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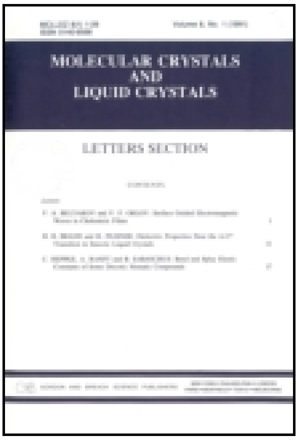

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Preparation of Single Phase $CuInSe_2$ Nanocrystals (NCs) via Phase Transformation of Cu-In-Se Compounds Formed by a Low Temperature Wet Chemical Route

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Cu-In-Se compounds were synthesized by wet chemical route using CuCl, $InCl_3$, and Se as precursors, and $CuInSe_2$ (CIS) was acquired via annealing of Cu-In-Se compounds. As-synthesized compounds exhibited $CuSe_2$-rich phases. The compounds synthesized below 95 °C transformed into CIS phase after the annealing above 450 °C, however the compounds synthesized above 100 °C exhibited different transitions from $CuSe_2$ to Cu_2Se. This could be explained by the excessive Se-loss in the surface of big rod. The size of the CIS was about 7.8 nm and the elemental ratio of (Cu:In:Se) in the NCs was 1:0.7:2.

Keywords Colloidal route; $CuInSe_2$; nanocrystal; phase transition; solar cell

Introduction

Chalcogenide nano-crystals (NCs) have attracted a great deal of attention in various fields. Especially, $CuInSe_2$ (CIS) has been investigated for many applications, including photovoltaic devices [1]. Over the past several years, several groups have reported the synthesis of many chalcogenide NPs using various synthetic routes, including thermolysis of single-source precursors, solvent-less thermolysis of various precursors, thermal decomposition of metal-surfactant complexes, and wet synthesis using precursors [2–4]. The wet synthesis processes can be classified into the colloidal and solvothermal routes by synthetic conditions, with the big differences between the two methods being the temperature and pressure. The colloidal route is operated at low temperature and pressure, while the solvothermal route is operated at high temperature and pressure. The wet solution routes have important advantages over the vacuum processes in forming the thin films; easy and simple process, large area applicability, and low temperature process [2–4]. Most of all, the low temperature process plays an important role in the fabrication of flexible solar cells. Generally, there are big problems in fabrication of flexible solar cells such as the absence of flexible substrate with a high thermal and chemical stability, high crystallization temperature of photon

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absorbing materials, and so on. Recently, organic substrates including polyimide films with high thermal stability have been developed, but the temperature stability is still low to apply these substrates to the solar cells. Thus, another approach is needed to accomplish the low temperature process and wet depositions using single phase CIS NCs can be the one of candidate for low temperature process. In wet depositions, a dispersed precursor liquid is needed to deposit desired films and the preparation of well-dispersed NCs before film depositions plays an important role to make good dispersed liquid.

In this study, Cu-In-Se compounds were synthesized using a low temperature wet chemical route, and single phase CIS NCs were acquired after the annealing of synthesized Cu-In-Se compounds. The synthesis conditions were analyzed in terms of pressure, and the effects of growth temperature on the Cu-In-Se compound formation were studied. After the annealing process, the structural variations of Cu-In-Se compounds grown at different growth temperatures were investigated, and the properties of CIS NCs investigated to understand the phase transition from Cu-In-Se compounds to single phase CIS NCs.

Experimental Details

Cu-In-Se compounds were synthesized by relatively straight-forward liquid-phase reactions at low temperatures. Copper(I) chloride (CuCl, Aldrich 99%), indium(III) chloride ($InCl_3$, Aldrich 98%) and Se (Aldrich 99.5%) were used as precursor materials, and ethylenediamine ($C_2H_4(NH_2)_2$, Aldrich 99%), n-propyl alcohol (n-C_3H_7OH, Duksan Chemicals 99.5%) and ethanol (C_2H_5OH, Duksan Chemicals 94%) were used as solvent chemicals. The precursors were dissolved in solvents, and the prepared solutions were then combined to form a homogeneous solution with Cu-In-Se compounds, and NC formations from the Cu-In-Se solutions were carried out for 24 h under an inert atmosphere. The reaction vessel with three bottle necks was closed to apply the pressure during the experiments, and the pressure was monitored using a digital manometer. The reaction vessel was purged using argon gas before the synthesis, and the growth temperatures were kept at 85, 95, 105, and 110 °C, respectively. The prepared precipitates were washed with methanol and acetone to remove impurities, and then stored in methanol to prevent the oxidation and aggregation of as-synthesized NCs. For thermal treatment and measurement, the solution of the NCs were dried using a vacuum oven, and the vacuum oven was purged and filled by nitrogen gas. The annealing of the NCs was performed for 30 min under N_2 atmosphere, and the annealing temperature was varied from room temperature to 550 °C.

The compositional ratio of the CIS NCs was analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES), and the structural properties of the CIS NCs were investigated by X-ray diffractometer (XRD, PANalytical MPD). The size and morphology of the NCs were characterized by a scanning electron microscope (SEM, Hitachi S-4200) and a transmission electron microscope (TEM, Hitachi H-7600). The optoelectronic properties of CIS NCs were measured by photoluminescence (PL) using Ar ion laser at a wavelength of 514.5 nm.

Results and Discussion

Figure 1 shows the SEM images of the as-synthesized Cu-In-Se compounds at different growth temperatures. As the growth temperature increased, the morphology of the as-synthesized materials was dramatically changed from a small sphere to a big rod shape. The reason for the change in the morphology was thought to be from that the synthetic conditions

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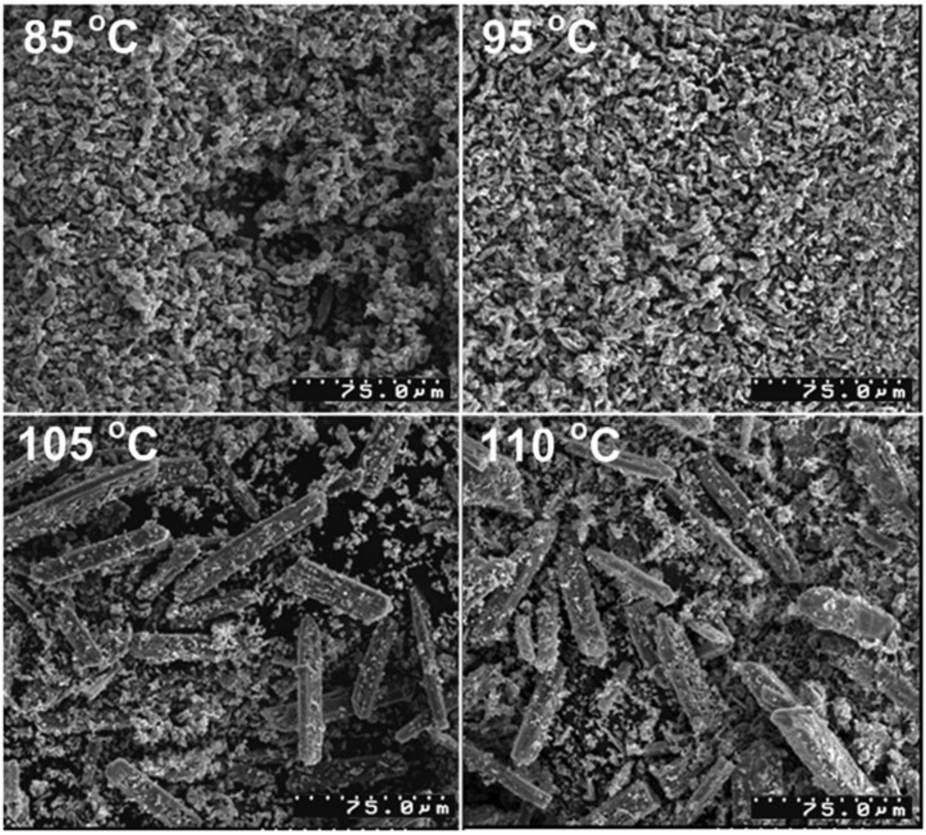

Figure 1. Scanning electron microscope (SEM) images of CIS NCs at different growth temperatures; the growth temperature of (a) 85 °C, (b) 95 °C, (c) 105 °C, and (d) 110 °C.

gradually changed from a colloidal route to a solvothermal route due to the change in vessel pressure [3,5]. The variation of pressure is proportional to the temperature in the closed vessel. In this experiment, the rising ratio of pressure as a function of temperature was about 0.028 bar/ °C, and the pressure in the reaction vessel increased from 1.84 to 2.57 bar, when the temperature was increased from 85 to 110 °C. This implied the chemical reaction was gradually changed from colloidal to solvothermal route and this change caused to accelerate the aggregation between synthesized particles during growth process. Consequently, the structures and shapes of particle grains were significantly affected from the change of temperature and pressure inside reaction vessel. Therefore, it is possible that there existed more active chemical reactions within the vessel, leading to changes in the structures and shapes of the NCs due to fast nucleation processes. Figure 2 shows the variation of pressure in reaction vessel as a function of growth time at different growth temperatures.

Figure 3 shows elemental mole ratios of as-synthesized nanoparticles according to the growth temperatures. The elemental ratio of as-synthesized Cu-In-Se compounds seldom changed with the change in growth temperature, and the elemental ratio of Cu:In:Se was about 1:0.9:1.4. This ratio was similar to the ratio of precursor (1:1:1.3), because the synthesis has been carried out in a closed reaction vessel. This meant that the compositional ratio of the compounds could be easily controlled by adjusting the ratio of precursors.

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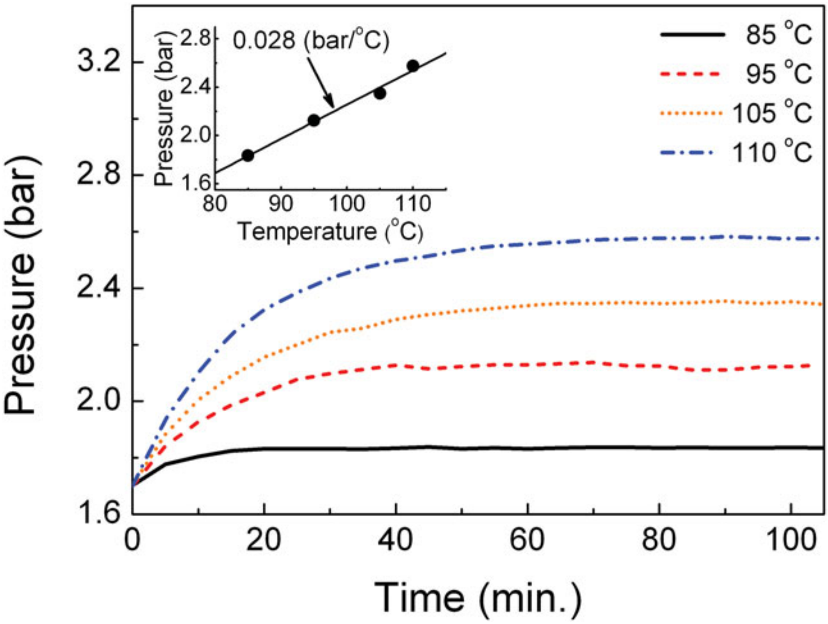

Figure 2. The variation of pressure in reaction vessel as a function of growth time at different growth temperatures and the variation ratio of pressure with varying temperatures (inset).

Figure 4 shows the X-ray diffraction patterns (XRD) of Cu-In-Se compounds synthesized at different growth temperatures. The Cu-In-Se compounds, synthesized at the temperature of 85 °C, possessed mostly $CuSe_2$ phases before annealing process, and there were predominantly $CuSe_2$ phases even after the annealing at or below 350 °C. The phase transition from $CuSe_2$ to $CuInSe_2$ gradually began above 350 °C, and single phase CIS NCs were formed over 400 °C (not shown here). The CIS NCs above 400 °C possessed

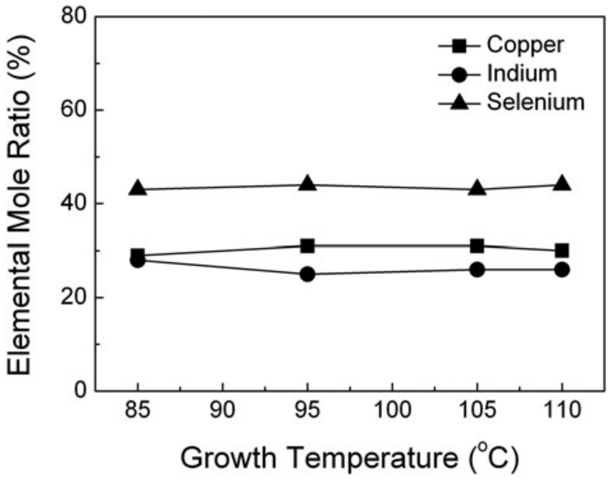

Figure 3. Elemental mole ratio of as-synthesized CIS NCs according to growth temperatures.

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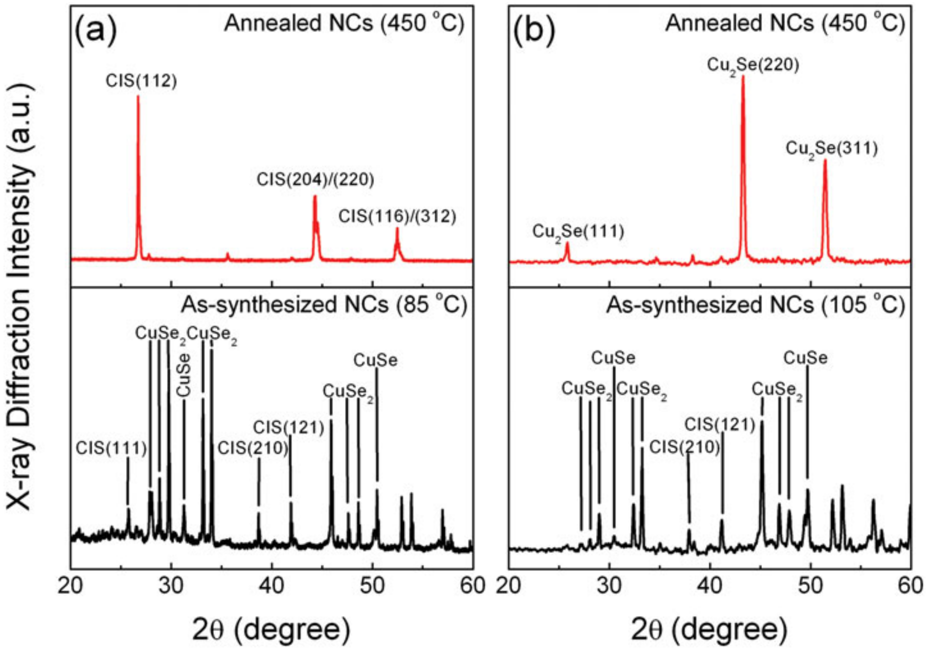

Figure 4. X-ray diffraction patterns (XRD) of annealed NCs at sintering temperature of 450 °C (top) and as-synthesized NCs (bottom); (a) the growth temperature of 85 °C and (B)105 °C.

the single $CuInSe_2$ phase with tetragonal (chalcopyrite) structures, with preferred orientations of (112), (204)/(220), and (116)/(312), respectively. On the other hand, the CIS NCs, synthesized above the temperature of 100 °C, $CuSe_2$ phases were transformed to Cu_2Se phases with cubic structures [6]. In this case, the phase transition from $CuSe_2$ to Cu_2Se

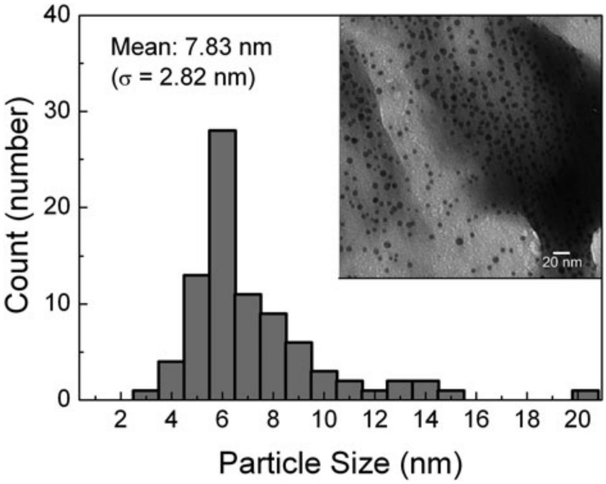

Figure 5. The size distribution and transmission electron microscope (TEM) image (inset) of a single phase CIS NCs (Growth temperature: 85 °C and annealing temperature: 450 °C).

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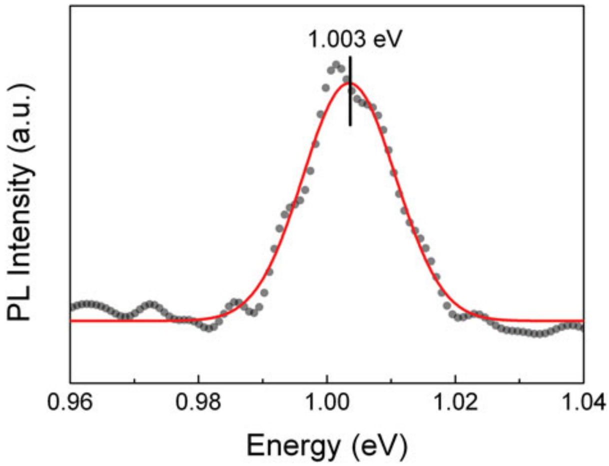

Figure 6. Room temperature photoluminescence (PL) spectrum of a single phase CIS NCs (Growth temperature: 85 °C and annealing temperature: 450 °C).

occurred above 350 °C because of the Se-loss in $CuSe_x$ phase [7,8]. In this experiment, the reason for Cu_2Se transition can be explained as follows; the morphology of as-synthesized CIS materials above the growth temperature of 100 °C was of big rod shape, and excessive Se-loss occurred in surface regions led to the phase transition of Cu_2Se phase and also Se-deficiency caused not to make InSe related phase during annealing process. Thus, this phase did not completely change into single phase CIS even after the annealing.

Figure 5 shows the size distribution and TEM image of annealed CIS NCs (synthesized temperature: 85 °C) at the annealing temperature of 450 °C. The shape of CIS NCs was close to a sphere, and the size of NCs was relatively mono-dispersed. The mean value of the particle size was approximately 7.83 nm with a standard deviation (σ) of 2.82 nm. The atomic composition ratio of this CIS NCs was 0.3:0.2:0.5 (Cu:In:Se), and the Cu-rich CIS NCs had a value of Cu/In of 1.5 and a value of (Cu+In)/Se of 1. Figure 6 shows the PL spectrum of the CIS NCs (synthesized temperature: 85 °C) at the temperature of 450 °C. The PL spectrum was measured using an Ar ion laser at a wavelength of 514.5 nm with the power of 0.1 W. The PL spectrum of the annealed particles exhibited the strong peak at around 1.0 eV, and this value was in well agreement with previous results [9,10].

Conclusion

In this study, CIS NCs were synthesized by a wet chemical synthesis at various growth temperatures. The growth temperature strongly affected the NCs synthesis conditions, and the shape of as-synthesized NCs gradually changed from a sphere to a rod shape as the growth temperature increased. As-synthesized CIS NCs mainly contained $CuSe_2$ phases as binary phases. These binary phases of the NCs synthesized below 100 °C, were dramatically changed into the single phase of CIS above an annealing temperature of 400 °C, which then seldom changed at annealing temperatures above 400 °C. The annealed CIS NCs were of the tetragonal (chalcopyrite) structure, with the preferred orientations of (112), (204)/(220) and (116)/(312). The size of the NCs were approximately 7.8 nm (σ =2.8 nm), and the elemental ratio of (Cu:In:Se) in the single phase CIS NCs was approximately 1:0.7:2. The PL spectrum of the annealed particles exhibited the strong peak at around 1.0 eV. The developed method is a relatively easy process to synthesize Cu-In-Se compounds, which does not require the typical Se environment annealing process to transform from Cu-In-Se compounds to single phase CIS NCs. In addition, the CIS NCs can be easily applied in preparing the ink containing CIS NCs because of mono-dispersed size of the NCs. Most of all, the low temperature process in film formations was possible in this method using CIS NCs, because the CIS NCs already had not only semiconductor properties but also high absorption properties prior to the post-annealing process. Thus, we believe that the CIS NCs formed using the method developed in this study can be used successfully utilized as materials for an absorption layer in the flexible solar cells.

Acknowledgments

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