



Novel fabrication route for carbon-free and dense CuInSe₂ (CIS) thin films via a non-vacuum process for solar cell application



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ABSTRACT

Carbon-free CuInSe₂ (CIS) thin film with a dense microstructure has been prepared using a novel non-vacuum based fabrication route. Cu_xS_y and In₂Se₃ binary nanoparticles, approximately 10 nm in size, were synthesized by a low temperature colloidal process. The precursor film was deposited using the coating ink formulated with the binary nanoparticles and pyridine, and then annealed in the rapid thermal annealing (RTA) chamber at 540 °C for 15 min under selenium (Se) atmosphere. Scanning electron micrographs, X-ray diffraction patterns and Raman spectra showed a phase pure carbon-free and dense CIS thin film was prepared in this method. A solar cell device fabricated using this CIS thin film showed the following photovoltaic characteristics: $V_{OC} = 350$ mV, $J_{SC} = 24.72$ mA cm⁻², FF = 38.73% and $\eta = 3.36\%$ under standard AM 1.5 condition.

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1. Introduction

Among thin film solar cells, Cu(In_{1-x}Ga_x)Se₂ (CIGS) solar cells are one of promising candidates because of their high efficiency [1,2]. In spite of the excellent performance of CIGS solar cells, however, the high production costs of conventional vacuum-based fabrication processes, such as a multi-stage co-evaporation and a two-step process for sputtering and selenization, are hurdles to the widespread commercialization of CIGS thin film solar cells [3]. Thus, non-vacuum-based CIGS fabrication processes have been investigated over the past several years [4–15].

Non-vacuum-based CIGS thin films have been fabricated by the drop-, spin-, and doctor blade-deposition of chemically prepared inks on substrates followed by high temperature annealing under selenium (Se) vapor or an inert atmosphere. Many research groups have dedicated their own efforts to developing the inks via various technologies to obtain high quality CIGS thin films [4–15]. Nanoparticles represent one suitable precursor material for such inks because they have the advantages of high purity and easy

composition control. Despite these advantages, nanoparticles have the poor wetting and film formation properties which should be improved. The addition of organic binders to the nanoparticles to formulate inks is one solution. However, carbon residues from organic binders likely remain in CIGS thin films in spite of high temperature annealing [12–14]. These residues may degrade solar cell performance stability and lead to the poor adhesion of CIGS thin films to molybdenum (Mo) contacts. Recently, Q. Guo et al. reported the synthesis of binder-free nanoparticle-based inks and the fabrication of a CIGS solar cell exhibiting 12.0% efficiency [9–11]. Although the results are very impressive, the nanoparticle synthesis method employed by Guo et al., called the 'hot injection process', is intricate and may not be suitable for mass production.

Another disadvantage of nanoparticles as a precursor for CIGS thin film is the insufficient grain growth. In general, sintering or coalescence is a process for eliminating interparticle pores. They occur at relatively high temperature, $T > 0.8T_m$, where T_m is the melting point, because they need the atomic migration between the nanoparticles. Such a high temperature can lead to the thermal shock of glass substrate and is not applicable to the fabrication of CIGS thin films. To address this concern, a suitable fluxing agent for promoting inter-particle sintering at lower temperature has been added to formulate the inks [16–19]. It has been shown that the addition of copper selenide and copper–thorium selenide

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(CuThSe₂) as fluxing agents to the Cl(G)S-based inks promotes the inter-particle sintering, however, the final composition of the films were Cu-rich [16–18]. Another approach for producing CIGS thin films from particulate precursors employs binary or ternary selenide nanoparticles, such as copper selenide, indium selenide and gallium selenide [19]. The objective of this formulation is to access the liquid-assisted sintering by the Cu–Se phase while retaining overall Cu-poor composition in the final films. Nanosolar has reported total-area efficiency of 15.3% CIGS solar cell using mixed selenide nanoparticles, however, the detail process parameters have not been revealed yet.

Here, we propose a new approach to solve the issues previously described. The organic binders which have a high molecular weight and a strong electronegative group are likely to remain as carbon residues in the final CIGS thin films. Thus, we have tried to find a monomeric coating additive having a relatively weak electronegative group to obtain carbon-free films. In addition, a fluxing agent leading to the liquid assisted sintering as well as volume expansion has been adopted to make film density higher. We present a novel fabrication route for a carbon-free and dense CuInSe₂ (CIS) thin film solar cells using a nanoparticle-based ink. Cu_xS_y and In₂Se₃ binary nanoparticles synthesized by the simple low temperature colloidal process were used to prepare CIS absorbers. A carbon-free precursor film was obtained using those binary nanoparticles and pyridine as a coating solvent. The precursor film changed to a dense CIS thin film by rapid thermal annealing (RTA) under Se vapor. A solar cell device fabricated using this CIS thin film demonstrated a power conversion efficiency of 3.36% under standard AM 1.5 condition.

2. Experimental section

2.1. Materials

Copper(I) iodide (CuI, 99.999%), indium(III) iodide (InI₃, 99.999%), sodium sulfide (Na₂S, 99.8%), and sodium selenide (Na₂Se, 99.8%) were purchased from Alfa Aesar, pyridine (99.9%), tetrahydrofuran (THF, 99.9%) and methanol (99.6%) from Aldrich, and elemental Se (99.999%, 3 mm shot) from Cerac. All chemicals were used as received without further purification.

2.2. Synthesis of Cu_xS_y nanoparticles

Cu_xS_y nanoparticles were synthesized according to the low temperature colloidal process reported by Schulz [12,13,15]. In a nitrogen-filled glove box, CuI (0.380 g, 2 mmol) and Na₂S (0.078 g, 1 mmol) were dissolved in pyridine (90 ml) and methanol (20 ml), respectively. Each solution was stirred overnight to thoroughly dissolve the solid precursor. After precursor dissolution, the solutions were transferred from the glove box to an ice bath in a fume hood and mixed together. The reaction mixture was stirred for 7 min, resulting in a black colloidal solution, which was centrifuged at 10,000 rpm for 10 min. The supernatant, a mixture of solvent and by-product, was decanted, and the nanoparticles were redispersed in methanol. This centrifugation process was carried out several times to obtain clean Cu_xS_y nanoparticles.

2.3. Synthesis of In₂Se₃ nanoparticles

In₂Se₃ nanoparticles were also synthesized according to the low temperature colloidal process. In a nitrogen-filled glove box, InI₃ (0.990 g, 2 mmol) and Na₂Se (0.380 g, 3 mmol) were dissolved in THF (90 ml) and methanol (20 ml), respectively. Each solution was stirred overnight. After precursor dissolution, the solutions were transferred from the glove box to an ice bath in a fume hood and

mixed together. The reaction mixture was stirred for 7 min, resulting in a yellowish colloidal solution, which was centrifuged at 10,000 rpm for 10 min. The supernatant was decanted, and the nanoparticles were redispersed in methanol. This centrifugation process was carried out several times to obtain clean In₂Se₃ nanoparticles.

2.4. Precursor film deposition

A coating ink was prepared by adding pyridine as a solvent to Cu_xS_y and the In₂Se₃ nanoparticles. The mixture of the two nanoparticles and pyridine was stirred by a magnetic stirrer for over 2 h and sonicated for 10 min. The ink was deposited on a 1-mm-thick Mo-coated soda-lime glass substrate by the spin coating. The films were then dried at 150 °C for 10 min to remove the solvent. When thicker films were desired, the spin coating and drying process were repeated several times.

2.5. CIS thin film fabrication

The as-deposited film was annealed under Ar and Se vapor to obtain CIS thin films. The film and Se pellets were placed in a rapid temperature annealing (RTA) chamber. The chamber was initially evacuated to a base pressure of 5E-6 torr, and then Ar gas was blown into the chamber to adjust the pressure to 1E-3 torr. The sample and Se pellets were then heated by a quartz lamp heater to 540 °C for 15 min for selenization.

2.6. Solar cell fabrication

The fabrication of the solar cell devices was completed by the chemical bath deposition of a 50-nm layer of CdS, followed by the radio-frequency sputtering of a 50-nm layer of intrinsic ZnO, and a 350-nm layer of Al₂O₃-doped ZnO. An Al top contact was deposited by thermal evaporation. The final devices possessed a Mo/CIS/CdS/i-ZnO/n-ZnO/Al structure and were isolated by mechanical scribing to yield an active area of 0.44 cm².

2.7. Characterization

Bright-field (BF) transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images of the nanoparticles were obtained using JEM-2000FXII and JEM-2100F (JEOL, Japan) with an operating voltage of 200 kV, respectively. Elemental mapping images and energy-dispersive X-ray spectra were obtained by energy-dispersive X-ray spectroscopy (EDS, Oxford, X-Max SDD) established in scanning transmission electron microscopy (STEM, JEM-2100F); a high-angle annular dark-field detector was used at an operating voltage of 200 kV. The Raman spectra of the nanoparticles were obtained in the quasi-backscattering geometry using the 514.5 nm and 632.8 nm of laser as the excitation source. The scattered light was filtered with a holographic edge filter, dispersed by a Spex 0.55-m spectrometer, and detected with a liquid-nitrogen-cooled back-illuminated charge-coupled-device (CCD) detector array. The morphologies of the as-deposited and the CIS films were investigated by high-resolution scanning electron microscopy (HRSEM, XL30SFEG Phillips Co., Holland at 10 kV). Compositional depth profiles of the as-deposited films were obtained by Auger electron spectroscopy (AES, Perkin Elmer, SAM 4300). The crystal structures of the CIS films were analyzed by X-ray diffraction (XRD, Rigaku Japan, D/MAX-2500) using CuK α radiation. The solar cell device performances were characterized using a class AAA solar simulator (WXS-155S-L2, WACOM, Japan).

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