Fabrication of CIGS nanoparticle-ink using ball milling technology for applied in CIGS thin films solar cell

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A B S T R A C T

A copper–indium–gallium–diselenide layer was formed from the binary-alloy nanoparticles of In_2Se_3, Ga_2Se_3, and CuSe. Copper–indium–gallium–diselenide thin films were fabricated using the precursor nanoparticle-ink based on non-vacuum technology. The ink was fabricated by a ball milling procedure and the size of agglomerated copper–indium–gallium–diselenide powder after milling was less than 100 nm. Crystallographic, morphological, stoichiometric, and photovoltaic properties of the films were characterized by sintering the precursor copper–indium–gallium–diselenide samples with different holding times in a non-vacuum environment without selenization. Analytical results indicate that the copper–indium–gallium–diselenide absorption layer prepared with a holding time of 7.5 min has a chalcopyrite structure and favorable compositions. The obtained compositions of the sample are $Cu_{0.976}In_{0.811}Ga_{0.277}Se_{1.935}$, and the ratios of Ga/(In + Ga) and Cu/(In + Ga) are 0.254 and 0.896, respectively. The photovoltaic properties of this sample are E_g of 1.185 eV, V_{oc} of 0.643 V, N_{ds} of 1.3×10^{15} cm^{-3}, and Ga of 0.277 mol, respectively.

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1. Introduction

Copper–indium–gallium–diselenide (CIGS)-based solar cells are highly promising for portable applications owing to their high absorption coefficient, wide absorbing spectrum, and high stability. The highest conversion efficiency of CIGS solar cells that has been reported to date is 20.3% [1].

The absorption layer of thin-film CIGS-based solar cells is normally fabricated by co-evaporation [2] or selenization [3]. However, the conventional vacuum co-evaporation process has several limitations, including a highly complex process, prohibitively high production costs, and difficulty in scaling up production. Additionally, highly toxic H_2Se is commonly used during selenization, and the thin films do not adhere well to substrates. Recent studies have thus fabricated a CIGS absorbing layer by using nanoparticle-ink [4–8] and by other coating methods. Two approaches for the nanoparticle-based process are one in which the precursor film is prepared by synthesizing CIGS powders [4–7] and another one in which a mechanical alloying method is implemented before the non-vacuum coating is performed while the agglomerated CIGS powder size is around 140 nm [8]. Sintering subsequently allows for the precursor films to form the dense absorbing film used in solar cells [9]. All steps performed in a non-vacuum environment make this approach relatively simple and inexpensive with several advantages, including ease of scale-up production [10] and excellent control of the ratios among metal concentrations.

However, the crystallographic, morphological, and stoichiometric properties of the CIGS layer obtained by the above method may inhibit the formation of a chalcopyrite structure during sintering. Therefore, this work presents a novel sintering method in which the holding time of heat treatment is adjusted when the precursor sample is sintered. The precursor ink of CIGS sample is prepared first by mixing nanoparticles with some solvents, followed by printing and baking. Additionally, adjusting the holding time of heat treatment forms the required CIGS absorption layer, which has a chalcopyrite structure and whose surface is dense and flat, subsequently allowing us to determine the optimal contents of Cu, In, Ga, and Se.

2. Experimental

2.1. Preparation of precursor films

2.1.1. Precursor ink

Three commercially available binary-alloy powders of In_2Se_3, Ga_2Se_3, and CuSe (whose sizes are around 74 μm) are used as starting materials to fabricate the precursor films of CIGS absorption layer in a non-vacuum environment. According to the initial stoichiometric ratio of 39% CuSe, 45% In_2Se_3, and 16% Ga_2Se_3, all three binary-alloy powders were mixed with appropriate solvents and then ground into nanoscale-sized pieces by using a ball mill to obtain the required ink for preparing the precursor films. The ink was printed onto a Mo/soda lime glass substrate and baked at a low temperature to remove solvents to form a dry

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precursor. Next, the required absorption layer of $CuIn_{0.7}Ga_{0.3}Se_{2.0}$ used in solar cells was obtained by thermally treating the precursor through means of rapid sintering to reduce the weight loss of the Se components.

An attempt was made to obtain the ink to manufacture CIGS precursor films by mixing the three binary compounds of 20 g CuSe, 23 g In_2Se_3, and 8 g Ga_2Se_3 with 500 ml solvent of propanol and zirconium beads; each zirconium bead has a size of 0.5 mm and a mass of 100 g, which were mixed together into a ball mill for grinding. After of coarse grinding, the zirconium beads were replaced with smaller ones. The smaller zirconium beads have the diameter of 0.1 mm but the total mass remains the same as that of the larger beads. An hour later, an additional 50 ml of propylene glycol and 10 ml of diethanolamine were added into the ball mill to grind continuously for an hour to obtain the required ink. Scanning electron microscopy (SEM) revealed the average size of the agglomerated CIGS powder after milling to be lower than 100 nm (Fig. 1).

2.1.2. Precursor films

Following printing of the ink on the Mo/soda lime glass substrate, the sample was baked in an oven at a heating rate of 20 °C/min from 25 to 80 °C and maintained at 80 °C for 5 min, to remove solvents within the sample. The sample was then heated continuously from 80 to 180 °C at the same heating rate and maintained at 180 °C for 10 min. Once the sample naturally cooled down to 25 °C, the required dry precursor films were obtained.

Next, the performance of the precursor films was evaluated by using X-ray diffractometry (XRD), and SEM, with those results summarized in Fig. 2(a)–(c). According to the XRD pattern in Fig. 2(a), the precursor films lacked CIGS crystals after baking, indicating that the expected CIGS film had not formed yet. The SEM photograph of Fig. 2(b) revealed no cracking on the sample surface, demonstrating that the precursor materials prepared in a solution are feasible for fabricating the CIGS absorption layer. According to the SEM photograph of cross-sectional in Fig. 2(c), the film thickness of CIGS precursor sample was 5 μm.

2.2. Sintering

The prepared precursor samples were heated in a rapid thermal annealing (RTA) furnace to yield an excellent crystalline state of CIGS. Each sample was first heated with an increasing rate of 15 °C/s to 550 °C, with this temperature maintained and subsequent cooling to room temperature. During sintering of thermal treatment, the film structure of CIGS sample could have changed by varying the holding time from 1 to 8 min and facilitating an analysis of the sample properties.
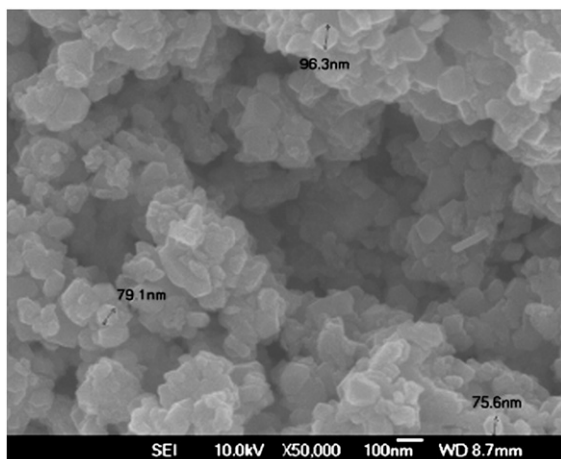

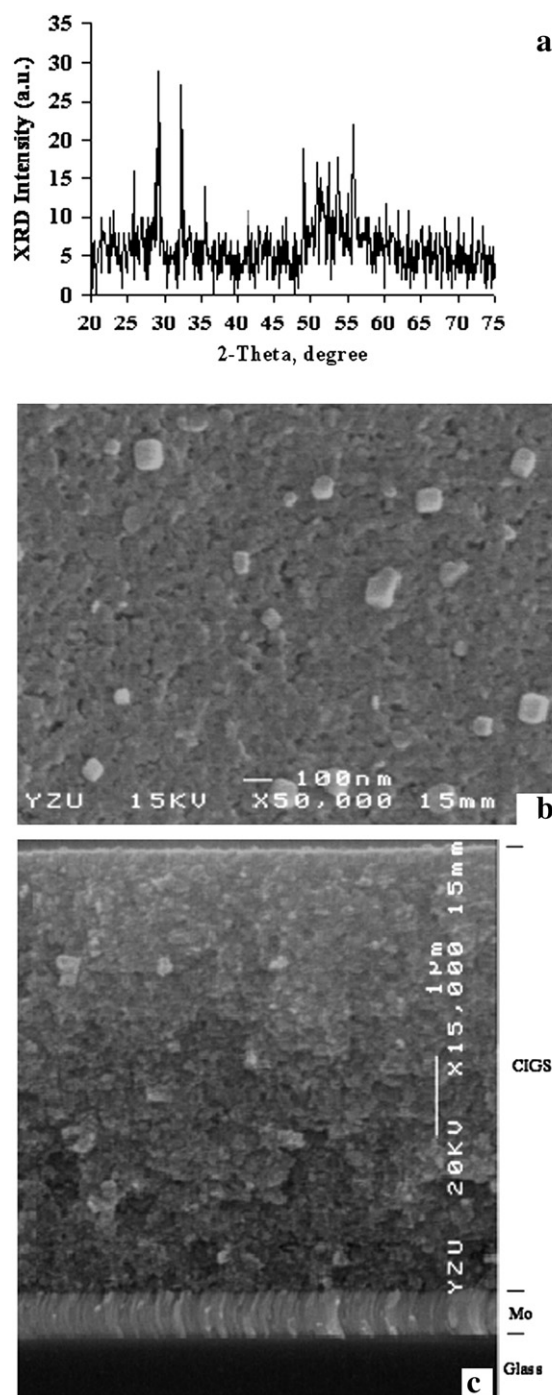Fig. 1. SEM photograph of nanoparticles after milling.

Fig. 2. Properties of the precursor CIGS thin film: (a) XRD pattern, (b) SEM photograph of sample surface, and (c) SEM photograph of sample's cross-sectional.

3. Results and discussion

3.1. Film compositions

The stoichiometric compositions of CIGS samples sintered with various holding times were determined from energy dispersive spectrometry (EDS) data (Table 1). However, verifying the sample compositions requires re-computing the at.% data of Cu, In, Ga, and Se without contents of C and Na. Notably, carbon is a highly probable residue because organic solvent and polymer binder are generally used in the preparation of paste or ink [11]. Among the diverse reasons for the low efficiencies it has been considered that residual impurities (e.g. carbon, oxygen, and other elements from precursors)