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## A single source three-stage evaporation approach to CIGS absorber layer for thin film solar cells



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### ABSTRACT

A novel single source three-stage evaporation process has been developed to deposit  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  absorber layers well suited for thin films solar cells. By varying the electron beam current and substrate temperature for each stage, the film structure, texture, morphology, composition and composition profile can be controlled precisely. The thin films are well crystallized with compact and faceted grains, with sizes ranging from 1 to 1.5  $\mu\text{m}$  and also predominantly textured along [112] direction. The elemental compositions are well controlled with Cu:(In+Ga) of 0.85:0.87 and Ga:(In+Ga) of 0.25:0.26, which is within the range for the highest efficiency CIGS solar cells. Photoluminescence and Raman spectra verify that the as-deposited thin films have desired optical properties, and secondary ion mass spectra composition depth profiling suggests that the thin films have graded bandgaps. Thin film solar cells fabricated with such films achieved a power conversion efficiency of 10.6%. This approach avoids the complexity and large area uniformity issues of co-evaporation, and therefore is promising for in-line CIGS film fabrication using the evaporation method.

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### 1. Introduction

Chalcopyrite  $\text{Cu}(\text{InGa})\text{Se}_2$  (CIGS) is touted as being one of the most promising absorber materials for thin film solar cells due to its high absorption coefficient ( $\alpha \sim 10^5 \text{ cm}^{-1}$ ), tunable band gap and long-term stability [1–4]. CIGS thin films have been deposited by both vacuum (either co-evaporation or sputtering followed by selenization) [5–10] and non-vacuum (using either particulate or molecular precursors) methods [11–17]. Among all these approaches, the co-evaporation approach has been proven to be the most successful for high-efficiency CIGS thin film solar cell fabrication, achieving a record efficiency of 20.3% [18–20]. All high performance CIGS absorbers in solar cells have common qualities. They are overall Cu deficient [21], which increases the majority carrier (hole) concentration by increasing the density of Cu vacancies. The optimal Cu/(In+Ga) elemental ratio is typically from 0.8 to 0.9 [22,23]. Ga incorporation increases the band gap of  $\text{CuInSe}_2$  [24]. The Ga/In ratio is typically about 0.3, resulting in a band gap of 1.1 eV [21]. A Ga/In composition grading is also determined to be beneficial to reducing recombination at the back contact and increase open circuit voltage  $V_{oc}$ . It is also recognized that at the surface of the Cu deficient CIGS films there is an ordered defect compound (ODC) with a stoichiometry of  $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ .

The ODC is n-type, forming a p–n homojunction at the interface between the chalcopyrite and the ODC, reducing the interface recombination. A preferential texture of either (112) or 220/(204) is also required for high efficiency devices [25,26]. These qualities can be achieved by a three-step co-evaporation method developed at National Renewable Energy Laboratory (NREL): the first step is co-evaporation of In, Ga, and Se; in the second step, Cu and Se are deposited at a higher temperature to allow for diffusion and intermixing of the elements; in the final step, In, Ga, and Se are again deposited to make the overall composition Cu deficient [22,23]. The high efficiency achieved by the co-evaporation technique makes the performance of CIGS thin film solar cells compare favorably even with crystalline Si solar cells. However, several issues associated with the co-evaporation make this process difficult to be scaled up for commercial applications. Among them, large area uniformity and the related difficulty of co-evaporating elements in an inline system, large capital expense for the multisource co-evaporation equipment, and high thermal budget. It is therefore highly desirable to develop an approach that can reproduce the film qualities by the NREL method, while circumventing its drawbacks. Recently a two-step, one-source process for CIGS thin film deposition has been reported, where a non-stoichiometric amorphous CIGS film was first deposited by electron beam evaporation and then annealed in a separate vacuum chamber to crystallize the film [27]. However, device quality films with the right stoichiometry and band gap grading have not been obtained, and no solar cell performance was reported.

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Herein, we report a novel single source three-stage evaporation route to fabricating device-quality CIGS thin films. We use a conventional electron beam (e-beam) evaporator equipped with a substrate heater and a compound source with a nominal composition of  $\text{Cu}_1\text{In}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  for CIGS thin film deposition. The beam current ( $I_B$ ) and substrate temperature ( $T_s$ ) were varied for each stage to control the composition, composition gradient and phase. Both parameters were determined by systematic investigations of the structure and composition for films obtained from each stage. The aim is to achieve an overall composition of Cu/(In+Ga) ratio of 0.8–0.9, Ga/(In+Ga) ratio of 0.2–0.3 and graded composition along film normal, all of which are requirements for high performance CIGS absorbers. We show that the crystal structure, texture, morphology, overall composition, and composition gradient of the films deposited with this technique closely mimic those obtained by the co-evaporation method. Applying this technique, we fabricated CIGS thin film solar cells with a power conversion efficiency of 10.6%. This technique enables the deposition of CIGS thin films using a conventional one-source-at-a-time evaporator, and device quality films are formed *in situ* without selenization. This method circumvents the high cost associated with co-evaporation equipment and most importantly, could solve the large area uniformity issue associated with co-evaporation, thus could open up a facile pathway to large scale commercial application of CIGS thin film solar cells.

## 2. Experimental methods

### 2.1. Sample fabrication

CIGS thin films were deposited on 3 mm thick SLG substrates coated with a 450 nm molybdenum layer or on bare SLG substrates by a conventional e-beam evaporator equipped with a substrate heater in a base vacuum of  $2 \times 10^{-7}$  Torr. The Mo layer acting as a back electrode was sputtered on SLG substrates using a DC sputtering system, with a sheet resistance  $< 1 \Omega \text{ sq}^{-1}$ . For high efficiency solar cell applications, an optimized amount of sodium in the form of a 3-nm-thick NaF layer was deposited onto the Mo-coated SLG substrates by e-beam evaporation prior to the three-stage deposition. CIGS powder with a nominal composition of Cu, In, Ga and Se in atomic ratio of 25, 12.5, 12.5 and 50 were evaporated from a single crucible. The thickness of the as-deposited film was controlled to be 1.5  $\mu\text{m}$ . In order to check the effects of evaporation power on chemical composition, single layer thin films were deposited by varying the beam current from 20 mA to 110 mA at a fixed voltage of 6.8 kV. Once optimal deposition parameters were obtained, device quality thin films were deposited with different beam current and substrate temperature based on a three-stage evaporation approach shown in Fig. 1. The deposition time for the three stages were 15 min, 40 min, and 10 min, respectively, to obtain the desired overall composition and composition gradient. During the first stage, the substrate was heated at 340 °C; during the second and third stages, the substrate temperature was ramped up to and kept at 550 °C. The beam current was fixed at 30 mA, 110 mA and 20 mA for each stage, respectively. For solar cell fabrication, a 50 nm thick CdS layer was deposited onto the as-deposited CIGS thin film via chemical bath deposition and then annealed at 200 °C for 60 s; subsequently, an i-ZnO/ZnO:Al bilayer was sputter deposited and the cells were completed using Ag paste contact fingers.

### 2.2. Characterizations

The thickness, morphology and chemical composition of the films were examined in a Carl Zeiss Auriga CrossBeam focused ion beam/field-emission SEM (FIB/SEM) system. The crystal structure

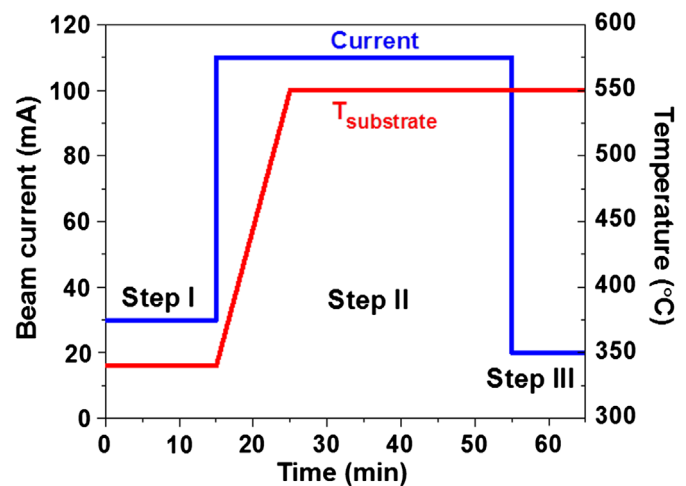


Fig. 1. A typical process profile of the single source three-stage evaporation approach.

was analyzed by an X-ray diffractometer operated at 40 kV and 30 mA using Cu- $\kappa\alpha$  radiation a Bragg-Brentano geometry using a Rigaku Ultima IV instrument with Cu KR radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The PL measurements were performed by exciting the thin film samples with a 780 nm laser radiation. Raman scattering experiments were conducted in back scattering geometry with a 514.5 nm Ar-ion excitation source using a Jobin-Yvon Horiba Labram HR instrument coupled to an Olympus BX41 microscope. The depth profiles of the elemental composition were studied by SIMS measurements using an Ion-ToF V 5-100 time-of-flight secondary ion mass spectrometer equipped with  $\text{Cs}^+$  as a primary ion with an acceleration voltage of 3 kV. The electrical properties of the as-deposited films were evaluated by a four-point probe and Hall measurement system. Current–voltage ( $I$ – $V$ ) characteristics were measured by Keithley 2400 using simulated sunlight at AM-1.5 produced by a 300 W Oriel Solar Simulator.

## 3. Results and discussion

As mentioned in the introduction, the CIGS composition is the key to high efficiency solar cells. To determine deposition parameters to be used in each stage of the three-stage process, the film composition as a function of beam current is systematically investigated. The film composition as measured by energy dispersive X-ray (EDX) spectroscopy as a function of  $I_B$  is shown in Fig. 2a. It can be seen that Cu composition increases monotonically with increasing  $I_B$ , initially slowly then rapidly at  $I_B > 70$  mA. Less than 7 at% of Cu is incorporated into the films when  $I_B$  is lower than 70 mA. As  $I_B$  goes up to 80 mA, the content of Cu increases significantly to 15.58 at%, which is due to the enhanced vapor pressure at higher beam current since Cu has the highest melting point and the lowest vapor pressure compared to other three elements In, Ga and Se. As  $I_B$  further increases to 110 mA, the content of Cu increases to 27.05%. On the other hand, the Se content remains nearly constant at about 50% for  $I_B$  of 30–50 mA and above 80 mA, while reaching up to 60% at the range of 60–70 mA, suggesting the formation of different Se compounds. These compounds can be identified by X-ray diffraction (XRD) as discussed later. The In content increases as  $I_B$  goes up to  $\sim 50$  mA and then decreases with further increasing  $I_B$ . The Ga content shows more complicated behavior: it first decreases with increasing  $I_B$  as  $I_B$  goes up to 60 mA, increases with  $I_B$  between 60 and 80 mA; then decreases again for  $I_B > 80$  mA. It is more illustrative by plotting Cu/(In+Ga) and Ga/(In+Ga) ratios as a function of  $I_B$ , as shown in

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