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

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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 $CuIn_{0.7}Ga_{0.3}$ and Se nanoparticles precursor following laser treatment. The $CuIn_{0.7}Ga_{0.3}Se_2$ thin films obtained in both cases were consistent with the initial constitution of the precursor materials used in terms of the Ga/(Ga+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.

## 1. Introduction

$CuIn_{1-x}Ga_xSe_2$ (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

*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.

*Inks from CIGS nanoparticles*: A commercially available $Cu(In_{0.7}Ga_{0.3})Se_2$ (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.

*Inks from nanopowders of CIG metallic alloy and Se*: Nanopowders of the metallic alloy $Cu(In_{0.7}Ga_{0.3})$ (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

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was used as the organic binder to tailor the rheology of the above mixture for the doctor blade technique.

*Deposition of precursor films*: Films of dimensions 0.8 cm × 0.5 cm were applied by the doctor blade technique on a microscopic glass slides using the precursor inks described in "*Nano-ink preparation*" Prior to applying the films, the glass slides were cleaned by degreasing with acetone and IPA in an ultrasonicator.

*Laser treatment*: A 6 kW 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 "*Inks from CIGS nanoparticles*" were treated using the laser with the beam tailored to yield a 8 mm × 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/s was found to yield the best results. Hence, detailed characterization was carried out on CIGS films treated with the above specified laser conditions.

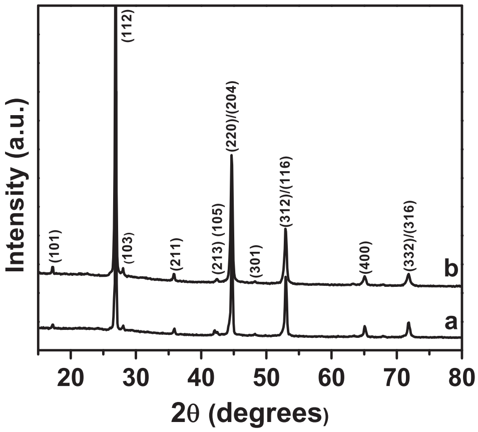

**Fig. 1.** XRD pattern of (a) CIGS nanoparticle material before laser treatment and (b) dense CIGS film obtained after laser treatment.

*Characterization of films*: The phase constitution of the obtained films was determined using X-ray diffraction (XRD) analysis (XRD; Cu *K*α 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.

*Films using CIGS nanoparticles as precursor*: The dense CIGS thin films prepared on a glass substrate using $CuIn_{0.7}Ga_{0.3}Se_2$ 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 $CuIn_{0.7}Ga_{0.3}Se_2$ 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 $CuIn_{0.7}Ga_{0.3}Se_2$ as evident from the good agreement with the reference pattern (JCPDS NO.

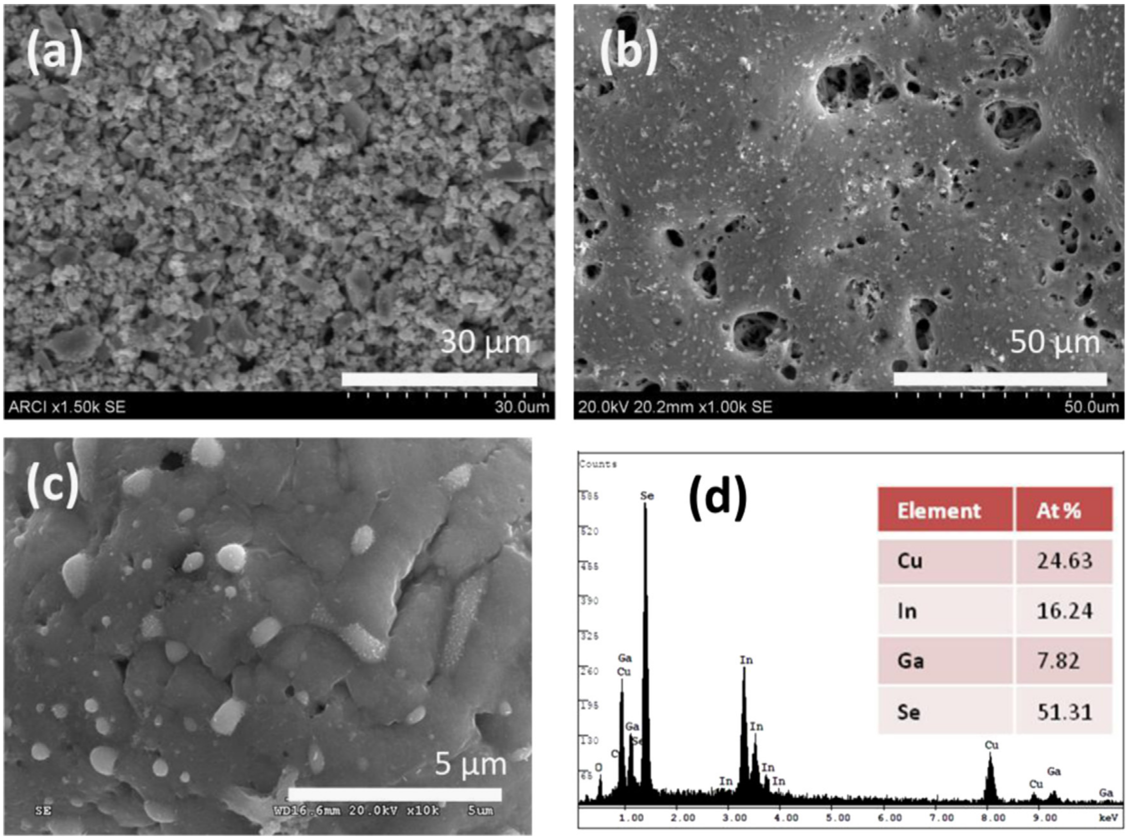

**Fig. 2.** SEM surface morphology of (a) untreated CIGS particles films (b) after laser treatment (c) image at higher magnification and (d) EDS result of the CIGS thin film after laser treatment.