

Effect Of Grain Size, Morphology and Deposition Temperature on Cu(InGa)Se₂ Solar Cells

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ABSTRACT

Cu(InGa)Se₂ films have been deposited by multisource elemental evaporation at substrate temperatures from 550 to 400°C to determine the effect of temperature on grain size and morphology and on solar cell performance. Films were deposited with different flux profiles to compare cases where a Cu_xSe_y phase is formed during different stages of growth or not at all. The films are characterized by atomic force microscopy to determine the grain size and surface area. With the Cu-rich growth, the mean lateral grain area decreases from 1.8 to 0.3 μm² as substrate temperature decreases. Sodium incorporation into the films via diffusion from the glass substrate is greater at the lower temperature when there is a larger grain boundary density. Device efficiency decreases with the lower temperature but cannot be simply attributed to changes in grain size or surface area. Instead the decrease in open circuit voltage and fill factor are attributed to a greater density of intra-grain trap states in the Cu(InGa)Se₂.

INTRODUCTION

For Cu(InGa)Se₂ based solar cells to achieve their promise for low cost photovoltaic power generation, manufacturing costs need to be reduced while maintaining high yield, reproducibility, and performance. Lowering the processing temperature for the Cu(InGa)Se₂ can reduce costs and increase yield by decreasing the heat load and stress on the deposition system and by allowing faster heat-up and cool-down. The highest efficiency solar cells utilize Cu(InGa)Se₂ deposited at substrate temperatures (T_{SS}) greater than 550°C onto soda lime glass which softens at such temperatures. This could create significant problems when handling large area substrates for module manufacturing. In addition, if T_{SS} is reduced to ~400°C, high temperature polyimide could be used as a substrate enabling roll-to-roll processing.

We have previously shown a decrease in Cu(InGa)Se₂ device efficiency from 16.4% to 14.1% due to decreasing the substrate temperature during evaporation from 550 to 400°C [1]. The most significant change in the Cu(InGa)Se₂ films deposited at lower T_{SS} was a smaller grain size. Other groups have also shown a simultaneous decrease in efficiency and grain size with lower T_{SS} using an in-line evaporation process [2] and with a three stage evaporation process which begins with an In-Ga-Se layer [3]. In this paper, changes in Cu(InGa)Se₂ films and devices are characterized as a function of substrate temperature to determine the causes for the drop in device performance as T_{SS} is reduced.

EXPERIMENTAL DETAILS

Cu(InGa)Se₂ films were deposited by thermal evaporation from independently controlled elemental sources for Cu, In, Ga, and Se. Three temporal deposition flux profiles were used to give depositions with: (1) uniform fluxes so that the films composition is never Cu-rich, (2) Cu-rich flux, Cu/(In+Ga) > 1, at the start of the run followed by only In, Ga, and Se fluxes to give the desired Cu-deficient final composition, and (3) Cu-rich flux in the middle of the run. The Cu/(In+Ga) ratios as a function of time through the deposition are shown in Figure 1 which

illustrates the fact that the endpoint compositions were the same in all cases. The process with the Cu-rich flux in the middle is intended to determine if the effects of Cu-rich growth specifically require the presence of a Cu_xSe_y phase during the initial nucleation of the film on the glass/Mo substrate. The In, Ga, and Se fluxes were kept constant throughout each deposition so there were no gradients in Ga content or bandgap, and were the same for each flux profile and substrate temperature. The deposition time for all films was 44 min resulting in final film thicknesses of $\sim 2 \mu\text{m}$. Film compositions, measured by energy dispersive x-ray spectroscopy (EDS), were $\text{Cu}/(\text{In}+\text{Ga}) = 0.8 - 0.9$ and $\text{Ga}/(\text{In}+\text{Ga}) = 0.3$, giving a bandgap $E_G = 1.2 \text{ eV}$. For this work, $\text{Cu}(\text{InGa})\text{Se}_2$ films have been deposited by multisource elemental evaporation at $T_{\text{SS}} = 400, 480, \text{ and } 550^\circ\text{C}$. At 480°C the soda lime glass substrate is below all glass transition temperatures.

In addition to EDS, films are characterized by atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS). The AFM measurements, using a Digital Instruments 3100 Scanning Probe Microscope, are used to determine grain size and surface area. SIMS measurements done at the National Renewable Energy Laboratory are used to compare the Na incorporation and to verify that all samples had uniform depth profiles of Cu, In, and Ga. Devices with a soda lime glass / Mo / $\text{Cu}(\text{InGa})\text{Se}_2$ / CdS / ZnO:Al / Ni-Al grid structure, with no anti-reflection layer, were fabricated using a baseline process described in [4]. The solar cells are measured on a total area basis under $100 \text{ mW}/\text{cm}^2$ AM1.5 illumination.

RESULTS

Grain Size and Morphology

The surface morphologies of films grown at $T_{\text{SS}} = 400, 480, \text{ and } 550^\circ\text{C}$ with a Cu-rich flux at the beginning of the deposition are shown by AFM images in Figure 2. The surface roughness appears to decrease as grain size gets larger with higher temperature. Since the grains are generally columnar [1], the structure can be characterized by the surface area of the grains. The average grain area has been determined for films deposited with the 3 processes described above and at the three temperatures. This characterization uses contrast-enhanced AFM images of the top surface to create a map of the grain boundaries [1] which is then digitized. The enclosed grain areas are then determined using NIH Image software [5].

For each sample the lateral grain areas were determined over 3 randomly selected $100 \mu\text{m}^2$ regions. In all cases the grain areas (A) are well described by a log-normal distribution, i.e., a normal distribution of the logarithm of A [6]:

$$f_n(\ln A) = \frac{1}{(\ln A)\sqrt{2}} \exp -\frac{(\ln A - E(\ln A))^2}{2 (\ln A)^2}, \quad (1)$$

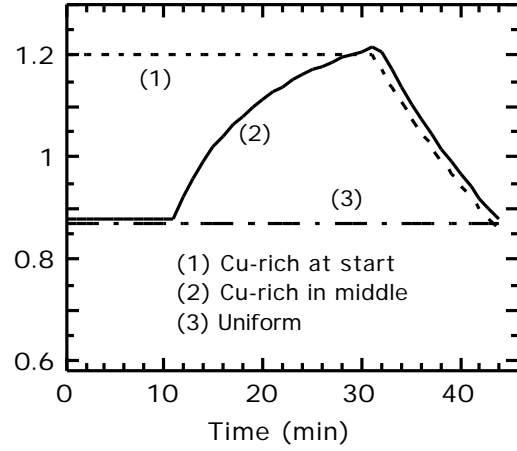


Figure 1. Relative Cu concentration during deposition using different flux sequences.

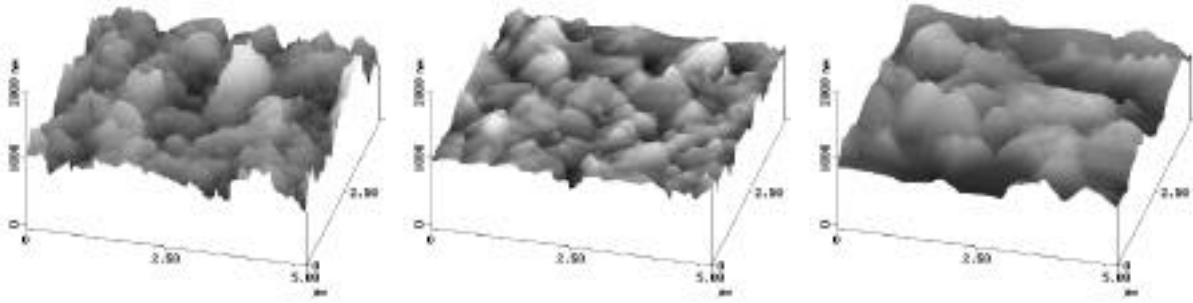


Figure 2. AFM images showing 5 μm x 5 μm areas of films deposited with Cu-rich flux at $T_{\text{SS}} = 400, 480, \text{ and } 550^\circ\text{C}$.

where $E(\ln A)$ is the expected value or mean of $\ln A$ and $(\ln A)$ is the standard deviation of the distribution. The mean grain area, \bar{A} , and length, \bar{d} , are given by:

$$\bar{A} = E(A) = \exp\left[E(\ln A) + \frac{1}{2} (\ln A)^2\right] \quad \text{and} \quad \bar{d} = \sqrt{4\bar{A}}. \quad (2)$$

These are weighted grain size measures since the probability of finding grains of a given area is proportional to the relative area rather than just the number of grains. Figure 3 shows the measured grain area distribution and log-normal fit for the samples shown in Figure 2 deposited at different T_{SS} . The parameters which describe the distribution, $E(\ln A)$, $(\ln A)$, and \bar{A} are listed in Table I for all processes and temperatures along with \bar{d} which can be compared to the length typically observed in cross-sectional micrographs.

Figure 3 shows that the median, or mid-point of the log-normal distribution, is the same for the films deposited at the two higher temperatures. However, the film at 550 $^\circ\text{C}$ has a larger mean area, 1.8 μm^2 , due to the larger standard deviation and occurrence of grains with $A > 1 \mu\text{m}^2$ which dominate the distribution. For $T_{\text{SS}} = 550^\circ\text{C}$, the mean area is larger with Cu-rich growth than with the uniform process. With $T_{\text{SS}} = 400$ and 480 $^\circ\text{C}$, the mean grain size is independent of the growth process.

The surface roughness is important because the open circuit voltage in a device is a function of junction area, as addressed below. The surface roughness is characterized by

$A_{\text{surf}} = (A_{\text{surf}} - A) / A$ where A_{surf} is the total surface area and A the planar area. Experimentally, A_{surf} was determined from AFM measurements over an area $A = 100 \mu\text{m}^2$. This is also listed in Table I.

Table I. Grain size and surface area with different deposition processes and temperatures.

T_{SS} ($^\circ\text{C}$)	Process	$E(\ln A)$	$(\ln A)$	\bar{A} (μm^2)	\bar{d} (μm)	A_{surf} (%)
400	Cu-rich at start	-1.9	1.1	0.3	0.6	54
	Cu-rich in middle	-1.9	1.2	0.3	0.6	76
	Uniform	-1.9	1.1	0.3	0.6	28
480	Cu-rich at start	-0.7	1.0	0.8	1.0	23
	Cu-rich in middle	-0.9	1.0	0.7	0.9	40
	Uniform	-0.4	0.7	0.9	1.0	32
550	Cu-rich at start	-0.7	1.6	1.8	1.5	26
	Cu-rich in middle	-0.6	1.2	1.2	1.1	33
	Uniform	-1.0	1.1	0.7	0.9	19

Sodium Incorporation

Depth profiles of the total Na content, measured by SIMS, in samples deposited at $T_{SS} = 400$ and 550°C using Cu-rich flux at the beginning or uniform flux are shown in Figure 4. The films deposited at 400°C have greater average Na concentrations than those deposited at higher T_{SS} . It is assumed that this is due to the greater density of grain boundaries, and that nearly all the Na resides along those boundaries [7]. The lower T_{SS} films have smaller grains so the Na might more easily diffuse into the bulk grains. Thus, these measurements only confirm the availability of Na but not the intra-grain concentration.

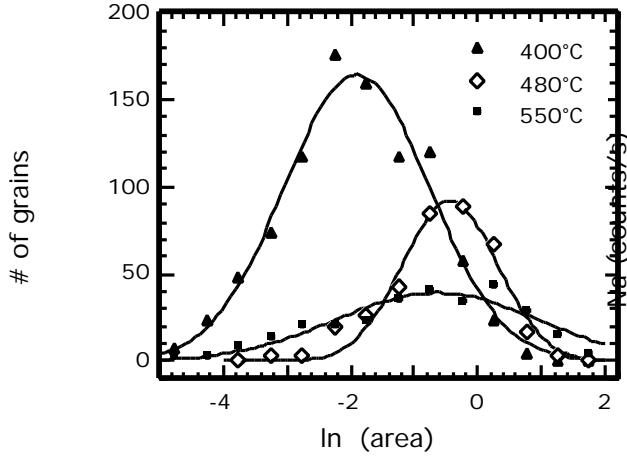


Figure 3. Grain size distributions for films deposited with Cu-rich flux and log-normal fits to each distribution.

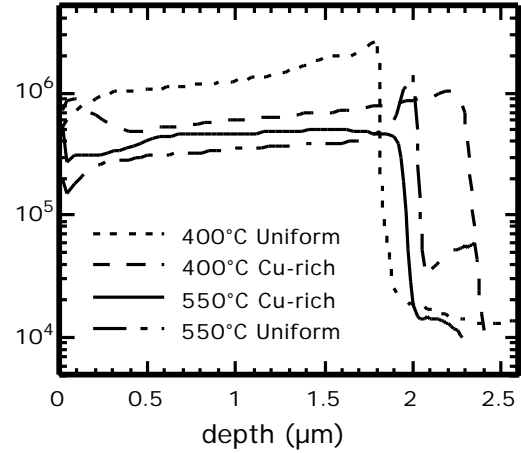


Figure 4. Sodium content measured by SIMS in films deposited at $T_{SS} = 400$ and 550°C .

Device Results

Current-voltage (J-V) parameters for the best cells fabricated with $T_{SS} = 400, 480,$ and 550°C and the three deposition processes are listed in Table II. The uniform deposition process gives poorer device performance at $T_{SS} = 400^\circ\text{C}$ than the Cu-rich growth processes, but at higher temperatures, 480 and 550°C , there is no advantage to the Cu-rich growth. V_{OC} and FF increase with T_{SS} for all three deposition processes, despite the comparable grain sizes in the films deposited at higher temperatures.

The J-V curves under illumination and in the dark are shown in Figure 5 for the cells deposited with Cu-rich flux at the start. To further characterize the losses as T_{SS} is reduced, the J-V data was analyzed assuming a standard diode equation:

$$J = J_0 \exp \frac{q}{nkT} (V - R_S J) - J_L. \quad (3)$$

The diode quality factor, n , and series resistance, R_S , were determined from the slope and intercept, respectively, of the derivative dV/dJ vs. $(J+J_{SC})^{-1}$. Then the recombination current, J_0 , was determined from the intercept of $\ln(J+J_L)$ vs. $V-R_S J$. This plot is shown in Figure 6 for the same data as in Figure 5 with $T_{SS} = 400$ and 550°C . With the lower T_{SS} , there is a difference between the data measured in the dark and the data under illumination which can be attributed to a voltage dependent light generated current collection [4]. There is much better agreement between the dark and light J-V curves for the sample with $T_{SS} = 550^\circ\text{C}$. The device parameters

Table II. Device results with different substrate temperature and evaporation process.

T_{SS} (°C)	Process	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	eff. (%)
400	Cu-rich at start	0.59	33	71	13.7
	Cu-rich in middle	0.60	33	71	13.8
	Uniform flux	0.56	29	69	11.3
480	Cu-rich at start	0.62	32	72	14.4
	Cu-rich in middle	0.63	30	71	13.4
	Uniform flux	0.60	32	72	14.0
550	Cu-rich at start	0.65	32	76	16.0
	Cu-rich in middle	0.65	32	75	15.5
	Uniform flux	0.65	33	74	15.9

R_s , n , and J_0 determined from the dark J-V data for all temperatures are listed in Table III. The devices have comparable values of n consistent with Shockley-Read-Hall recombination but decreasing J_0 with higher T_{SS} , as expected for the drop in V_{OC} .

Table III. J-V parameters with different substrate temperature.

T_{SS} (°C)	R_s (Ω-cm ²)	n	J_0 (mA/cm ²)
400	0.4	1.8	14×10^{-6}
480	0.2	1.7	2×10^{-6}
550	0.2	1.6	0.9×10^{-6}

DISCUSSION AND CONCLUSIONS

By comparing different deposition sequences at fixed T_{SS} , it is clear that differences in grain size do not simply correlate to device efficiency. This can be seen at $T_{SS} = 400^\circ\text{C}$ where the uniform deposition gives lower device efficiency but comparable grain size to the growth processes that incorporate a Cu-rich step. At $T_{SS} = 550^\circ\text{C}$ an increase in mean grain size does not result in an increased efficiency.

There are several other possible reasons for the lower V_{OC} that occurs with lower T_{SS} . An increase in surface area can result in a loss in V_{OC} since J_0 is proportional to the surface area A_{surf} . With constant n and J_L , the change in V_{OC} with surface area can be written as

$$V_{OC}(A_{surf1}) - V_{OC}(A_{surf2}) = \frac{nkT}{q} \ln \frac{A_{surf2}}{A_{surf1}} . \quad (4)$$

For a 50% increase in surface area, with $n = 1.7$, the loss in V_{OC} is 18 mV. Thus, the decrease in A_{surf} from 480 to 400°C reported in Table I can account for, at most, half of the decrease in V_{OC} . The films deposited at 480 and 550°C have comparable surface areas.

The increase in J_0 suggests an increase in the density of intra-grain defects that act as deep trapping states to control the recombination current in the Cu(InGa)Se₂. These intra-grain defects can also cause the light generated current collection to become more voltage dependent by reducing minority carrier diffusion length. Also, the J-V curves for devices made with $T_{SS} = 400^\circ\text{C}$ have hysteresis which indicates long relaxation times associated with defect states in the devices [1].

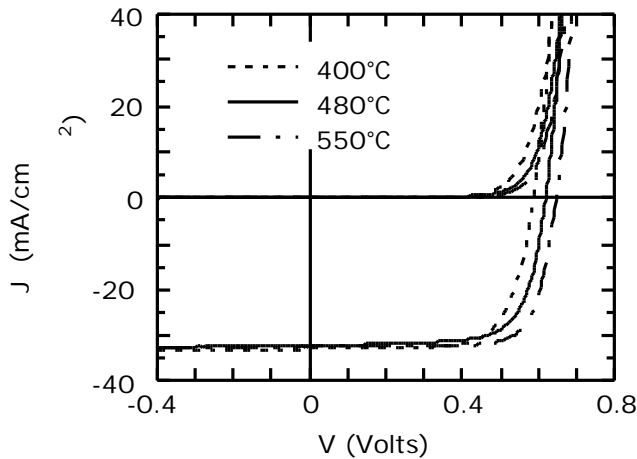


Figure 5. Current-voltage curves for devices with Cu(InGa)Se₂ deposited at different T_{SS} with Cu-rich growth at start.

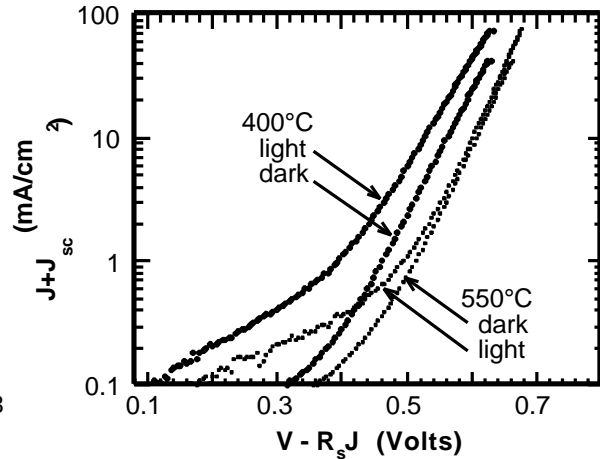


Figure 6. Logarithmic J-V behavior showing differences between light and dark curves for the 400°C case.

In conclusion, the effect of reducing substrate temperature during multisource evaporation of Cu(InGa)Se₂ on grain size and surface area has been characterized and related to the decrease in device efficiency. Comparing different flux profiles, it was shown that at T_{SS} = 400°C Cu-rich growth, whether at the beginning of the deposition or later in the process, is necessary to achieve good performance. However, at higher T_{SS} the device performance is insensitive to the growth sequence allowing greater process flexibility. With the Cu-rich growth, the mean lateral grain area decreases from 1.8 to 0.3 μm² as T_{SS} is reduced from 550 to 400°C, but only at the highest T_{SS} does the grain size depend on the growth process. In general, lower device efficiency with lower T_{SS} cannot be simply described by changes in grain size or surface area or by the availability of Na which is comparable at 400 and 550°C. Instead, the lower voltage and increased recombination current with lower temperature deposition indicate a greater density of intra-grain trap states in the Cu(InGa)Se₂ which can also lead to smaller minority carrier diffusion length and the voltage dependent current collection.

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REFERENCES

1. W. N. Shafarman and J. Zhu, *Thin Solid Films* **361-362**, 473 (2000).
2. M. Lammer, U. Klemm, and M. Powalla, *Thin Solid Films* **387**, 33 (2001).
3. S. Nishiwaki, T. Satoh, Y. Hashimoto, T. Negami, and T. Wada, *J. Mat. Res.* **16**(2), 394 (2001).
4. W.N. Shafarman, R. Klenk, and B.E. McCandless, *J. Appl. Phys.* **79**(9), 7324, (1996).
5. Web site: <http://rsb.info.nih.gov/nih-image/>.
6. K. Kurzydowski and B. Ralph, *CRC Series in Mat. Sci. & Tech.* (CRC Press, Boca Raton, FL, 1995) pp. 39-43.
7. D.W. Niles, M. Al-Jassim, and K. Ramanathan, *J. Vac. Sci. Technol. A* **17**(1), 291 (1999).