IN-SITU ANNEALING OF Cu(In,Ga)Se$_2$ FILMS GROWN BY ELEMENTAL CO-EVAPORATION

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ABSTRACT

The effect of in-situ post-deposition annealing on Cu(InGa)Se$_2$ films grown by elemental co-evaporation on microstructure and solar cell performance has been characterized. Films were deposited at a substrate temperature of 400°C and then annealed in-situ at 400°C, 475°C, 500°C and 550°C for times from 1 - 60 min. Devices made from films grown at 400°C and then annealed at 550°C for 1 minute had comparable efficiency to devices made from films grown at 550°C. Little or no grain growth was observed in SEM cross-section imagery for films annealed at 400°C, 475° or at 550°C for 1 minute but substantial grain growth was seen in films annealed at 550°C when the anneal time was increased to 10 minutes or more. Device performance also improved as a result of post-deposition annealing, but the improvement in $V_{OC}$ took place even when grain growth appeared stagnant. A decrease in the XRD (112) FWHM for such films, however, indicated that both post-deposition annealing and Cu-rich growth caused a change in the films. $V_{OC}$ was correlated with this measure of Cu(InGa)Se$_2$ film evolution for 0.55 $V < V_{OC} < 0.65 V$.

INTRODUCTION

For the highest efficiency devices, Cu(InGa)Se$_2$ films are deposited at the maximum substrate temperature ($T_{SS}$) allowed by the substrate, ~ 550°C for soda lime glass (SLG). A lower $T_{SS}$ would be desirable for a number of reasons, including more flexibility in substrate choice, a reduced energy budget of fabrication and a possible enabling of a CIGS-based tandem cell architecture. Decreased $T_{SS}$ during deposition, however, has been shown to result in films with reduced device performance [1,2,3].

In addition to reduced device performance, decreased $T_{SS}$ was also shown to yield films with smaller grains. If only the effects of deposition temperature were considered, then device performance and grain size were correlated, but introducing non-constant source fluxes during deposition (so that the deposited films were Cu-rich during part of the deposition) also increased grain size. By also considering films grown in this way, it was found that there was not a simple correlation between grain size - measured by atomic force microscopy (AFM) - and device behavior [1,2].

In this paper, we investigate the effect of in-situ annealing immediately after Cu(InGa)Se$_2$ deposition on grain size, crystallographic orientation, and device behavior and consider the issue of a relationship between microstructure and device performance.

EXPERIMENTAL APPROACH

Cu(InGa)Se$_2$ films were deposited on 1"x1" Mo-coated SLG substrates in a stationary bell-jar system using thermal evaporation from four Knudsen-type elemental sources (copper, indium, gallium and selenium). Source fluxes were held constant throughout the deposition and $T_{SS}$ during deposition was 400°C. After deposition was complete, the films were subjected to further in-situ post-deposition annealing (PDA) for different temperatures (400°C, 475°C, 500°C and 550°C) and times (1 – 60 min). Figure 1 shows temperature profiles for two 550°C / 1 minute post-deposition anneals. The ramp-up times were 4 and 10 minutes, respectively.

Figure 1. Time-temperature profiles for 550°C / 1 minute PDA with two different ramp-up rates.

We also examined some films deposited at $T_{SS}$=400°C with non-constant source fluxes during deposition. Growth of these films occurred in two stages. In the first stage, the film composition was Cu-rich with a Cu/(In+Ga) ratio greater than unity [1,2]. In the second stage, the Cu flux was terminated, so that the final film composition was Cu-poor.

All Cu(InGa)Se$_2$ films grown were 1.5 - 2 µm thick. Film compositions, measured using energy dispersive x-ray spectroscopy (EDS), gave Cu/(In+Ga) = 0.8 – 0.9 and Ga/(In+Ga) ≈ 0.3. Film microstructure was characterized with SEM cross-section images and with XRD. XRD reflections were acquired with 40 kV Cu K$_\alpha$ radiation and
(112) profiles were measured in 0.01° intervals from 25.0 to 28.0°. The Cu Kα2 component of the resulting data was stripped using the Rachinger correction before analysis.

For each 1”x1” sample Cu(InGa)Se2 film, six separate devices were fabricated. Each device had a structure of SLG/Mo/Cu(InGa)Se2/CdS/ZnO/ITO/(Ni/Al grid). No AR coating was used. Devices were characterized by J-V measurements under AM1.5 illumination at 25°C. All reported J-V results are averages of multiple devices for a given 1”x1” sample.

RESULTS

Cross-sectional SEM images of Cu(InGa)Se2 films deposited at T_{SS}=400°C (A) and T_{SS}=550°C (B) are shown in Figure 2. Without any PDA, the film deposited at 400°C had a characteristic small-grained microstructure in which the lateral dimension of the grains was much less than the film thickness. The film deposited at T_{SS}=550°C, on the other hand, had much larger grains, with lateral dimensions on the order of 1 μm.

Figure 2. Cross-sectional SEM images of Cu(InGa)Se2 films on Mo/SLG deposited at T_{SS}=400°C (A) and T_{SS}=550°C (B).

Figure 3 shows cross-sectional SEM images of films deposited under conditions identical to film A (i.e. at T_{SS}=400°C). After deposition was complete, however, these films were subjected to further in-situ PDA at 550°C. The substrate temperature increased from 400°C to 550°C in 10 minutes. Film (C) was held at that temperature for one minute (“slow ramp” in Figure 1), while Film (D) was held at that temperature for 60 minutes. It took about 15 minutes for the films to cool back down to 400°C after the heater was turned off.

Figure 3. Cross-sectional SEM images of Cu(InGa)Se2 films on Mo/SLG deposited at T_{SS}=400°C and then annealed at 550°C for one minute (C) and for 60 minutes (D).

For film (C), which experienced only the short 1 minute anneal at 550°C, there was little or no apparent change in grain size. In film (D), on the other hand, substantial grain growth has clearly taken place and the grains seen in this film appear comparable to those seen in film (B).

In addition to Cu(InGa)Se2 runs A-D, we also grew films at 400°C and exposed them to PDA at temperatures of 400°C and 475°C for 1, 10 and 60 minutes and at 500°C for 30 minutes. We also repeated run C (550°C / 1 minute) several times with different ramp-up and cool-down rates. Compared to films (B) and (D), there was no obvious grain growth for any of these runs and all films examined had small-grained microstructures that appeared qualitatively similar to films (A) and (C). Grain growth was observed for films grown at 400°C and then annealed at 550°C for 10 and 60 minutes.

Table 1 shows J-V measurements of devices made from the same Cu(InGa)Se2 runs as the films shown in Figures 2 and 3. The devices made from the film deposited at T_{SS}=400°C without any high temperature PDA (A) were comparable to previously reported results for uniform Cu-poor deposition [2]. The Voc of these devices were ~ 100 mV lower than devices made from films with a deposition temperature of T_{SS}=550°C (B).

PDA at 550°C significantly improved the performance of the resulting devices. In particular, only a short 1 minute anneal at 550°C (plus ramp-up and cool-down times) was sufficient to produce a film (C) that yielded a
device comparable to the device made from a film deposited at 550°C (B), even though there was little or no apparent Cu(InGa)Se₂ grain growth. Additional annealing time (D) did not yield any significant further device improvement.

Table 1. J-V results for Cu(InGa)Se₂ films deposited at different temperatures and with 550°C in-situ annealing.

<table>
<thead>
<tr>
<th>T&lt;sub&gt;SS&lt;/sub&gt; (°C)</th>
<th>PDA time (min)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>FF (%)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm²)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 400C</td>
<td>0</td>
<td>0.55</td>
<td>67</td>
<td>25</td>
<td>9.3</td>
</tr>
<tr>
<td>B 550C</td>
<td>0</td>
<td>0.64</td>
<td>76</td>
<td>33</td>
<td>15.9</td>
</tr>
<tr>
<td>C 400C</td>
<td>1</td>
<td>0.64</td>
<td>76</td>
<td>32</td>
<td>15.3</td>
</tr>
<tr>
<td>D 400C</td>
<td>60</td>
<td>0.65</td>
<td>78</td>
<td>31</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Table 2. Preferred orientations and FWHMs of Cu(InGa)Se₂ films deposited at different temperatures and with 550°C PDA.

<table>
<thead>
<tr>
<th>T&lt;sub&gt;SS&lt;/sub&gt; (°C)</th>
<th>PDA time (min)</th>
<th>I(112)</th>
<th>I(204,220)</th>
<th>(112) FWHM (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 400C</td>
<td>0</td>
<td>0.3</td>
<td>0.26</td>
<td>0.10</td>
</tr>
<tr>
<td>B 550C</td>
<td>0</td>
<td>100</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>C 400C</td>
<td>1</td>
<td>0.6</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>D 400C</td>
<td>60</td>
<td>3</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Most of the films that featured the characteristic small-grained microstructure in SEM images also had (112) peaks broadened from the instrument function. Films annealed at 400°C had FWHMs of > 0.20°. The (112) reflection sharpened for films annealed at 475°, decreasing to 0.17° (1 minute) and to 0.14° (60 minutes). For 550°C / 1 minute PDA, the (112) peak sharpened further to between 0.14° and 0.10°. A film grown at 400°C, but with a Cu-rich growth stage, had a FWHM=0.20°. In contrast, all of the films that showed clear evidence of grain growth in SEM images had sharp (112) peaks that could not be confidently distinguished from the XRD instrument function.

![Figure 4](image_url)  
Figure 4. XRD scans of, from top to bottom: (A): T<sub>SS</sub>=400°C, (B): T<sub>SS</sub>=550°C, (C): T<sub>SS</sub>=400°C plus 1 min anneal at 550°C, and (D): T<sub>SS</sub>=400°C plus 60 minute anneal at 550°C.

We also observed (112) peak broadening for some films. To quantify this, the Pearson VII function (a generalization of Cauchy and Gaussian distributions) was used to fit the measured (112) peaks [4]. Fitting the Pearson VII function to a (112) diffraction peak measured on a Cu(InGa)Se₂ film annealed at high temperature for many hours yielded a FWHM of 0.09°, which we considered to be the FWHM of our instrument function. (112) peaks with FWHM ≥ 0.11° were considered to be distinguishable from the instrument function.

![Figure 5](image_url)  
Figure 5. The FWHM of the (112) peak for the films grown at 400°C and subjected to PDA at 550°C for 10 minutes is less than 0.02° wider than the instrument function. Other PDA films have peaks distinguishable from the instrument function.

As already mentioned, PDA films in which grain growth appeared stagnant nevertheless yielded devices with increased V<sub>OC</sub>. These same films also had XRD (112) peak sharpening. Figure 6 shows a correlation between device V<sub>OC</sub> and FWHM of the Cu(InGa)Se₂ films from which the devices were made. The figure includes Cu(InGa)Se₂ films annealed at different temperatures and with slow and fast PDA ramp-up rates. It also includes
devices whose $V_{OC}$ was improved by using 2-stage (Cu-rich/Cu-poor) Cu(InGa)Se$_2$ deposition process.

The observation that $V_{OC}$ is improved to ~0.65 V by brief high temperature annealing while further annealing has no further effect on $V_{OC}$ suggests that there are multiple Cu(InGa)Se$_2$ defects controlling $V_{OC}$. Specifically, defects which lead to reduced $V_{OC}$ in films deposited at 400°C apparently have a relatively low activation energy for thermal annealing while the defects that limit high efficiency devices are more stable. Photocapacitance measurements showed additional deep defects in similar devices with 400°C Cu(InGa)Se$_2$ deposition compared to high efficiency devices [6].

**CONCLUSIONS**

A short 1 minute PDA at 550°C is capable of transforming a film originally deposited at 400°C into one that yields a device similar to a film deposited at 550°C.

Annealing improves Cu(InGa)Se$_2$ solar cells before it drives substantial grain growth. Device performance is uncorrelated to lateral grain size, at least above a minimum size that is much smaller than film thickness and also much smaller than the grain size typically observed in high efficiency devices.

In films that are improved by post-deposition annealing, $V_{OC}$ correlates with the (112) FWHM of the Cu(InGa)Se$_2$ film for 0.55 V < $V_{OC}$ < 0.65 V. The same correlation is also observed when the (112) FWHM is reduced by means of a Cu-rich growth phase.

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**REFERENCES**


