On the Effect of Indium Chloride Dose on the Recrystallization of $Cu(In,Ga)Se_2$ Thin Films and associated Devices

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***Abstract*— Cu(In,Ga)Se_2 thin films deposited by a single-stage co-evaporation process at 350 ºC on molybdenum coated soda lime glass substrate were annealed post-deposition in $InCl_3$ vapor. The amount of $InCl_3$ and Se was varied. The annealing treatment was done at 450 ºC for 30 minutes. Increase in grain size was observed after the treatment in all cases by X-ray diffraction. Device performance was low, but improved slightly after KCN etching.**

Keywords*— *Cu(In,Ga)Se_2, recrystallization, annealing, $InCl_3$

I. Introduction

High-throughput production process make thin film photovoltaics a potential alternate to silicon based solar cells. Such a process is the fabrication of CdTe photovoltaic modules. The high-rate deposition of CdTe layer includes the annealing in $CuCl_2$ vapor, recrystallizing the CdTe and resulting in enhanced cells performance [1, 2]. Similarly, the application of metal halides recrystallization in the case of $Cu(In,Ga)Se_2$ or CIGS could potentially produce high efficiency devices. One has to keep in mind that an optimum compositional profile, including proper gallium grading and ideal Cu content, is likely required for high device performance, while only large grain size does not always yield higher efficiency devices [3].

In this work, we explore the ex-situ recrystallization of CIGS using indium chloride vapor treatment at various doses and its effect on both thin film properties and device performance.

II. Experimental methods

CIGS thin films were deposited at substrate temperature of 350 ºC by a single-stage co-evaporation process onto molybdenum coated soda-lime glass. The composition of the samples determined by x-ray fluorescence (XRF). After deposition, half of the samples were placed in a quartz tube with different amount of $InCl_3$ for recrystallization (along with an amount of elemental Se to ensure overpressure of Se). The quartz tubes were then sealed and placed into a furnace. The annealing treatment was performed at a constant temperature of 450 ºC for 30 minutes. After annealing samples were cool to room temperature and were rinsed with deionized water to remove any deposit on the surface. The other half of the samples were kept as reference. Some of these samples were exposed to KCN etching for surface treatment.

The resulting samples were characterized by several methods. The crystallographic structures analysis was done by symmetric θ-2θ X-ray diffraction and analyzed using the International Center for Diffraction Data (ICDD) database. Cross-section morphological analysis were performed by scanning electron microscope (SEM). The photovoltaic characteristics were evaluated by external quantum efficiency (QE) measurements (QEX7, PV measurements Inc.) and current density-voltage (J-V) measurements (IV5, PV measurements Inc.) done under AM 1.5G with a light intensity of 100 mW/cm^2 at 25°C.

A summary of the various types of samples is presented in Table I. Both the dose of $InCl_3$ and Se were changed giving rise to 3 types of samples. The duration of annealing was kept constant at 30 minutes.

TABLE I. Process parameters for the Samples Recrystallized in the Annealing Chamber

Sample	Se (g)	$InCl_3$ (g)	Time (min)
I	0.25	0.25	30
II	0.10	0.10	30
III	0.03	0.03	30

III. Results and discussions

The amount of Se and $InCl_3$ was varied to optimize the vapor during recrystallization. The details of the amount included are indicated in Table I. The composition measured by XRF indicated a condensation of Se and In on the samples, when an excess quantity was used (as in sample I). The amount of Se and $InCl_3$ was then optimized (for sample II), but excess Se still appeared. Sample III had a more uniform composition. As can be seen in Figure 1, the cross section SEM taken on all samples revealed an evolution of the grain size, with samples annealed having larger crystallite sizes as compared to the reference samples.

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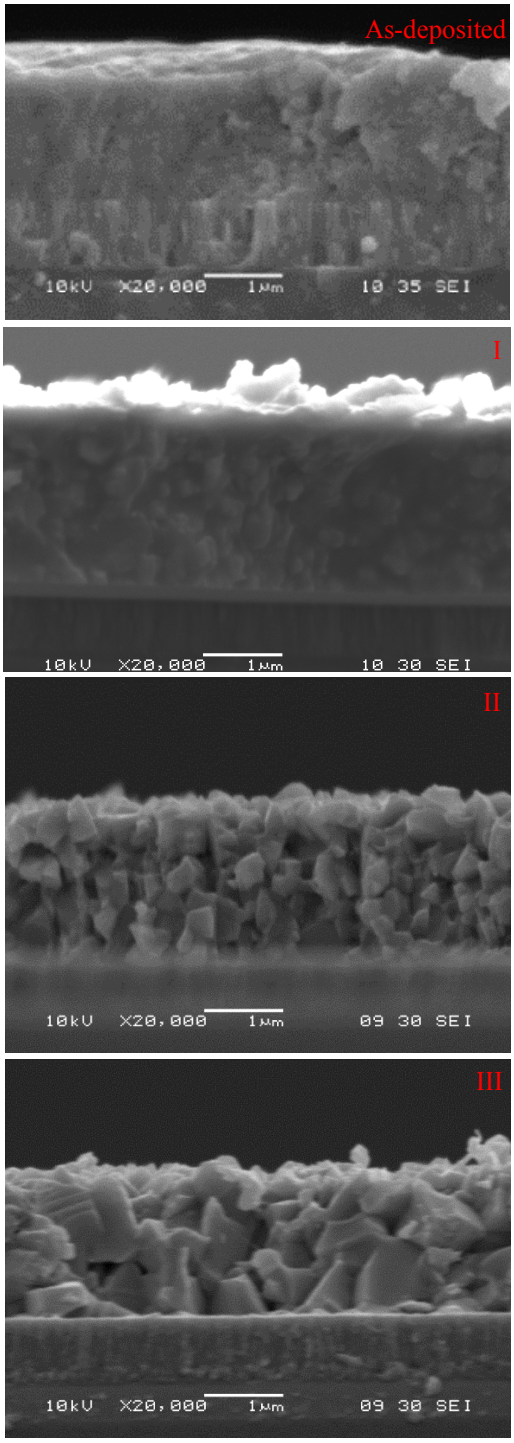


Fig. 1. Cross-section Scanning Electron Microscopy micrographs of CIGS films: as-deposited and recrystallized at 450 °C by $InCl_3$ vapor treatment at various doses (see Table I).

XRD characterization was performed on the films. XRD profiles of the samples annealed with $InCl_3$ with different doses are shown in Figure 2 and the peak properties are shown in Table II. XRD profiles shows that the samples have a strong (112) orientation and no change of preferential orientation occurs due to the recrystallization. All samples after recrystallization have larger peak intensities and smaller full width a half maximum (FWHM) indicating larger cystallite sizes for these samples.

TABLE II. XRD RESULTS FOR AS-DEPOSITED AND $INCL_3$ TREATED SAMPLES AT 450 °C

Sample	Peak (112)/(220)	Int.I	FWHM
As-deposited	26.7/44.6	395/73	0.41/0.73
I	27.0/44.9	703/128	0.22/0.51
II	26.9/44.7	1183/392	0.26/0.42
III	27.0/44.7	1188/216	0.33/0.35

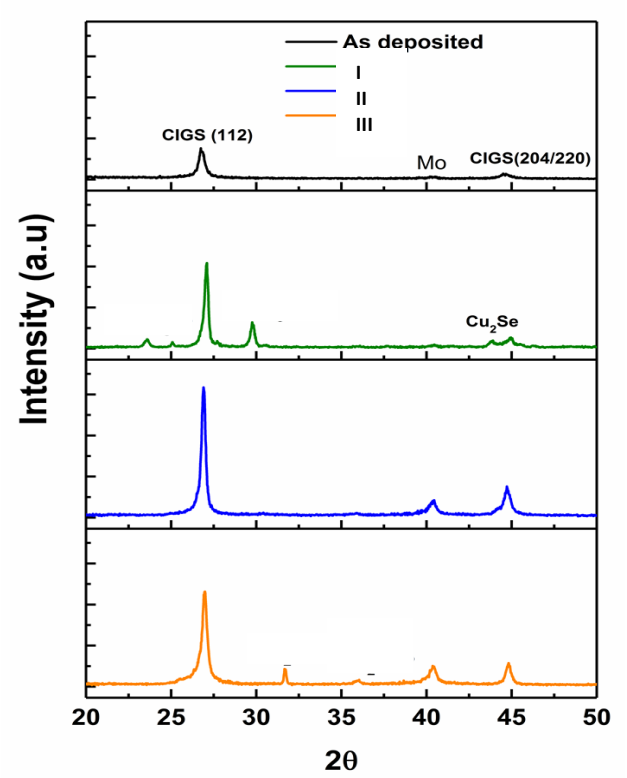


Fig. 2. XRD plots ((112) and (220)/(204) peaks) for as-deposited and $InCl_3$ treated CIGS samples.

A small shift in the peak position for all samples after recrystallization might indicate a change in gallium distribution or a change in the film strain. This will be confirmed by secondary ion mass spectrometry measurements.

Raman Spectra were measured at RT before and after annealing at 450 °C for samples of type III. The Raman spectra shows a clear intense peak ascribed to A1 mode of CIGS compound with a lower FWHM compared to the as-deposited samples due to better crystallinity. The A1 peak of the annealed sample shifted towards $CuInSe_2$. The peak at 252 cm^{-1} for the as-deposited sample might be related to $Cu_{2-x}Se$. The spectrum

also shows a broader peak or the as-deposited samples due to the contribution of E and B_2 modes of CIGS, implying the presence of In-Se and Ga-Se phases.

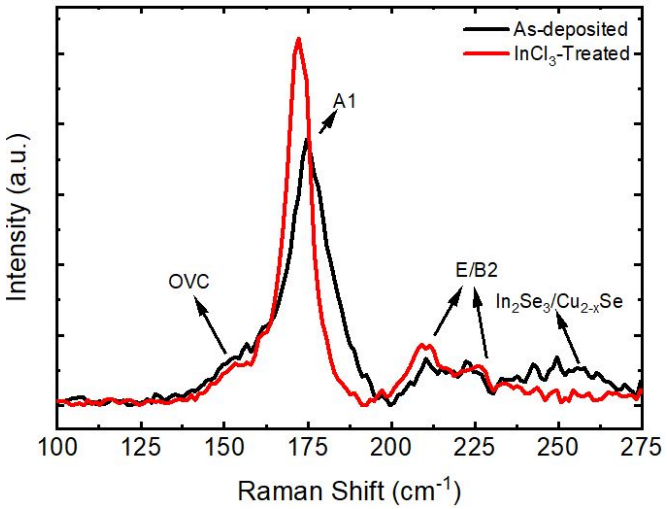
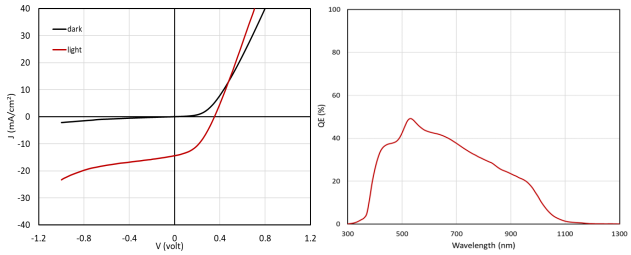


Fig. 3. Raman spectra of as-deposited and $InCl_3$ treated CIGS samples III at 450 ºC.

All types of samples were processed into full devices. However, most of the devices resulted in shunted devices, except for devices of Type III. The representative current-voltage and external quantum efficiency curve for devices of Type III are shown in Figure 3. Table III shows the corresponding photovoltaic parameters. The device performance was lower than expected. To improve the device performance, surface treatment with KCN was performed. KCN is known to remove metallic rich phase at interface, improve junction and mitigate shunting. While there can be a significant removal of alternate phases from the film's surface, the actual CIGS material remains generally untouched. The overall device performance increases after the KCN treatment as can be seen from Figure III and Table III, mostly due to an increase in short circuit current density.



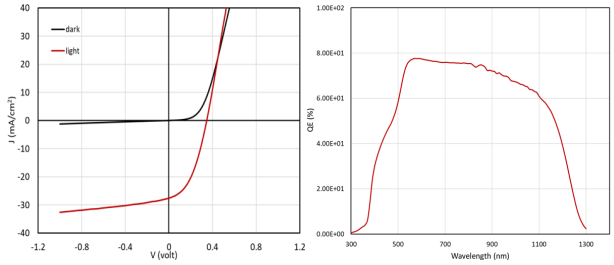


Fig. 4. Representative I-V and QE curves for samples of Type III with and without KCN treated CIGS samples.

TABLE III. XRD RESULTS FOR AS-DEPOSITED AND $INCL_3$ TREATED SAMPLES AT 450 ºC

Sample	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
$InCl_3$	0.35	14.4	42	2.1
KCN	0.34	27.5	42.6	4.0

IV. CONCLUSION

The recrystallization of CIGS thin films by $InCl_3$ vapor treatment at various doses was studied by morphological and structural analysis. Grain enhancement was observed by SEM in treated samples in all cases. A decrease in FWHM and an increase in peak intensity were observed by XRD, suggesting a change in crystallinity. The performance of most of the devices was poor, with a lot of shunting. The performance was slightly improved after KCN treatment, which tends to remove metallic phases and reduce surface roughness. Further improvement in the precise dose, annealing temperature and optimum composition is still needed to improve the grain quality and device performance.

ACKNOWLEDGMENT

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