Letter

Nearly carbon-free printable CIGS thin films for solar cell applications

Eunjoo Lee [a], Se Jin Park [a,c], Jin Woo Cho [a], Jihye Gwak [b], Min-Kyu Oh [c], Byoung Koun Min [a,*]

[a] Clean Energy Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Photovoltaic Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuesong-gu, Daejeon 305-343, Republic of Korea
[c] Department of Chemical and Biological Engineering, Korea University, Anam-dong Seongbuk-gu, Seoul 136-713, Republic of Korea

ABSTRACT

In order to fabricate low cost and printable $CuIn_xGa_{1-x}Se_yS_{2-y}$ (CIGS) thin film solar cells, a precursor solution based method was developed. Particularly, in this method, nearly carbon-free CIGS film was obtained by applying a three-step heat treatment process: the first for the elimination of carbon residue by air annealing, the second for the formation of CIGS alloy by sulfurization, and the third for grain growth and densification in the CIGS film by selenization. The film also revealed very large grains with a low degree of porosity, similar to those produced by the vacuum based method. A solar cell device with this film showed current–voltage characteristics of $J_{sc}=21.02$ mA/cm^2, $V_{oc}=451$ mV, $FF=47.3\%$, and $\eta=4.48\%$ at standard conditions.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Among the various thin film solar cells in the market, $CuIn_xGa_{1-x}Se_yS_{2-y}$ (CIGS) thin film solar cells have been considered to be the most promising alternatives to crystalline silicon solar cells because of their high solar to electricity conversion efficiency, reliability, and stability [1]. However the current fabrication methods of CIGS thin film, which is the most important component in CIGS solar cell devices, are based on vacuum processes such as co-evaporation and sputtering techniques. Even though these methods result in highly efficient CIGS solar cells, they generally require initially high capital investment as well as maintenance capital expense due to the necessity of vacuum equipment [1,2]. Moreover there is significant loss of resource material, which again increases the manufacturing cost [2]. In addition, the large scale production of photovoltaic panels is restricted due to the limiting size of vacuum equipment.

In order to solve the problems of the current CIGS film fabrication methods non-vacuum processes have been suggested, such as printing, electroplating, spraying, etc. [2–10]. In particular, paste or ink based coating methods, e.g. spin coating and doctor-blade, would be competitive in terms of processing capital costs, efficiency of resource material usage, and processing speed [2,3].

There are two main approaches in solution based CIGS thin film fabrication: nanoparticle based and precursor solution based [6–12]. For example $CuInS_2$ (CIS) or CIGS nanoparticles were synthesized by a solvothermal route, which was applied to the preparation of inks [6–8]. The CIS or CIGS thin films were then prepared by a drop- or spin-casting of these inks followed by annealing under Se vapor or inert environment [6,7]. Instead of CIGS nanoparticles, CuInGa oxide nanoparticles were also applied to the preparation of CIGS films for which the oxide film was selenized by H_2Se gas [13].

In precursor solution based approaches, metal nitrates, chlorides, or acetates are frequently dissolved in organic solvent followed by an addition of polymer binder to allow for suitable rheology. After being coated on a conducting substrate, the film was annealed under inert or Se environment [9,10]. Alternatively binary compound precursors such as Cu_2S, In_2Se_3, and Ga_2Se_3 were dissolved in a hydrazine solution to form ink, which was spin-casted on the substrate followed by annealing under inert atmosphere [11,12].

Inspite of several promising results (e.g. ~12% by Lui et al. [12]) of the solution based CIGS thin films in solar cell applications, to date their solar cell efficiencies are not high enough to compete with those from vacuum based processes. Among the diverse reasons for the low efficiencies it has been considered that residual impurities (e.g. carbon, oxygen, and other elements from precursors) in the films may play a detrimental role in solar cell operation [3,14]. In particular, carbon is a highly probable residue because organic solvent and polymer binder are generally used in the preparation of paste or ink. For example, CIGS thin film

* Corresponding author. Tel.: +82 2 958 5853; fax: +82 2 958 5809.
E-mail address: bkmin@kist.re.kr (B.K. Min).
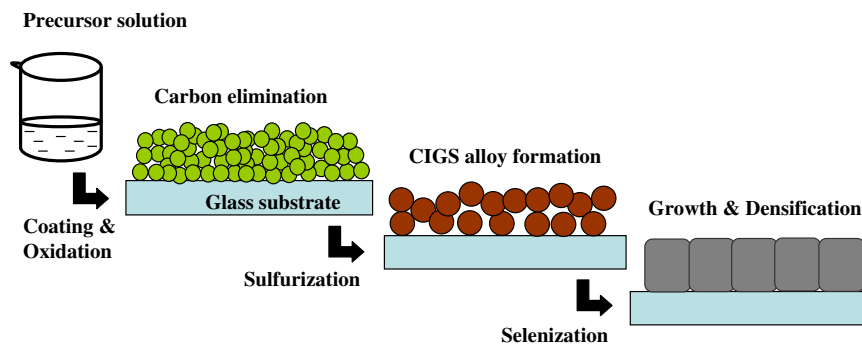
Precursor solution

Fig. 1. Schematic illustration of the CIGS thin film fabrication processes.

prepared by a precursor based paste was found to leave a thick amorphous carbon layer (∼2 μm) between the CIGS layer and the Mo coated glass substrate even after selenization with Se vapor [3,14]. This carbon layer would act as a high resistor, and would increase the series resistance of the cell. In addition, the carbon layer was observed to lead to poor adhesion of the CIGS film at the Mo interface [3,14]. Meanwhile, the residual carbon can exist in the entirety of the CIGS film when the annealing process is carried out under inert gas atmosphere. Previously we found that the carbon impurity prohibited crystal growth in the CIGS film during thermal treatment, which again deteriorated solar cell performance [10]. The hydrazine based deposition process suggested by Mitzi et al. [11] and Lui et al. [12] is a solution to minimize the residual carbon impurity in the CIGS film, because no carbon based organic chemicals are used in the precursor ink preparation. However, there may still be obstacles in this method for practical applications because hydrazine is known to be a highly toxic and explosive chemical.

In this study we suggest a precursor solution based method for the preparation of nearly carbon-free CIGS thin film (Fig. 1). To achieve it, a three-step annealing process was involved after coating of the paste on a glass substrate: the first process for the elimination of carbon residue by air annealing, the second for the formation of CIGS alloy by sulfurization, and the third for grain growth and densification in the CIGS film by selenization. We found that an amorphous mixed oxide film of Cu, In, and Ga and a polycrystalline CIGS film were formed by the first and the second and/or third annealing process, respectively. Notably, the amount of carbon residue was measured to be around the accuracy limit (∼3 at%) of our electron probe microanalyzer (EPMA) analysis in both cases. In addition, significant growth of CIGS crystal in the film was observed due to the third annealing process. Importantly, in this method, most procedures including paste preparation and film deposition were conducted in atmospheric conditions and not in restricted conditions (e.g. in a glove box), which will yield more potential for commercialization.

2. Experimental

A precursor mixture solution was prepared by dissolving appropriate amounts of $Cu(NO_3)_2xH_2O$ (99.999%, Alfa Aesar, 1.0 g), $In(NO_3)_3xH_2O$ (99.99%, Alfa Aesar, 1.12 g), and $Ga(NO_3)_3xH_2O$ (99.999%, Alfa Aesar, 0.41 g) in anhydrous ethanol (60 mL), followed by adding ethanol solution (20 mL) with terpineol (Fruka, 14.0 g) and ethyl cellulose (Aldrich, 0.75 g). After the mixture solution was condensed at 40 °C under reduced pressure, a viscous paste with rheological properties suitable for spin coating was prepared.

After the paste was coated on glass substrates, the sample was placed on a hot plate (∼150 °C) to dry for 5 min. The first annealing process was carried out at 350–450 °C under atmospheric

conditions for 1 h. The film thickness after the first annealing was adjusted to ∼2 μm. The second annealing process, sulfurization, was performed at 500 °C for 30 min under $H_2S(1\%)/N_2$ gas environment, and the third annealing process, selenization, was conducted at 500 °C for 10 min under Se vapor environment with an Ar gas flow using a furnace with a quartz tube.

Structural characterization of the films was performed by a scanning electron microscope (SEM, Nova, NanoSEM200) and X-ray diffraction (XRD, Shimadzu, XRD-6000). Composition analysis was carried out by an electron probe microanalyzer (EPMA, Jeol, JXA-8500F). The film thickness was measured using a surface profiler (Veeco, Dektak 8).

Solar cell devices were fabricated according to the conventional configuration (Mo/CIGS/CdS/i-ZnO/n-ZnO/Al). In our process a 60 nm thick CdS buffer layer was deposited on CIGS film by chemical bath deposition (CBD), and i-ZnO (50 nm)/Al doped n-ZnO (500 nm) were deposited by radio frequency (rf) magnetron sputtering on the CdS layer. An Al grid 500 nm thick was deposited as a current collector by thermal evaporation. The active area of the completed cells was 0.44 cm². The solar cell efficiency was measured using a class AAA solar simulator (WXS-155S-L2, Wacom, Japan) and an incident photon conversion efficiency (IPCE) measurement unit (Soma Optics, Japan).

3. Results and discussion

First of all, Cu, In, and Ga nitrates were dissolved completely in ethanol at room temperature to produce the precursor mixture solution. Ethanol solution containing terpineol and ethyl cellulose was also prepared followed by mixing with the precursor mixture solution. The composition of Cu, In, and Ga is easily adjustable, which would be an important merit of this method because the band gap of the film can be easily controlled. In the present study, the CIGS film with a composition ratio of 1:0.7:0.3:2 (Cu:In:Ga:Se:S) was primarily investigated.

Although a viscous paste with suitable rheological properties was prepared by condensing the mixture solution under reduced pressure at 40 °C, the reaction between the precursors to form the alloy of Cu, In, and Ga did not occur at this stage. The reaction between the metal ions in the precursor mixture occurred during the heat treatments of the spin casted paste on a soda–lime glass under ambient conditions. Structural changes of the films with respect to the heating temperatures were examined by X-ray diffraction (XRD; Fig. S1 in the Supporting Information). No apparent peaks corresponding to the crystalline structure of $CuInGa$ oxide (e.g. $CuInGaO_4$) were found up to 450 °C, indicating that only amorphous states of the mixed oxide were formed up to this temperature (Fig. 2a). The composition of the film analyzed by EPMA showed almost the same atomic ratio of Cu, In, and Ga as that of the precursor paste, implying no loss of elements during