing agent in ambient atmosphere. Ethylene glycol (EG) has been utilized in the synthesis of alloy nanoparticles.[9] EG also acts as a stabilizer in the reduction to prevent further growth of the formed nanoparticles.[10] Pastes from the obtained Cu–In alloy nanoparticles were coated on substrates, followed by the selenization of the thin films to synthesize $CuInSe_2$. The phases and sizes of the prepared nanoparticles were characterized. The effects of the selenization temperatures on the thin Cu–In alloy films were examined. The crystalline structure and the band gap of the thin $CuInSe_2$ films were analyzed via Raman and UV–visible–NIR spectroscopy, respectively.

For preparing the precursors of $CuInSe_2$, Cu–In alloy nanoparticles were prepared via chemical reduction in ethylene glycol. Copper(II) chloride dihydrate ($CuCl_2\cdot 2H_2O$) and indium chloride tetrahydrate ($InCl_3\cdot 4H_2O$) were dissolved in EG. The molar ratio of $CuCl_2\cdot 2H_2O$ to $InCl_3\cdot 4H_2O$ was set at 1:1. After stirring, sodium borohydride ($NaBH_4$) was added into the solution, followed by the addition of triethylamine (TEA). The molar ratios of Cu^{2+} and In^{3+} to $NaBH_4$ to TEA were set at 1:10:10. The synthesized powders were washed with methanol, concentrated via centrifugation, and dried in a vacuum oven at 70 °C. The obtained particles were mixed with OP-10 and 1-hexanol as the surfactant and the solvent to prepare the ink. The ink was coated on the soda-lime glass (SLG) substrates via a doctor-blading method. Selenium powders were used as the selenium source and put in a horizontal tube furnace. Once the selenium powders were heated, the selenium gas was carried by the carrier gas (5 vol % H_2 and 95 vol % N_2) to induce the selenization reactions of the coated films. The coated films were selenized in the reducing atmosphere at 250–450 °C for 30 min.

The phases of the synthesized particles and thin films were characterized employing an X-ray diffractometer (XRD, Philips X'Pert/MPD) with Cu Kα radiation at 45 kV and 40 mA. The sizes of the obtained particles were analyzed using a transmission electron microscope (TEM, Hitachi H-7100). The microstructures of the prepared thin films were observed utilizing a scanning electron microscope (SEM, Hitachi S-800). The compositions of the Cu–In alloy powders were characterized via inductive coupling plasma (Perkin-Elmer, ICP Optima 3100XL). The crystalline structure of thin films was examined employing a Raman spectroscope (HORIBA Jobin Yvon T64000) performed in a backscattering configuration with Ar ion laser (wavelength: 514.5 nm) as a light excitation source. The optical absorbance of the thin films was characterized using a UV–visible–NIR spectrophotometer (JASCO V-570).

Cu–In alloy nanoparticles were synthesized via chemical reduction in ambient conditions. Figure 1a illustrates the X-ray diffraction patterns of the obtained Cu–In alloy particles as-coated on the substrate. The XRD patterns of CuIn and Cu_2In were in agreement with the data in ICDD files (No. 35-1150 and 42-1475, respectively). It is inferred that the formation of Cu–In alloy powders are ascribed to high activities of formed metallic (Cu and In) nanoparticles.[11] The major formed compound was CuIn. However, a small amount of Cu_2In was also found. The formation of CuIn and Cu_2In is considered to be parallel reactions. The inset of Figure 1 shows the microstructures of the prepared Cu–In alloy particles. Secondary particles consisting of 40–60 nm original particles were prepared. It is reported that EG reacts with $NaBH_4$ to form a complex of $Na^+B^-(OCH_2CH_2OH)_4$, which acts as a stabilizer to inhibit the formed particles from growing.[12] Therefore, particles within the scale of nanometers can be obtained in the reduction process.

Figures 1b–1d illustrate the XRD patterns of the thin Cu–In alloy films selenized at various selenization temperatures for 30 min. After selenization at 250 °C (Figure 1b), $CuInSe_2$ was found to form with the existence of Cu_2In and In_2O_3. It is considered that some indium species did not participate in the reduction reactions and possibly remained as an amorphous phase in the powders. In this study, 1-hexanol and OP-10 were used as the solvent and the surfactant to prepare ink. During heating, these organic materials are decomposed at elevated

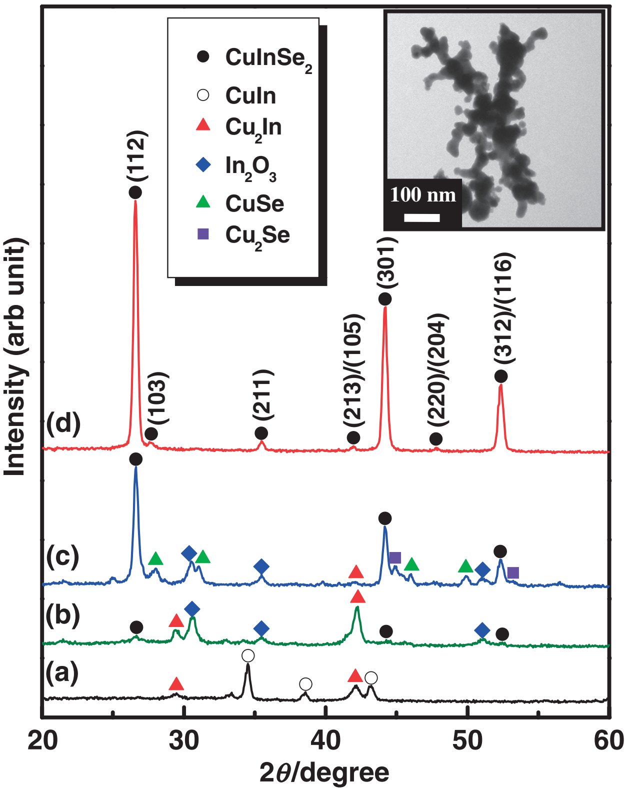

Figure 1. X-ray diffraction patterns of thin Cu–In alloy films (a) as-coated and selenized at (b) 250, (c) 350, and (d) 450 °C for 30 min. The transmission electron micrograph of the Cu–In alloy nanoparticles synthesized via chemical reduction is illustrated in the inset.

temperatures to produce oxygen species. The oxygen species will react with indium species to form In_2O_3. As the temperature was elevated to 350 °C (Figure 1c), the amount of $CuInSe_2$ was increased, and Cu–Se compounds (CuSe and Cu_2Se) were formed. After increasing the temperature to 450 °C (Figure 1d), single-phase $CuInSe_2$ was obtained. The XRD patterns of $CuInSe_2$ were consistent with reported data (ICDD card No. 89-5648). In addition, the formation of chalcopyrite $CuInSe_2$ was verified from the presence of (103), (211), and (213)/(105) planes, which are characteristic of chalcopyrite $CuInSe_2$.[13]

Figure 2 shows the Raman spectra of the thin Cu–In alloy films selenized at various temperatures for 30 min. After heating at 250 °C (Figure 2a), Raman peaks at 169 and 257 cm^{-1} indicate that chalcopyrite $CuInSe_2$ and Cu_2Se phase were formed, respectively.[14,15] As the temperature was elevated to 350 °C (Figure 2b), Raman peaks of chalcopyrite $CuInSe_2$ (169 cm^{-1}) and Cu_2Se phase (257 cm^{-1}) coexisted. At 450 °C (Figure 2c), only a Raman peak assigned to chalcopyrite $CuInSe_2$ (169 cm^{-1}) was observed. This indicates that monophasic chalcopyrite $CuInSe_2$ was successfully synthesized.

The absorbance spectra of the thin selenized Cu–In alloy films were measured to estimate the band gap energy of $CuInSe_2$. The band gap of the thin $CuInSe_2$ film was calculated according to the following formula:[16]

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

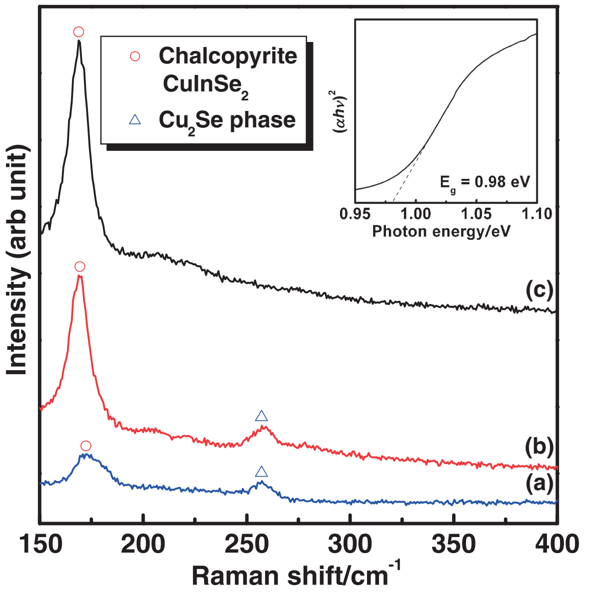

Figure 2. Raman spectra of thin Cu–In alloy films selenized at (a) 250, (b) 350, and (c) 450 °C for 30 min. The absorbance spectrum of the thin Cu–In alloy film selenized at 450 °C for 30 min is illustrated in the inset.

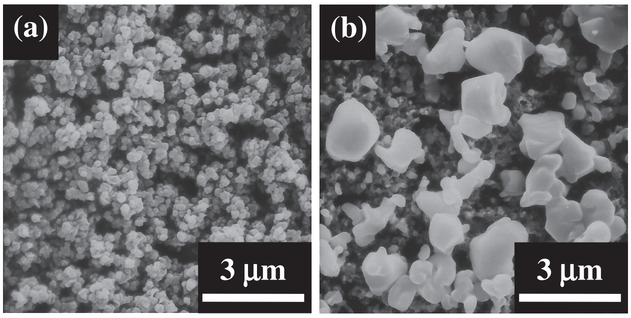

Figure 3. Scanning electron micrographs of thin Cu–In alloy films selenized at (a) 250 and (b) 450 °C for 30 min.

where α is the absorption coefficient, $h\nu$ is the photon energy, k is a constant, and E_g is the band gap energy. Via plotting $(\alpha h\nu)^2$ versus $h\nu$, the band gap value is obtained. The extrapolation of the straight line in the plot to $(\alpha h\nu)^2 = 0$ reveals the band gap value. The band gap of the thin Cu–In alloy film selenized at 450 °C for 30 min was 0.98 eV as depicted in the inset of Figure 2. This value corresponded with the reported value.[17]

Figure 3 shows the microstructures of thin Cu–In alloy films selenized at various temperatures for 30 min. After the thin film was selenized at 250 °C (Figure 3a), the particle sizes were about 150–250 nm. With elevating the selenization temperature to 450 °C (Figure 3b), the sizes of particles were increased significantly compared with those selenized at 250 °C. According to the Cu–Se phase diagram, CuSe and Cu_2Se will transform into the liquid phase at elevated temperatures.[18] The formed liquid phase will cover the surface of the grains and act as a fluxing agent to enhance the grain growth.[19–22] Based on the XRD results (Figures 1b and 1c), it was found that CuSe and Cu_2Se phases were formed at 250–350 °C. On heating at 450 °C, the liquid phase was formed and acted a fluxing agent to result in the significant grain growth of $CuInSe_2$ particles. The above results demonstrate that the thin $CuInSe_2$ films with large grains can be prepared via using Cu–In alloy nanoparticles.

In summary, thin $CuInSe_2$ films were prepared via coating Cu–In alloy nanoparticles on the substrates by selenization. The precursors composed of CuIn and Cu_2In were prepared via chemical reduction using ethylene glycol as the particle stabilizer. Nanoparticles with a size of around 40–60 nm were obtained. In the selenization, $CuInSe_2$ phase started to form at as low as 250 °C. By increasing the selenization temperatures, the particles in the thin films grew significantly because of the existence of Cu–Se compounds. After the thin film was selenized at 450 °C, single-phase $CuInSe_2$ with large grains was obtained. Chalcopyrite $CuInSe_2$ was formed as verified via Raman spectroscopy. Employing Cu–In alloy nanoparticles via the chemical reduction method gives a promising route to prepare the thin $CuInSe_2$ films.

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