

# Cu(In,Ga)Se<sub>2</sub> Thin Film Preparation from a Cu(In,Ga) Metallic Alloy and Se Nanoparticles by an Intense Pulsed Light Technique

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The main contribution of this paper is the development of a novel process for the formation of copper indium gallium diselenide (CIGS) films. CIGS films with a thickness of 4  $\mu\text{m}$  and grain size from 0.3  $\mu\text{m}$  to 1  $\mu\text{m}$  were prepared from a Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>) (CIG) metallic alloy and Se nanoparticles by the intense pulsed light (IPL) technique. The melting of the CIG and Se nanoparticles and nucleation of CIGS occurred in a very short reaction time of 2 ms. It is believed that the Se diffuses into the CIG lattice to form the CIGS chalcopyrite crystal structure. The tetragonal chalcopyrite crystal structure was confirmed by x-ray powder diffraction (XRD), while the microstructure and composition were determined by field-emission scanning electron microscopy (FESEM), energy-dispersive x-ray spectroscopy (EDAX), and x-ray fluorescence (XRF) spectroscopy.

**Key words:** CIGS thin film, chalcopyrite, intense pulsed light, solar cells

## INTRODUCTION

Chalcopyrite, a thin film of copper indium gallium diselenide (CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>), more often referred to as CIGS, has become the subject of considerable interest and study for semiconductor devices in recent years. These devices are also referred to as I-III-VI<sub>2</sub> devices, according to their constituent elemental groups. CIGS is of particular interest for solar cell absorber applications because its solar energy to electrical conversion efficiency exceeds 19.9% in active areas, which is quite high for current state-of-the-art solar cell technologies.<sup>1</sup>

For CIGS thin films, very few fabrication methods are reported in the literature. The most common method of fabricating a CIGS thin film is the sequential evaporation of metals.<sup>2,3</sup> Several researchers have attempted various techniques other than coevaporation to develop CIGS absorber

layers, for example, sequential sputtering of precursors,<sup>4</sup> reactive sputtering in H<sub>2</sub>Se,<sup>5</sup> hybrid sputtering and evaporation,<sup>6</sup> rapid thermal processing (RTP),<sup>7</sup> stacked elemental layer (SEL) technique,<sup>8</sup> selenization of amorphous CuIn-O precursors,<sup>9</sup> sprayed metal oxide precursors followed by selenization,<sup>10,11</sup> electrodeposition,<sup>12</sup> and CIGS thin film preparation from nanoparticle precursors.<sup>13</sup> However, in all the above-mentioned methods, toxic selenization and vacuum treatment are unavoidable. The general disadvantage of most of the direct absorber formation techniques is the fact that high substrate temperatures (i.e., 300°C to 550°C) need to be maintained during film growth. The high-temperature processing and selenization treatment used in solar cell fabrication are neither cost effective nor easily scalable to high-volume production.

The major drawback of selenization with H<sub>2</sub>Se or Se fluxes is the high toxicity of the gas, which presents serious hazards to humans in large-scale production environments. Furthermore, the

high-temperature reduction and selenization step makes it impractical to make CIGS solar cells on temperature-sensitive polymer substrates. The substrates would warp, melt or degrade at such high temperatures in the presence of reducing agents.

The use of bulk CIGS as the starting material is challenging, as bulk CIGS has a melting point around 1000°C. However, since most of the flexible substrates cannot withstand such a high temperature, it is not possible to melt bulk material directly onto a substrate. Even glass will have serious warping problems at this temperature. Moreover, the energy requirements needed for high-temperature manufacturing at 1000°C will incur substantial cost. Thus, there is a need for fabrication methods for CIGS thin film-based solar cells that address CIGS absorber layer preparation without selenization and vacuum treatment.

In this paper we report CIGS thin film preparation from CIG metallic alloy and Se nanoparticles using the intense pulsed light (IPL) technique and the characterization of prepared films by x-ray powder diffraction, SEM-EDAX, and XRF analyses. To the best of our knowledge, this is the first report of CIGS film preparation from CIG and Se nanoparticles without high-temperature vacuum technology and selenization treatment.

## EXPERIMENTAL PROCEDURES

The precursors, metallic alloy Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>) (CIG) nanoparticles (average particle size 50 nm) and Se nanoparticles (average particle size 80 nm), were used as received from QuantumSphere Inc. The metallic alloy CIG and Se nanoparticles were mixed in an appropriate molecular ratio with an organic binder (polyethylene glycol) to tailor the rheology of the mixture for the doctor blade method. Films of 1 cm<sup>2</sup> area were prepared by the doctor blade method on a microscopic glass slide substrate and allowed to dry in air. The microscopic glass slides used were cleaned and degreased with acetone in an ultrasonicator. The prepared films were covered with a glass slide before being exposed to an IPL lamp. The light energy used to prepare the films was 5 J cm<sup>-2</sup> to 20 J cm<sup>-2</sup>. All the experiments were performed in air and at room temperature.

A home-built IPL system consisting of a Xenon flash lamp, and a power and pulse supplier/controller was used for CIGS film preparation. The power and pulse controller is designed to adjust the light energy and the pulse width in the ranges of 1 J cm<sup>-2</sup> to 50 J cm<sup>-2</sup> and 0.1 ms to 30 ms, respectively.

The crystal phases of the prepared films were determined by an x-ray powder diffractometer (XRD) (X'pert, Cu K<sub>α</sub> radiation) with the Bragg angle ranging from 15° to 80°. Field-emission scanning electron microscopy (FE-SEM) (JEOL, JSM-67) was used to examine the surface morphology microstructure and cross-section of the

films. The composition was analyzed with energy dispersion by x-ray analysis (EDAX). The compositional uniformity of the samples was determined by x-ray fluorescence (XRF) spectroscopy with K<sub>α1,2</sub> intensity measurements. The K<sub>α1,2</sub> scans were recorded by a sequential XRF wavelength-dispersive spectrometer (SEA6000VX, SII Nanotechnology Inc.; 50 W tungsten tube, Vortex Silicon Drift Detector).

## RESULTS AND DISCUSSION

CIGS films can be prepared from CIG and Se nanoparticles by the IPL technique. Figure 1 shows the XRD pattern of Se nanoparticles, Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>) (CIG) metallic alloy nanoparticle precursors, and an as-prepared CIGS film at 20 J cm<sup>-2</sup> IPL light energy, clearly showing planar reflections of CIGS in good agreement with the reported references (JCPDS No. 35-1102) of Cu(In<sub>0.7</sub>Ga<sub>0.3</sub>)Se<sub>2</sub> with the tetragonal chalcopyrite structure. The CIG and Se nanoparticles are believed to form the CIGS tetragonal chalcopyrite structure via reactive sintering by IPL. It is expected that selenization can be done without changing the microstructure, and selenium may just diffuse into the CIG lattice. There is no evidence of selenium peaks in the XRD pattern of prepared CIGS films, which indicates that all of the Se nanoparticles were used off to diffuse into the CIG lattice. Figure 2 shows an XRD pattern of CIGS films prepared at 5 J cm<sup>-2</sup>, 15 J cm<sup>-2</sup>, and 20 J cm<sup>-2</sup> light energy, indicating that the minimum (5 J cm<sup>-2</sup>) light energy is sufficient to form CIGS from CIG and Se precursors. However, a small amount of unreacted CIG precursor remains in the film, as confirmed by the XRD patterns. The peaks marked with an asterisk in Fig. 2 correspond to unreacted CIG metallic alloy and do not correspond to other phases of CIGS or any other elements, as confirmed by XRD of CIG metallic alloy precursor particles. It is observed that the XRD peaks corresponding to unreacted CIG have a much lower intensity as compared with the CIGS phase. The amount of unreacted CIG in the film prepared at 20 J cm<sup>-2</sup> light energy was found to be almost negligible, as confirmed by the very small CIG peaks shown in Fig. 2.

Surface morphology images of a CIGS film prepared at 20 J cm<sup>-2</sup> light energy are shown in Fig. 3a and b. An overall surface morphology of compact grains separated by grain boundaries with very few voids is seen. The grain size of the CIGS film prepared at 20 J cm<sup>-2</sup> light energy is in the range from 0.3 μm to 1 μm, as shown in Fig. 3b. Grain size measurements was also carried out using the Scherrer equation,  $D = k\lambda/\beta\cos\theta$ , where  $D$  is the crystallite size,  $k$  is a constant (0.9),  $\lambda$  is the wavelength of the x-ray radiation,  $\beta$  is the line width (obtained after correction for instrumental broadening), and  $\theta$  is the angle of diffraction. The grain size obtained from XRD data is 0.76 μm. The

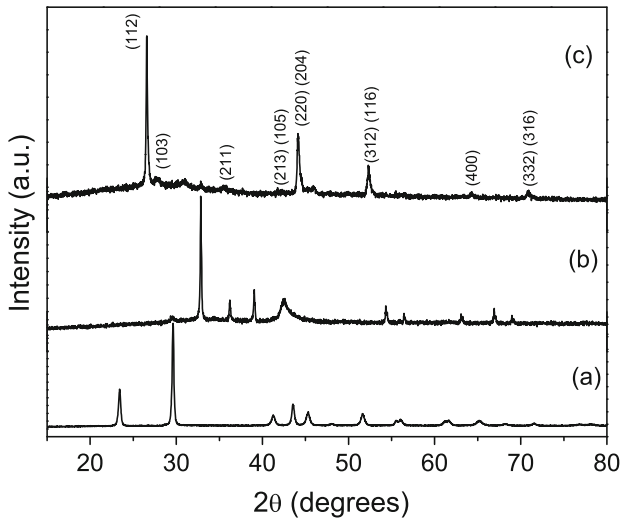


Fig. 1. XRD pattern of (a) Se, (b) CIG precursor materials, and (c) CIGS film prepared at  $20 \text{ J cm}^{-2}$  IPL light energy.

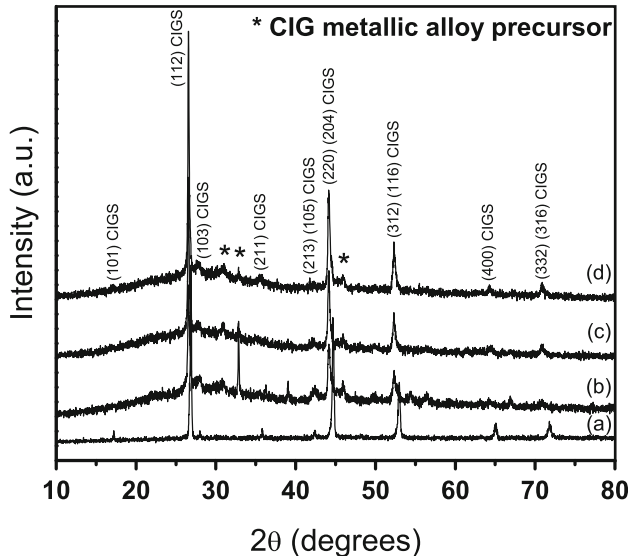


Fig. 2. XRD pattern of (a) commercially available CIGS nanoparticles, and CIGS films prepared from CIG and Se nanoparticles at various light energies: (b)  $5 \text{ J cm}^{-2}$ , (c)  $15 \text{ J cm}^{-2}$ , and (d)  $20 \text{ J cm}^{-2}$ .

morphology of larger grains clearly indicates diffusion and sintering of the particles in the film. The mechanism of CIGS formation and crystallization by IPL is not yet clear. However, it may be explained based on the melting point of CIG ( $550^\circ\text{C}$ ) and Se ( $217^\circ\text{C}$ ). The melting of the CIG and Se nanoparticles and nucleation of CIGS occurred in a very short reaction time. Figure 3c shows a cross-sectional SEM image of a CIGS film prepared at  $20 \text{ J cm}^{-2}$  light energy, where large grains extending from the back to the front of the film are seen. The thickness of the film is about  $4 \mu\text{m}$ , and adhesion between the CIGS film and glass substrate is found to be reliable.

This qualitative analysis of the films was confirmed by EDAX. Figure 3d shows a representative EDAX spectrum of a CIGS film prepared at  $20 \text{ J cm}^{-2}$  light energy, confirming the near-stoichiometric composition of  $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$  of the film. The presence of only Cu, In, Ga, and Se in Fig. 3d confirms that no oxidation of the respective elements occurred during the CIGS formation process using the IPL technique. The composition of elements in the film prepared at  $20 \text{ J cm}^{-2}$  light energy nearly matches the ratio of elements in the starting materials precursors, i.e.,  $\text{Cu}:\text{In}:\text{Ga}:\text{Se} = 25:17.5:7.5:50$ . This was confirmed by XRF studies, which reveal a high degree of compositional uniformity. The average value derived after several scans done at one point of the printed area is  $25.04:15.99:7.67:51.3$  (Table I). The elemental analysis confirms that the composition is very close to that of the starting materials. The thickness of the film was about  $4 \mu\text{m}$  throughout the printed area. It is observed that the Cu, In, Ga, and Se concentrations remained virtually constant through the entire layer of the film. This result confirms that the IPL process eliminates the grading of gallium and indium in the CIGS structure and resulted in homogeneous single-phase material. The elemental composition and the thickness across the printed area confirmed by XRF are in good agreement with the SEM and EDAX results.

The formation mechanism of CIGS from CIG and Se nanoparticles by IPL is not fully understood. However, it may be described based on the absorption of light by CIG and Se nanoparticles. CIG and Se nanoparticles are black and therefore very light absorbing. These particles have very high surface-area-to-mass ratio; hence, very little light is needed to heat the particles. The intense pulsed light from the xenon flash lamp can form a CIGS film from CIG and Se nanoparticles in a very short time of a few milliseconds. Such a short reaction time prevents oxidation of the elements and second phase generation. Another valuable benefit of reactive IPL sintering is that the CIG and Se materials can be sintered to form CIGS without damaging the glass or temperature-sensitive flexible polymer substrate materials. Another possible reason might be the sintering time of a few milliseconds, which is much shorter than the thermal equilibration time required to heat the substrate.

## CONCLUSIONS

CIGS films were prepared from CIG metallic alloy and Se nanoparticles using the intense pulsed light technique. XRD, SEM-EDAX, and XRF analysis results support the formation of CIGS films without toxic selenization or vacuum conditions. The advantages of the current process are a very short reaction time (milliseconds) and compatibility with temperature-sensitive flexible substrates without vacuum or selenization treatment. The prepared

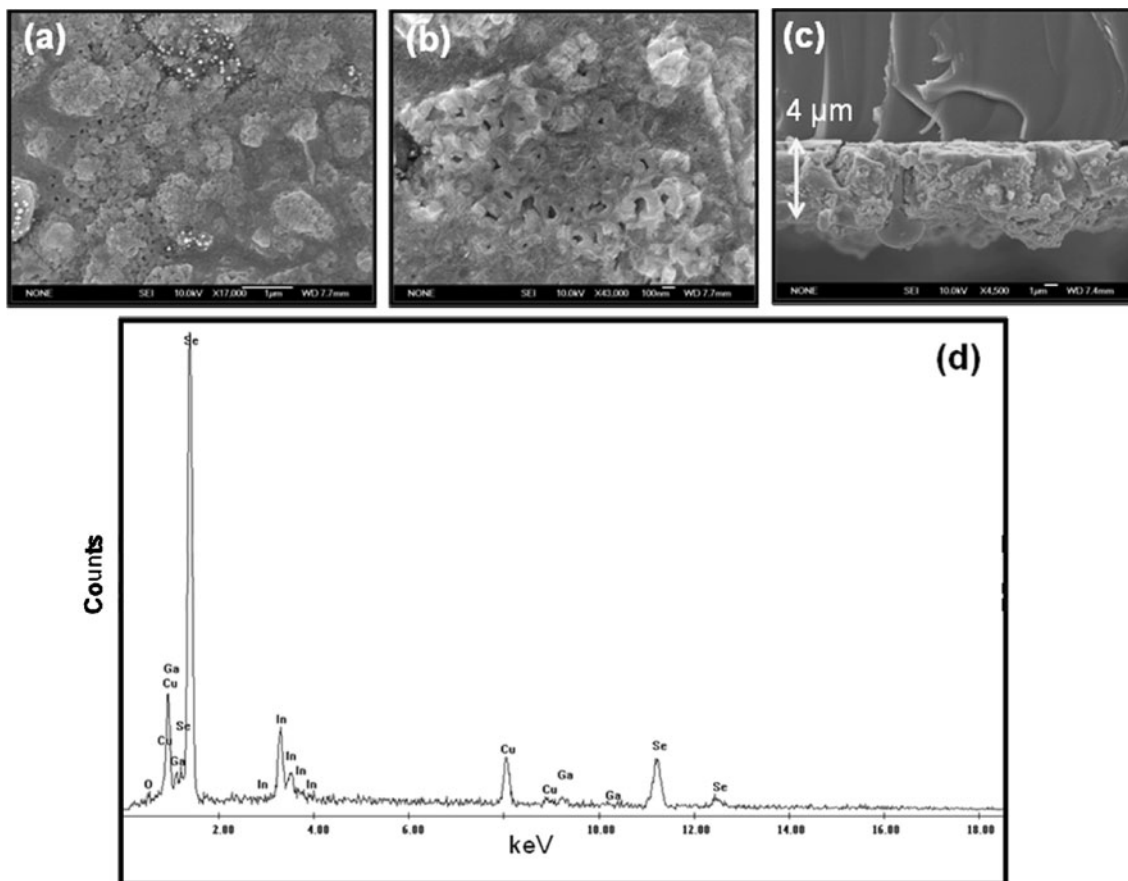


Fig. 3. (a) Overall surface morphology SEM image, (b) image at higher magnification, (c) cross-section SEM image, and (d) EDAX spectrum of CIGS film prepared on glass substrate at 20 J cm<sup>-2</sup> light energy.

**Table I. XRF analysis of as-prepared CIGS film at 20 J cm<sup>-2</sup> light energy**

Scan	CIGS Thickness (μm)	Elemental Analysis (%)			
		Cu	In	Ga	Se
1	3.90	25.36	16	7.83	50.81
2	3.89	25.14	16.3	7.69	50.86
3	4.1	25	15.69	7.45	51.85
4	4.02	24.93	16.75	7.47	50.85
5	4.01	24.94	15.21	7.72	52.13
6	3.85	25.05	16.35	7.92	50.68
7	3.9	25.3	16.12	7.9	50.68
8	4.41	23.9	14.39	7.3	54.41
9	3.88	25.54	16.38	7.69	50.38
10	4.02	25.2	16.73	7.69	50.38
Average	3.99	25.04	15.99	7.67	51.3
Std. deviation	0.166	0.445	0.729	0.203	1.237

CIGS film can potentially be used as an absorber layer for solar cells. Presently the material's photoactivity is low because a minute amount of unreacted CIG precursor remained in the film. The detailed mechanism for CIGS formation by the intense pulsed light technique is under investigation.

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