

Synthesis and Selenization of CIGS particle with different copper ratios fabricated by solvothermal refluxing method

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Abstract

The purpose of this study was to investigate the effect of different copper ratios on the quality of $\text{Cu}_x\text{In}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ (CIGS) film, where $x=0.8, 0.9, 1, 1.1, 1.2$, and to find the copper ratio that is most suitable for growing CIGS crystals, thereby improving the quality of the overall CIGS film.

We use a two-stage process to prepare CIGS films. In the first stage of the process, we provide a simple, non-toxic and low-cost method for the preparation of CIGS solution: through the direct use of metal powder as reaction materials, and the use of polyetheramine (D400) as a solvent in a non-vacuum process. A nano-solution of CIGS was prepared using a solvothermal refluxing method, and then CIGS film was prepared on a glass substrate by a doctor's blade method.

In the second stage of the process, we placed the CIGS film in a two zone tube furnace to perform pressurized closed selenization, while having nitrogen gas filled up the entire tube. The selenium powder is heated with the condition of 550°C for 30 minutes to provide selenium compensation. The CIGS film after the pressurized closed selenization process will be analyzed by XRD, SEM, EDS, Raman and UV-Vis to discuss the best selenization conditions. According to the analysis of material properties, CIGS films with good crystallinity were obtained at a copper ratio of 1.1 (Cu-rich).

***Keywords* – CIGS, solvothermal refluxing method, copper-rich, selenization, copper content**

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I. INTRODUCTION

Over the past few decades, polycrystalline copper indium diselenide (CISe) thin films and their alloys, especially with gallium (CIGSe) have been considered as the potential absorbers in the field of photovoltaics [1-3]. The $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) system has been known to have advantages, such as non-toxicity, long time stability and high conversion efficiency [4]. The chemical composition of the resulting film can be easily controlled by adjusting the initial composition of the precursor. Due to the adjustable band gaps, long-term radiation stabilities and high optical absorption coefficient, chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) has been considered as one of the most promising candidates as absorber materials for photovoltaic applications[5,6]. Also the best CIGS thin film solar cell has already reached a confirmed conversion efficiency for about 20% [7]. However, devices fabricated with vacuum processes have disadvantages such as high production cost and the scale of production. In this study, we report a non-vacuum solvothermal synthesis under a thermal-refluxing environment using polyetheramine as solvent, which has a greater stability due to the higher boiling point. The toxic elements won't even release or lose in the process at a high temperature. Our purpose was to investigate CIGS selenization situation under different copper ratio.

II. EXPERIMENTAL

This study used solvothermal refluxing method to synthesize different copper ratios of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ nano-ink. 0.116 mol of copper (Cu) powder, 0.0812 mol of indium (In) powder, 0.0348 mol of gallium (Ga) powder, and 0.232 mol of selenium (Se) powder were added in a three neck flask with 150ml of polyetheramine (D400, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2[\text{OCH}_2\text{CH}(\text{CH}_3)]_6.\text{NH}_2$). Heat and stir at 250°C for 20 hours in the nitrogen atmosphere. After that, deposit the as-synthesized nano-ink on clean glass substrates using the doctor's blade method to prepare CIGS thin film, where the glass substrates were ultrasonically cleaned with ethanol and acetone, and rinsed with deionized water. Redo the process but change the copper powder into 0.0928, 0.104, 0.1276, and 0.1392 mol, which corresponds to copper ratio 0.8, 0.9, 1.1, and 1.2, respectively.

Next, place the CIGS thin film into a carbon block, and surround the thin film with selenium powder, which act as a selenium compensation. Anneal the carbon block in a two zone tube furnace with the condition of 550°C for 30 minutes. The prepared samples were characterized by X-Ray Diffractometer (XRD, Bruker D8 Advance Diffractometer with $\text{CuK}\alpha$ radiation, $\lambda=1.5418 \text{ \AA}$), Raman spectrometer (Renishaw with 633 nm Laser wavelength), Field Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7000), Energy Dispersive Spectrometer (EDS, Bruker EDS QUANTAX) and UV-Vis-NIR Spectrophotometer (HITACHI U-4100).

III. RESULTS AND DISCUSSIONS

In the XRD patterns showed in Fig. 1, CIGS thin films were selenized at 550°C for 30 minutes. As could be seen from the XRD spectra in Fig. 1, the three main diffraction peaks due to (112), (220) and (312) planes correspond to CIGS, which are identified by comparison with the JCPDS data card 35-1102. (a), (b), (c), (d), and (e) represents the copper ratio 0.8, 0.9, 1, 1.1, and 1.2, respectively. Table 1 shows the full width at half maximum (FWHM) of (112) peak of the film and calculates the approximate grain sizes of different copper ratios. The FWHM decreases with the increase of copper ratio, which may be attributed to the crystalline quality improvement and grain growth. Due to the sharpest and the most intense peak, Sample (d), as in copper ratio 1.1, has a better crystallinity. Note that in Fig. 2, as we focus on (112) peak, there appears to have a ternary phase, which correspond to $\text{CuIn}_2\text{Se}_3.5$ (JCPDS #35-1349). This indicates the reaction has over reacted, results in the excessive copper ions, later on formed CIS.

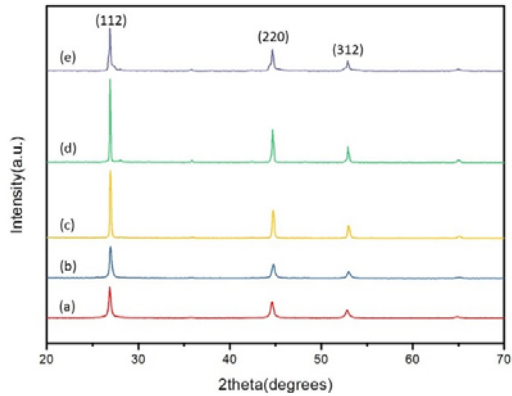


Fig. 1. XRD patterns of selenized CIGS films fabricated by using different copper ratios (a)0.8 (b)0.9 (c)1 (d)1.1 (e)1.2

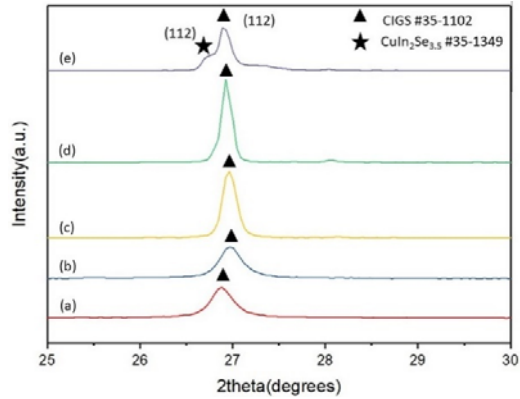


Fig. 2. XRD patterns of peak (112) for different copper ratios (a)0.8 (b)0.9 (c)1 (d)1.1 (e)1.2

Table 1. FWHM and approximate grain size (calculated from fig. 1)

Cu ratio	Degree	FWHM	Grain Size (nm)
0.8	26.886	0.3	26.3
0.9	26.968	0.299	26.39
1	26.966	0.174	45.34
1.1	26.933	0.13	60.69
1.2	26.899	0.228	34.6

To further investigate the structural properties of CIGS thin films, Raman spectroscopy was adopted. Raman spectra of selenized CIGS films with different copper ratios are presented in Fig. 3. Theoretically, the peak position of CIGS should be between 175 (CIS)-186 (CGS) cm^{-1} [8], but due to the A1 signal position is related to the mass of Se atom, the bond strength of Cu-Se and In-Se [9], and an additional phonon loss caused by defects, the A1 signal moved to low frequencies. For all copper ratios, there only appears one strong peak at 170 cm^{-1} , which associated with the A1 mode of lattice vibration of the chalcopyrite structures [10,11], with no indication of an additional second phase.

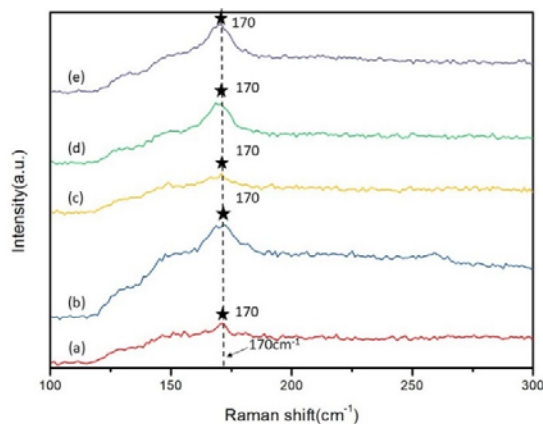


Fig. 3. Raman spectra of selenized CIGS films fabricated by using different copper ratios (a)0.8 (b)0.9 (c)1 (d)1.1 (e)1.2

Surface SEM images of CIGS films selenized from precursor films with different copper-ratios are presented in Fig. 4. From Fig. 4(a-d), the crystallinity of the films improves noticeably as the copper ratio increases, but slightly disintegrates when it comes to Fig. 4(e), which also consistent with the XRD analysis. Table 2 shows the composition of each sample measured by EDS analysis. Copper ratio of 0.8 and 0.9 are categorized as Cu-poor, copper ratio of 1 is categorized as slightly Cu-poor, and copper ratio of 1.1 and 1.2 are categorized as Cu-rich. The Cu-rich films exhibit a granular surface morphology, whereas a scattered bulk-like surface morphology is observed for the Cu-poor films. In comparison of the Cu-poor and the Cu-rich films, the Cu-rich films have a larger grain size. When the copper ratio is 1.1 or above, the surface morphology of Cu-rich films exhibit closely packed grains which are approximate 1 μm wide. According to the growth model proposed by Klenk et al. [12], a low-temperature liquid Cu-Se phase is present for the Cu-rich films during selenization and can aid the film growth. Therefore, the difference of Cu content between two films could result in different morphology and grain size.

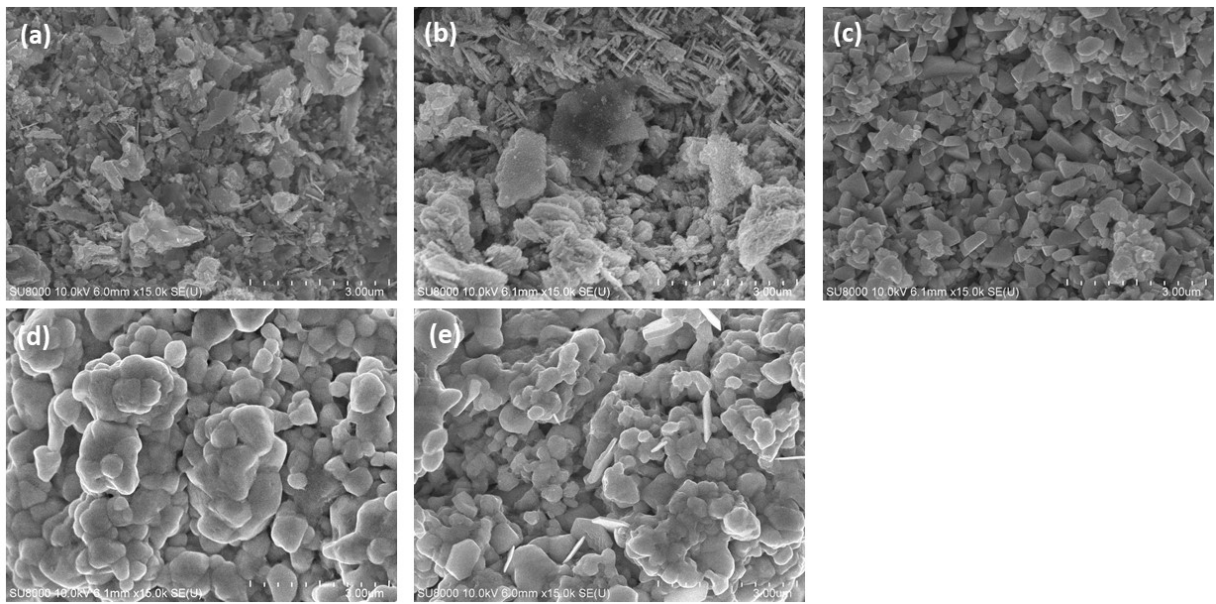


Fig. 4. SEM images of selenized CIGS films fabricated by using different copper ratios (a)0.8 (b)0.9 (c)1 (d)1.1 (e)1.2

Table 2. Chemical compositions (measured by EDS) of the selenized CIGS films fabricated by using different copper ratios

Cu ratio	Cu(at%)	In(at%)	Ga(at%)	Se(at%)	Cu/(In+Ga)
0.8	19.78	17.26	9.63	53.02	0.73
0.9	21.8	18.8	5.76	53.65	0.89
1	24.69	18.8	8.66	47.85	0.90
1.1	24.69	16.78	6.66	51.87	1.05
1.2	26.77	17.83	6.45	48.95	1.10

We measured the absorption α as a function of wavelength using UV-vis to determine the band gap of the selenized CIGS films, as shown in Fig. 5. The quaternary system $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) allows the band gap of the semiconductor to be adjusted over a range of 1.04–1.67 eV [13]. The band gap decreases as the copper ratio increases, and then bounces up a little when it

reaches 1.2. For the range of 1.25-1.4 eV, there is a minimum band gap of 1.25 eV for the copper ratio of 1.1. The crystalline quality has effects on optical performance. Refer to the SEM images of Fig. 4, as the surface morphology becomes more compact and the grain size becomes bigger, the band gap becomes smaller. In general, the Cu-rich ones have a smaller band gap than the Cu-poor ones.

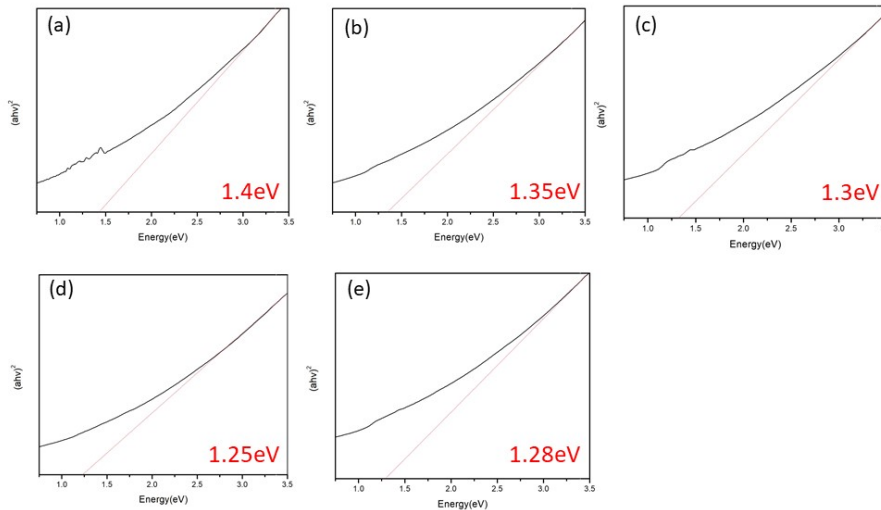


Fig. 5. UV-Vis-NIR absorption spectrum of selenized CIGS films fabricated by using different copper ratios (a)0.8 (b)0.9 (c)1 (d)1.1 (e)1.2

IV. CONCLUSIONS

A two stage process has been developed to prepare CIGS films using solvothermal refluxing method and Se-vapor selenization. Different copper ratios have been discussed. XRD shows the copper ratio of 1.1 has the sharpest and the most intense (112) peak (FWHM=0.13) and the biggest grain size (60.69nm). Raman analyze shows all samples with no indication of an additional second phase. SEM images show the Cu-rich films have a better uniformity, flatness and more compact than the Cu-poor films. UV-vis also shows the Cu-rich films have smaller band gaps, epically the copper ratio of 1.1 for 1.25 eV. Above all, it is safe to say the CIGS absorber grown in copper-rich will further improve the performance of a solar cell.

V. ACKNOWLEDGMENT

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