



# Synthesis and characterization of copper gallium diselenide powders prepared from the sol–gel derived precursors

Zhi-Liang Liu, Fu-Shan Chen, Chung-Hsin Lu\*

*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC*

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## Abstract

Copper gallium diselenide ( $\text{CuGaSe}_2$ ) powders were synthesized via the sol–gel method followed by a selenization process. The sol–gel process can effectively reduce the required synthesis temperature to  $400\text{ }^\circ\text{C}$  due to enhanced reactivity and improved composition homogeneity. The amount of  $\text{Cu}_2\text{Se}$  impurity phase was decreased when sufficient  $\text{Ga}^{3+}$  was added to the precursors.  $\text{CuGaSe}_2$  powders were successfully prepared when the  $\text{Ga}^{3+}/\text{Cu}^{2+}$  molar ratio was increased to 2. The formation of  $\text{CuGaSe}_2$  with a pure chalcopyrite structure was confirmed via the Rietveld refinement analysis. With decreasing  $\text{Ga}^{3+}/\text{Cu}^{2+}$  molar ratios, the particle size of the prepared  $\text{CuGaSe}_2$  powders was significantly enlarged because the copper selenide phase acted as a flux for the particle growth. The optical absorption spectra revealed the obtained  $\text{CuGaSe}_2$  to have a band gap of 1.68 eV. The sol–gel method combined with the selenization process was demonstrated to provide a potential approach for fabricating  $\text{CuGaSe}_2$  materials.

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## 1. Introduction

Thin-film solar cells have been developed as the second-generation solar cells because the absorption materials are cost effective. Because of the direct band gap and high absorption coefficient, chalcopyrite semiconductors are considered to be the promising candidates for thin-film solar cells.  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) with a CIGS/CdS/ $\text{ZnO}$  junction was demonstrated to exhibit high efficiency as reported by NREL and ZSW [1,2]. For further improving the efficiency, the tandem-structure solar cells connect two cells in series. The bottom and top cells absorb the red and blue sunlight portion, respectively. The chalcopyrite material  $\text{CuGaSe}_2$  (CGS) with a large band gap is considered as a potential material for the top cell in multi-junction devices [3]. It has been reported that a tandem structure with CGS as the top cell and CIGS as the bottom cell can increase the conversion efficiency [4].

CGS and CIGS based absorbers are usually obtained via the vacuum routes [5–7]. However, the conventional vacuum systems have several drawbacks including the high production costs, difficulty in scaling up, and process complexity. Because of its' relatively simple procedure, low cost, and flexibility in scaling up [8,9], a particle based coating process is considered as an alternate process for CGS and CIGS absorber films.

CGS and CIGS powders are usually synthesized via the solvo-thermal [10,11] or solid-state process [12]. The required reaction temperature in the solid state process is at least  $800\text{ }^\circ\text{C}$  to form the pure phase [13]. In addition, the particle size of CGS and CIGS is difficult to control via the solid-state process. In the particle-based process, the particle sizes of CGS significantly affect the morphology and the surface state of absorption films. Hence, the way to control the particle size is important in particle-based deposition methods. To reduce the reaction time and temperatures, a sol–gel method utilizing polymerizing agents followed by a selenization process was used in this study. The molar ratios of  $\text{Ga}^{3+}$  to  $\text{Cu}^{2+}$  in the precursor of CGS powders were modified to form the pure phase and control the morphology.

\*Corresponding author. Tel.: +886 2 23651428; fax: +886 2 23623040.

E-mail addresses: [chl@ntu.edu.tw](mailto:chl@ntu.edu.tw), [chl@ccms.ntu.edu.tw](mailto:chl@ccms.ntu.edu.tw) (C.-H. Lu).

## 2. Experimental

CuGaSe<sub>2</sub> powders were prepared via the sol–gel route employing citric acid and ethylene glycol as the polymerizing agents. Copper nitride and gallium nitride were dissolved in deionized water. The molar ratios of Cu(NO<sub>3</sub>)<sub>2</sub> to Ga(NO<sub>3</sub>)<sub>3</sub> were varied from 1:1 to 1:2. Afterward, citric acid was added in the solution. After stirring for 1 h, ethylene glycol was then added into the mixed solution. The mixed solution was stirred and heated at 100 °C for 1 h to remove the excess water, followed by increasing the temperature to 200 °C to initiate the polymerization reaction. During the polymerization reaction, citric acid was used to chelate the metal ions and polymerize with ethylene glycol to form the gels. The brownish gels were formed after the polymerization reaction. To remove the organic residuals, the brownish gels were heated in air at 420 °C for 2 h. After the heating process, the precursors were formed. The precursors were selenized at temperatures ranging from 450 °C to 550 °C using a gas mixture (5 vol% H<sub>2</sub> and 95 vol% N<sub>2</sub>) with selenium vapor to form CuGaSe<sub>2</sub> particles.

The phases of the prepared samples were examined using an X-ray diffractometer (XRD, Philips X' Pert/MPD, Tokyo, Japan) using CuK $\alpha$  radiation at 45 kV and 40 mA. The morphology of the CuGaSe<sub>2</sub> powders was observed using a scanning electron microscope (SEM, Hitachi S-800, Tokyo, Japan). The band gap of the CuGaSe<sub>2</sub> particles was measured using a UV/vis/NIR spectrophotometer (UV, Jasco V-570). The prepared products were characterized via X-ray photoelectron spectra (XPS, VG Scientific ESCALAB 250, UK).

## 3. Results and discussion

### 3.1. Compositional effects on the formation and morphology of CuGaSe<sub>2</sub> powders via the sol–gel route

The CuGaSe<sub>2</sub> sol–gel derived precursors were selenized at different reaction temperatures for 1 h. The Ga<sup>3+</sup>/Cu<sup>2+</sup> molar ratio was set to 1. Fig. 1 illustrates the X-ray diffraction patterns of the precursors and resultant compounds. CuO and Ga<sub>2</sub>O<sub>3</sub> phases were observed in the sol–gel derived precursors as shown in Fig. 1(a). After selenization at 450 °C, the phase of CuGaSe<sub>2</sub> started to form (Fig. 1(b)). In addition, a small amount of Cu<sub>2</sub>Se was found to coexist with CuGaSe<sub>2</sub>. As the reaction temperature was increased to 500 °C and 550 °C (Fig. 1(c) and (d)), the amount of CuGaSe<sub>2</sub> increased monotonously. However, the impurity phase of Cu<sub>2</sub>Se remained to coexist with CuGaSe<sub>2</sub> in the samples. The formation of Cu<sub>2</sub>Se implies that the Ga species were insufficient during the reactions.

The precursors of CuGaSe<sub>2</sub> were selenized to form CuGaSe<sub>2</sub> powders. A reducing atmosphere (5% H<sub>2</sub> and 95% N<sub>2</sub>) was used during the selenization process. The hydrogen gas caused the reduction of Ga<sub>2</sub>O<sub>3</sub> (Fig. 1(a)) to form Ga metal. The metallic gallium is easily vaporized because of the low melting point of Ga metal (29.7 °C). The evaporation of gallium species will result in the gallium loss in the selenization process. In order to compensate for the gallium loss and supply

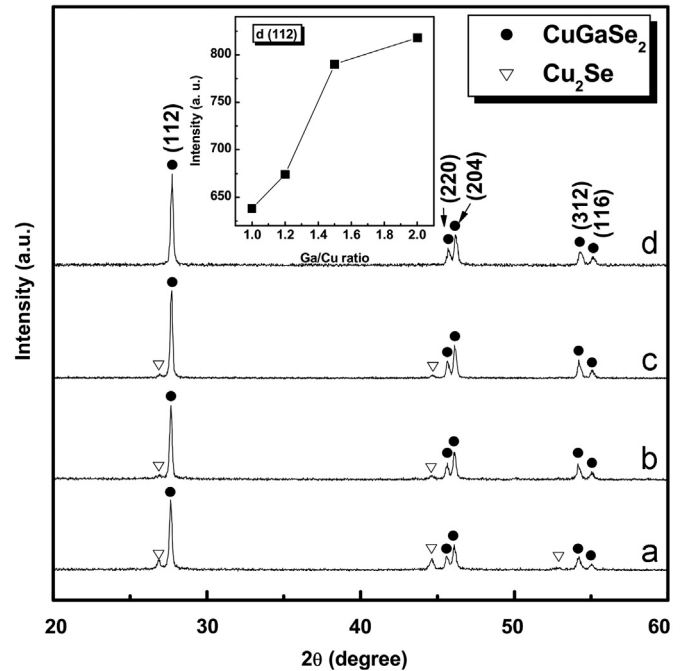


Fig. 1. XRD patterns of CuGaSe<sub>2</sub> powders prepared with the Cu<sup>2+</sup> to Ga<sup>3+</sup> molar ratio of 1.0 at (a) precursor, (b) 450 °C, (c) 500 °C, and (d) 550 °C for 1 h in the sol–gel process.

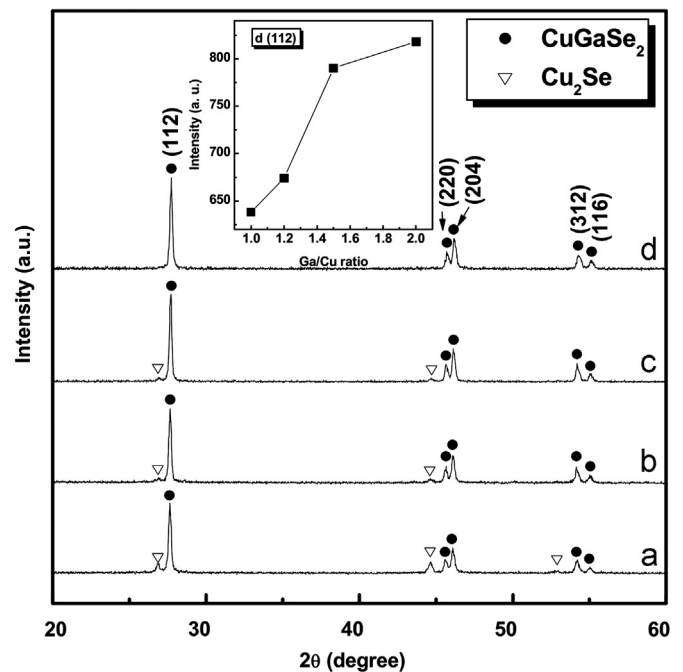


Fig. 2. XRD patterns of CuGaSe<sub>2</sub> powder prepared at 550 °C for 1 h with the Ga<sup>3+</sup> to Cu<sup>2+</sup> molar ratios of (a) 1.0, (b) 1.2, (c) 1.5, and (d) 2.0 in the sol–gel process. Inset: the relation between the Ga<sup>3+</sup>/Cu<sup>2+</sup> molar ratios and the diffraction peak intensity of CuGaSe<sub>2</sub>.

sufficient Ga during the reactions, the Ga<sup>3+</sup>/Cu<sup>2+</sup> molar ratio in the precursors should be increased.

To investigate the effects of Ga<sup>3+</sup>/Cu<sup>2+</sup> molar ratio on the formed phase, the Ga<sup>3+</sup>/Cu<sup>2+</sup> molar ratio was varied to 1, 1.2,

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