Fabrication of CIGS thin film absorber by laser treatment of pre-deposited nano-ink precursor layer

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Abstract

A process to prepare Copper Indium Gallium Selenide (CIGS) absorber thin films by laser treatment of pre-deposited nano-inks has been investigated. Two approaches were followed, one using an ink of CIGS nanoparticles and other employing an ink comprising a mixture of a CIG metallic alloy and Se nanoparticles. Laser post treatment of the film applied with the CIGS ink was found to retain the chalcopyrite structure following melting and recrystallization, with no additional phases being generated during the process. Single-phase, highly crystalline CIGS thin films were also found to result from the ink made of $\text{CuIn}_{0.7}\text{Ga}_{0.3}$ and Se nanoparticles precursor following laser treatment. The $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin films obtained in both cases were consistent with the initial constitution of the precursor materials used in terms of the $\text{Ga}/(\text{Ga}+\text{In})$ ratio. The prepared films were comprehensively characterized using XRD, SEM-EDS and XRF. Results reveal that the above non-vacuum approach obviating the need for a selenization step is simple, quick and expected to have a large impact on the overall process economics for fabrication of CIGS thin film solar cells.

Keywords: CIGS thin film, Solar energy, Laser treatment, Non-vacuum, Nano-ink

1. Introduction

$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) thin film solar cells are among the most promising candidates for solar cell applications and have already reached high power conversion efficiencies above 20 % [1,2]. However, in recent years, the photovoltaic manufacturing technology has demanded low-cost processing techniques because of growing competitiveness of the solar cells market. Thus, in an effort to increase the cost-effectiveness of CIGS solar cells, several solution-based approaches have been explored. These have included electrochemical routes [3,4], spraying or spin coating of organometallic precursors [5], screen printing CIGS metal pastes [6], and printing nanoparticle-derived precursors [7,8]. The above mentioned approaches have yielded power conversion efficiencies in the range of 14–17% for CIGS thin film solar cells [9]. However, either a post-treatment in vacuum or a selenization step is essential in case of all the above mentioned processes to make a device-quality CIGS absorber thin film. In this context, to overcome the drawbacks of vacuum and toxic selenization processes, realization of a CIGS thin film absorber by intense pulsed Light (IPL) treatment of an applied CIGS layer has already been reported as a single step technique [11, 12]. In the present study, post-processing using a high-power laser has been explored to take advantage of its unique benefits, particularly in terms of rapid large area treatment. The successful use of this novel atmospheric process, which obviates the need for vacuum and eliminate the selenization step, to obtain dense, highly crystalline CIGS films from a CIGS precursor as well as from CIG and Se precursors without any additional heat treatment is highlighted herein.

2. Experimental details

2.1 Nano-ink preparation

Two approaches were adopted to formulate inks, one using CIGS particles and another using CIG metallic alloy and Se nanoparticles as described in the sections below.

2.1.1 Inks from CIGS nanoparticles

A commercially available $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$ (CIGS) powder (100 mesh) was used (American Elements, USA). The as-received powder was ball milled for 48 h to reduce particle size to sub micron size. Detailed milling experiments are discussed and reported by us [13]. The resulting CIGS powder was then mixed with polyethylene glycol to tailor its rheology and make it suitable for application by the doctor blade technique.

2.1.2 Inks from nanopowders of CIG metallic alloy and Se

Nanopowders of the metallic alloy $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})$ (CIG) (average particle size 50 nm) and Se (average particle size 80 nm), were procured (QS company, USA). As in case of the CIGS powder, polyethylene glycol was used as the organic binder to tailor the rheology of the above mixture for the doctor blade technique.

2.2. Deposition of precursor films

Films of dimensions 0.8 cm x 0.5 cm were applied by the doctor blade technique on a microscopic glass slides using the precursor inks described in Section 2.1. Prior to applying the films, the glass slides were cleaned by degreasing with acetone and IPA in an ultrasonicator.

2.3 Laser treatment

A 6kW fiber-coupled diode laser (Model: LDF 1000-6000, Laserline GmbH), integrated with a 6 axes robotic system, was used for the experimentation. The films applied by doctor blade technique on glass substrates as described in Section 2.1.1 and 2.1.2 were treated using the laser with the beam tailored to yield a 8 mm x 5 mm rectangular spot. Preliminary experiments were conducted by varying the laser power and scanning speed to achieve uniform treatment over the entire coating. Post treatment employing a laser power of 200 W and a scan speed of 125 mm/sec was found to yield the best results. Hence, detailed characterization was carried out on CIGS films treated with the above specified laser conditions.

2.4 Characterization of films

The phase constitution of the obtained films was determined using X-ray diffraction (XRD) analysis (XRD; $\text{Cu K}\alpha$ radiation, D8 Advancem, Bruker, Germany). Field emission scanning electron microscopy (FE-SEM; S-4300 SE/N, Hitachi, Japan) with EDS analysis was used to examine the surface morphology, microstructure and elemental composition analysis. The thickness of the films was measured using X-ray fluorescence spectroscopy (XRF; XDV-SDD, Fischer Switzerland).

3. Result and discussion

The prominent results obtained from the two approaches adopted to fabricate CIGS absorber films, using laser treatment of pre-placed inks prepared from either CIG metallic alloy and Se nanoparticles or CIGS particles, are discussed below.

3.1 Films using CIGS nanoparticles as precursor

The dense CIGS thin films prepared on a glass substrate using $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ powder as precursor were fully characterized after laser treatment. Recrystallization of CIGS was confirmed by XRD analysis, which also revealed that the annealed quaternary CIGS alloy films were monophasic with no evidence of

other/secondary phases. The XRD patterns of the CIGS precursor material and the $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin film obtained after laser treatment are shown in Fig 1. All the peaks in Fig 1b correspond to the chalcopyrite tetragonal polycrystalline structure of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ as evident from the good agreement with the reference pattern (JCPDS NO. 35-1102) for $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ and CIGS prior to laser treatment. The extremely sharp, well-defined chalcopyrite peaks are indicative of increase in grain size and crystallinity of CIGS alloy. This result indicates that the laser-treated CIGS ink retains the chalcopyrite structure even after melting and recrystallization, with no other phases being generated during the process.

The surface morphology of the obtained $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ film is shown in Fig 2 (b) and (c). The SEM images show that the CIGS thin film prepared is compact and dense. It is important to note that the morphology is indicative of melting and homogenization during the laser treatment compared to the CIGS particles that constituted the ink (Fig. 2(a)). The constitution of the obtained $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin film is consistent with the constitution of the CIGS precursor material in terms of the selected Ga/(Ga+In) ratio. Fig 2(d) shows the EDS analysis reveals a high degree of compositional uniformity with an average elemental composition of 24.63 at% Cu, 16.24 at% In, 7.82 at% Ga and 51.31 at% Se, closely matching the starting alloy composition of $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$. **The average thickness of the film measured by XRF was found to be 5.3 μm with standard deviation of 4.3%.** Although the laser treatment was carried out in air, no oxidation or phase segregation was observed. This could be attributed to both the very short interaction time of few milliseconds as well as the fact that the CIGS particles in the ink were coated with PEG. Further investigations are in progress to assess process parameter impact and to fully optimize the process to achieve best CIGS film quality.

3.2 Films using CIG metallic alloy and Se nanoparticles as precursor

CIGS thin films prepared on glass substrates employing an alternate approach of using $\text{CuIn}_{0.7}\text{Ga}_{0.3}$ and Se powders as precursors were also characterized following laser treatment. The XRD patterns of the CIG and Se precursor materials are shown in Fig 3(a) and Fig 3(b), respectively, while the XRD pattern of the obtained CIGS thin film is shown in Fig 3(c). The XRD pattern of the CIGS thin film reveals diffraction peaks corresponding to single-phase chalcopyrite CIGS without any impurity phases, consistent with the standard bulk crystal structure pattern of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ (JCPDS NO. 35-1102). The constitution of the obtained thin film after laser treatment also found to correspond to $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$, as separately confirmed by EDS. Its constitution is noted to be consistent with the constitution of the CIG and Se precursor materials in terms of the Ga/(Ga+In) ratio. The surface morphology of the $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ film is also shown in Fig 4 and found to be dense. **The average thickness of the film measured by XRF was found to be 3.6 μm with standard deviation of 3.5%.** In this case, the mechanism responsible for formation of CIGS from CIG and Se nanoparticles following laser treatment, despite the short interaction time of only few milliseconds, is yet to be understood and demands further investigation. However, a plausible explanation could be the high absorption of light by CIG and Se nanoparticles [12]. By virtue of the very high surface area-to-mass ratio of the precursor powders on account of their fine particle size, little energy is needed for reaction between these particles to form the final CIGS alloy. Moreover, the very low melting temperature of Se (217 °C) is expected to additionally drive the diffusion of Se and CIG and nucleation of CIGS [14]. Although the incorporation of Se is difficult to control during the alloying due to its low boiling point and high volatilization, the short interaction time during laser treatment process in the present investigation is helpful in alloying CIGS. The simple and quick single-step laser treatment process is expected to have a large impact on overall process duration for fabrication of CIGS thin film solar cells.

4. Conclusions

Dense CIGS thin films were prepared by laser treatment of pre-deposited inks, formulated using both CIGS particles as well as a mixture of CIG and Se particles as precursors. Melting and recrystallization of

monophasic CIGS was found to take place with no indication of any other/secondary phase generation. Highly crystalline, dense chalcopyrite structured $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin films were found to result from this novel non-vacuum method which does not require a separate selenization step. The laser treated CIGS films exhibited high crystallinity and compositional homogeneity with desired stoichiometry.

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Figure captions

Fig 1. XRD pattern of (a) CIGS nanoparticle material before laser treatment and (b) dense CIGS film obtained after laser treatment

Fig 2. SEM surface morphology of (a) untreated CIGS particles films (b) after laser treatment (c) image at higher magnification and (d) EDS result of the CIGS thin film after laser treatment.

Fig 3. XRD patterns of (a) Se nanoparticle precursor material (b) CIG metallic alloy precursor material and (c) CIGS film obtained by laser treatment

Fig 4. SEM micrograph of the surface morphology of a CIGS film obtained from CIG and Se precursor by laser treatment

Figure 1

Figure 2

Fig 2.

Figure 3

Figure 4

Fig 2.