

# **Cu(In,Ga)Se<sub>2</sub> Thin-Film Evolution During Growth— A Photoluminescence Study**

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# Cu(In,Ga)Se<sub>2</sub> THIN-FILM EVOLUTION DURING GROWTH - A PHOTOLUMINESCENCE STUDY

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## ABSTRACT

An in-depth understanding of the defect formation and resulting changes in material quality occurring during the Cu(In,Ga)Se<sub>2</sub> growth process is vital to the successful and widespread use of this photovoltaic material. In an attempt to develop such an understanding, we investigated the growth of Cu(In,Ga)Se<sub>2</sub> thin films from (In,Ga)<sub>2</sub>Se<sub>3</sub> precursors. This was achieved by using energy- and time-resolved photoluminescence spectroscopies to characterize a series of thin films, each removed at a different point along the reaction pathway of the “three-stage” growth process. The resulting thin films are representative of the absorber layer as it proceeds from a Cu-rich to Cu-poor state. The experimental results support a growth model incorporating changes in the dominant defect states and improvement in the recombination lifetime during this final stage of the growth process as the material transitions to a Cu-poor phase.

## EXPERIMENTAL

The Cu(In,Ga)Se<sub>2</sub> thin films were deposited on molybdenum-coated glass substrates by physical vapor deposition in a multisource bell jar system. The specific time-dependent fluxes for each of the independent source materials are shown schematically in Figure 1. This “three-stage” process [1] starts with the formation of an (In,Ga)<sub>2</sub>Se<sub>3</sub> layer. As growth proceeds, this layer is reacted with Cu and Se to form a mixed composition of Cu(In,Ga)Se<sub>2</sub> and Cu<sub>2-x</sub>Se. The growth process is completed by the addition of In, Ga, and Se to remove the Cu<sub>2-x</sub>Se phase and adjust the Cu(In,Ga)Se<sub>2</sub> composition to slightly Cu-poor. This process results in extremely high-quality material and has produced the highest-efficiency CIGS solar cell ever reported [2].

The samples, labeled **a** through **d** in Figure 1, were extracted at varying times during the third stage of the growth process. Consequently, these thin films are representative of the absorber layer as it proceeds from a Cu-rich to Cu-poor state. Two separate sets of thin films were grown for this study. One set of low-Ga absorbers was grown such that the Ga/(In+Ga) was about 0.26, and one set of high-Ga absorbers was grown with a Ga/(In+Ga) ratio of about 0.56. Specific Cu/(In+Ga) ratios are listed in Table 1.

In an attempt to understand the effect of Cu<sub>2-x</sub>Se on the material quality, companion pieces from each set of samples were immersed in a NaCN solution for 4 minutes. This

chemical etch removes any Cu<sub>2-x</sub>Se phase at the surface and between the network of grains in the film. It should be noted that the Cu/(In+Ga) value for sample **a** is strongly influenced by the Cu<sub>2-x</sub>Se phase present in the film. Removal of this Cu<sub>2-x</sub>Se phase results in a measured Cu/(In+Ga) value of 1.02, implying that the actual Cu(In,Ga)Se<sub>2</sub> composition is near stoichiometric to slightly Cu-rich. By sample **b**, the film composition is clearly Cu-poor.

The samples were characterized with energy-resolved photoluminescence (PL) and time-resolved photoluminescence (TRPL). The PL technique used a HeNe laser (623.8 nm) excitation source and an InGaAs diode array or silicon charge-coupled device (CCD) array detector. The sample temperature was varied from 4.5 to 300 K, and the laser power was varied from 0.1 to 10 mW. The spot size was about 0.25 mm in diameter, resulting in an excitation density ranging from about 0.2 to 20 W/cm<sup>2</sup>. The TRPL characterization was performed at room temperature using the time-correlated single-photon counting technique [3]. The excitation source was a cavity-dumped dye laser pumped by a mode-locked Nd:YAG laser. The output of this system was a 1-MHz pulse train of 5-ps-wide pulses and a wavelength of 650 nm (1.9 eV). The average excitation power was 10 mW, corresponding to an initial excitation density of about 5x10<sup>16</sup> cm<sup>-3</sup>. The time-dependent PL was detected by a photomultiplier tube with a minimum system response of about 100 ps. The resulting TRPL spectra provide a measure of the excited minority-carrier concentration as a function of time.

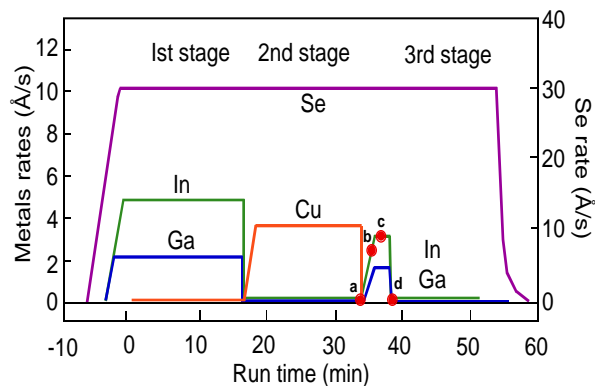


Fig. 1. The “three-stage” growth process.

Table 1. Measured parameters for the low-Ga samples.

	as-grown samples				NaCN-etched samples			NaCN-etched devices				
	Cu/(In+Ga)	PL Peak (eV)	PL Intensity @ 250K	E <sub>a</sub> (meV)	(ns)	PL Intensity @ 250K	E <sub>a</sub> (meV)	(ns)	efficiency	V <sub>oc</sub> (V)	J <sub>sc</sub> (ma/cm <sup>2</sup> )	(ns)
a	1.24	1.137	1.4e2	16	0.1	7.1e2	11	0.1	7.4	0.499	29.5	0.4
b	0.95	1.087	1.1e4	55	1.0	1.5e4	58	0.9	12.7	0.631	31.0	11.9
c	0.93	1.092	3.8e4	62	1.6	3.7e4	65	1.6	15.8	0.680	34.2	19.6
d	0.88	1.097	0.7e4	56	1.7	1.0e4	64	1.6	14.8	0.661	34.4	17.7

## RESULTS AND DISCUSSION

### Low-Ga samples

The normalized low-temperature (4.5 K) PL spectra for the samples with Ga/(In+Ga) fraction less than 0.26 are shown in Figure 2. From these data, it is evident that a shift in the dominant emission energies takes place as the sample transitions from being Cu-rich to Cu-poor. Specifically, as additional In and Ga are incorporated into the thin film, the dominant transition is shifted about 40-50 meV lower in energy and is broadened. This behavior is consistent with a change in the PL process to one involving new localized donor or acceptor states [4]. The peak locations for these spectra are summarized in Table 1.

Concurrent with this change in the dominant PL emission of the absorber material is an increase in the integrated PL intensity, by a factor of about 10<sup>2</sup>, between sample **a** and samples **b**, **c**, and **d** (see Table 1). This increase can be attributed to an increase in the material quality due to an increase in the minority-carrier lifetime and/or an increase in the radiative recombination rate due to an increase in the majority-carrier concentration. The latter possibility is not supported by capacitance-voltage measurements on companion pieces processed into devices [5].

A better understanding of the recombination process is obtained through temperature-dependent PL measurements. An example spectra of the integrated PL intensity as a function of inverse temperature for the low-Ga sample **d** is plotted in Figure 3. Evident from these data is the reduction of the luminescence intensity as the temperature is increased.

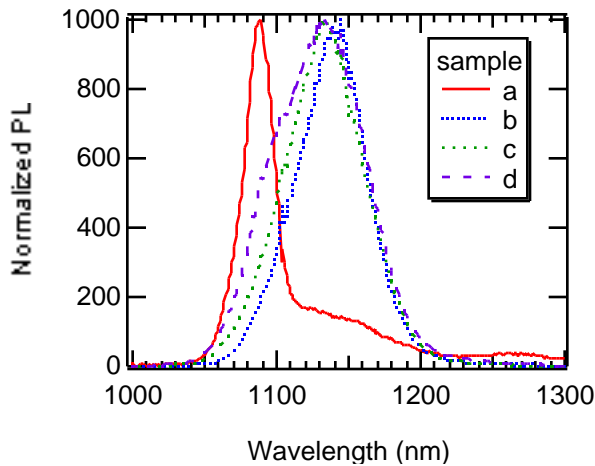


Fig. 2. PL spectra at 4.5 K for the low-Ga samples.

The standard model for explaining this thermally quenched behavior results in the following analytical expression for the temperature-dependent PL intensity [6]

$$PL(T) = PL(0) / ( 1 + C \cdot \exp(-E_a/kT) ) \quad (1)$$

where PL(T) is the integrated PL intensity at a temperature T, C is a constant fitting parameter, k is Boltzmann's constant, and E<sub>a</sub> is a thermal activation energy. The exponential term in Equation 1 originates from the ratio of  $\tau_r / \tau_{nr}$ , where  $\tau_r$  is the radiative lifetime and  $\tau_{nr}$  is the nonradiative lifetime. In the derivation of Equation 1, it is typically assumed that the nonradiative recombination process is thermally activated and the corresponding exponential temperature dependence will dominate any temperature dependence associated with the capture cross sections of the nonradiative recombination center or the radiative recombination process.

A plot of Equation 1 is fit to the data and included in Figure 3. The resulting E<sub>a</sub> of this analysis for each of the low-Ga samples is included in Table 1. Of particular note is the change in E<sub>a</sub> between sample **a** and samples **b**, **c**, and **d**. It appears that as the material transitions to a Cu-poor state, the dominant nonradiative recombination process shifts to one involving a larger thermal barrier.

A more direct measure of the dominant recombination process can be obtained from the TRPL measurements. In this case the PL intensity, which is proportional to the minority-carrier density, is measured as a function of time. The simplest form of analysis is to extract an exponential decay time (  $\tau$  ) that is representative of the removal rate of minority

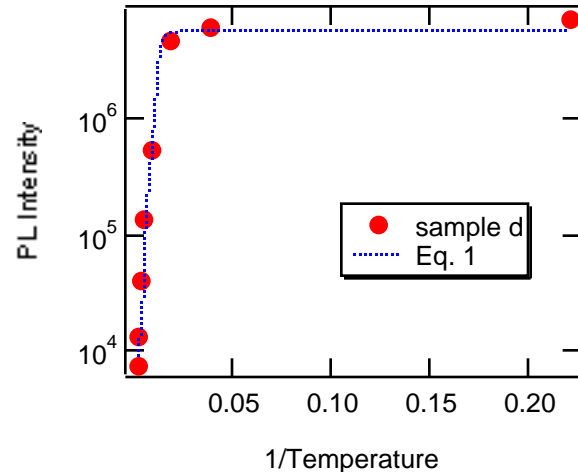


Fig. 3. Integrated PL intensity for low-Ga sample **d**.

carriers at that particular density or time. This decay rate can be influenced by bulk and surface recombination, as well as capture and emission from trap states. Figure 4 contains the TRPL spectra for the low-Ga samples, and Table 1 contains the decay times obtained from fits to the long single exponential region of each spectra. It is important to note that the system response is about 100 ps, making the true decay time for sample **a** lower than the measured value included in Table 1.

At this point, a distinct trend in the observed properties of these samples is forming. In all cases, the differences between the samples is manifested mainly between sample **a** and the others. The differences between samples **b**, **c**, and **d** are much more subtle. These differences include a distinct shift in the PL peak energy, PL intensity, PL temperature dependence, and TRPL decay time. All of this evidence supports the idea that (1) a significant change in the defect structure is occurring and (2) this change is associated with an improvement in the material quality of the Cu(In,Ga)Se<sub>2</sub> absorber layer.

One possible important difference between sample **a** and samples **b**, **c**, and **d** is the presence of a Cu<sub>2-x</sub>Se phase that is known to exist within the Cu-rich samples. To test the influence of this phase on the measured properties of the absorber layers, each sample was etched for 4 minutes in a NaCN solution. The removal of the Cu<sub>2-x</sub>Se phase is supported by compositional measurements and the observation of large voids in the etched sample where the Cu<sub>2-x</sub>Se once resided [7]. The integrated PL intensity, the thermally quenched activation energy (E<sub>a</sub>), and the TRPL decay time for the NaCN-etched samples are listed in Table 1 for direct comparison to the values for the companion as-grown samples. The most significant change associated with the removal of Cu<sub>2-x</sub>Se is an increase in the PL intensity of sample **a** by a factor of 5. More importantly, the removal of the Cu<sub>2-x</sub>Se phase did not result in sample **a** becoming more like samples **b**, **c**, and **d**. This suggests that the dominant defects and recombination processes are intrinsic to the Cu(In,Ga)Se<sub>2</sub> phase.

To directly compare the preceding measurements with the standard solar cell figures of merit, completed solar cells

were fabricated from each of the NaCN-etched samples. Use of the NaCN-etched absorbers was necessitated by the presence of Cu<sub>2-x</sub>Se in some of the as-grown samples. If present, the Cu<sub>2-x</sub>Se phase will tend to short-circuit the device, not allowing for a measure of device performance that is representative of the underlying absorber material quality. Table 1 contains the resulting device efficiency, open-circuit voltage (V<sub>oc</sub>), short-circuit current density (J<sub>sc</sub>), and TRPL decay time (τ) for each device. From the data, it is clear that there is a large change in device performance between sample **a** and samples **b**, **c**, and **d**. Furthermore, the measured decay time correlates well with device performance, as shown in Figure 5.

A comparison between the measurements performed on the absorber layers and the corresponding devices reveal a few interesting changes. The first is that there is an increase in the overall PL intensity by a factor of about 200 for samples **b**, **c**, and **d** when they are processed into finished devices (not shown here). Possible causes for this are an increase in the base carrier concentration and/or a decrease in the recombination rate. Also apparent is an increase in the TRPL decay time by about a factor of 10 for these same samples. This increase in the decay time could be the result of defect or surface passivation of the as-grown absorber layer. There is also the possibility that the charge separation occurring at the depletion edge and the resulting return to equilibrium are affecting the decay process. Although it is not clear why this would be associated with an increase in the overall PL intensity, or why the resulting decay time would correlate so well with device performance, it is worth noting. Further theoretical and experimental work are under way to sort these possibilities out.

In summarizing the low-Ga results, there are several important observations that deserve emphasis. First, there is a significant change in the measured parameters between sample **a** and the others. This is consistently observed in all of the material and device measurements performed here. Compositionally, it is known the sample **a** is Cu-rich whereas the others are Cu-poor, and sample **a** possesses substantially more Cu<sub>2-x</sub>Se than the others. Removal of the Cu<sub>2-x</sub>Se phase does not significantly improve material or device

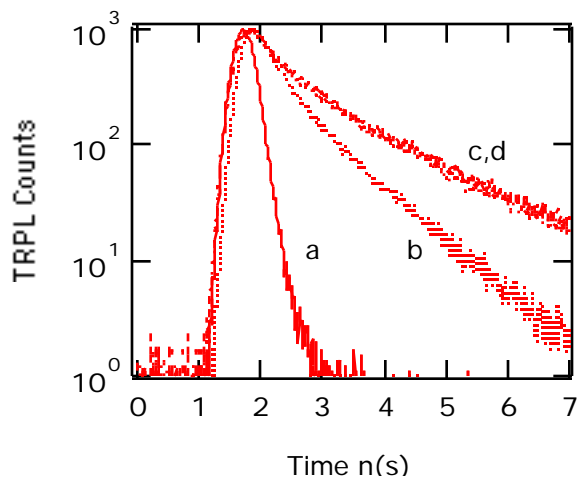


Fig. 4. TRPL spectra for the low-Ga samples.

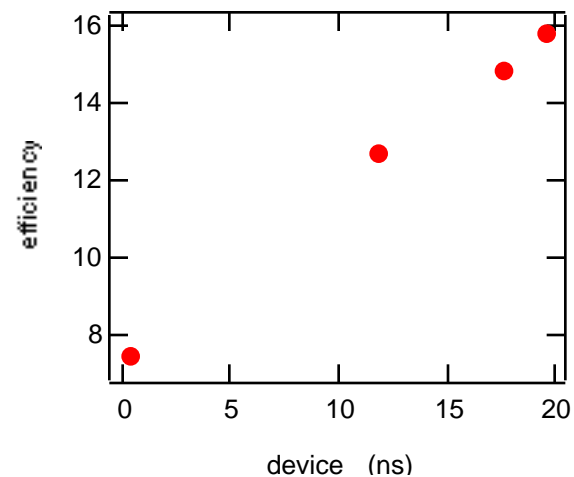


Fig. 5. Conversion efficiency for the low-Ga devices.

performance, shifting the focus of a compositional related link with material quality to the change in stoichiometry in going from Cu-rich to Cu-poor. During this change, the dominant PL energy is abruptly reduced by about 50 meV – an amount in general agreement with that expected for shallow-donor-to-acceptor or band-to-acceptor transitions involving a  $V_{cu}$  [8]. Correspondingly, the thermally quenched activation energy changes from about 16 meV for sample **a** to about 55-60 meV for samples **b**, **c**, and **d**. Finally, and perhaps most importantly, there is a significant increase in the material quality as measured by the factor of  $10^2$  increase in the PL intensity, the increase in the TRPL decay time, and the device performance as the material transitions to a Cu-poor phase.

### High-Ga samples

Similar measurements were performed on a set of high-Ga samples where the Ga/(In+Ga) ratio was about 0.56. The trends observed in the low-Ga set were also observed in the high-Ga set, with a few exceptions concerning the processed devices.

Specifically, the as-grown samples exhibited a marked change in PL peak position at 4.5 K and PL intensity (by about  $10^2$  to  $10^3$ ) in transitioning from sample **b** to sample **c**. The Cu/(In+Ga) ratios for these films reveal that, in this case, sample **a** is rich with  $Cu_{2-x}Se$  (ratio of 1.31) and sample **b** is very near stoichiometry (ratio of 0.99). Not until sample **c** does the sample becomes appreciably Cu-poor (ratio of 0.95). The NaCN treatment resulted in enhanced PL intensity for each sample relative to the as-grown film, but the difference between samples **a**, **b** and **c**, **d** remained. The measured TRPL decay times for the films also showed a similar trend of 0.1, 0.1, 0.9, and 1.6 ns for samples **a** through **d**, respectively.

Processing the films into completed devices, as before, resulted in an increase in the PL intensity and TRPL decay time, but, with the exception of sample **b**, not to the extent observed for the low-Ga samples. In particular, the measured TRPL decay time for processed devices **c** and **d** only increased by a factor of about 4 (Table 2). Correspondingly, the  $J_{sc}$  and efficiency of these devices fall below that obtained for sample **b**. It is possible that the processing conditions arrived at after years of optimizing the performance of the low-Ga absorber material are not optimal for use with higher Ga-containing films – especially when the Cu/(In+Ga) ratio falls much below 1.

### CONCLUSION

The final stage of the “three-stage” growth process is rich with changes in the defect chemistry and transport properties of the growing absorber layer. This analysis provides evidence of several of these, including a shift in the emission and activation energy of the PL process, an increase in the material quality, and an increase in device performance. Furthermore, these transitions occur abruptly in going from a Cu-rich to a Cu-poor material.

Table 2. Measured Parameters for the high-Ga samples.

	eff. (%)	$V_{oc}$ (V)	$J_{sc}$ ( $ma/cm^2$ )	(ns)
a	6.1	.582	22.76	0.2
b	13.6	.750	26.25	2.0
c	10.1	.762	23.31	4.0
d	7.8	.750	20.03	7.5

### ACKNOWLEDGEMENTS

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