Project Title: Development of a Low Cost Insulated Foil Substrate for Cu(InGaSe)₂ Photovoltaics

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Working Partners: DOW Corning Corporation

Cost-Sharing Partners: DOW Corning Corporation

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DOE Project Team: DOE Field Contracting Officer - Andrea Lucereo
DOE Field Project Officer - Jim Payne
Project Engineer - Leon Fabick
EXECUTIVE SUMMARY

The present project validated the use of stainless steel flexible substrate coated with silicone-based resin dielectric, developed by Dow Corning Corporation, for Cu(InGa)Se₂ based photovoltaics. The project’s driving force was the high performance of Cu(InGa)Se₂ based photovoltaics coupled with potential cost reduction that could be achieved with dielectric coated SS web substrate.

First, 430SS was shown to be the preferred substrate based on the suitable thermal expansion coefficient. However, randomly distributed shunt paths through the silicone-based resin had to be burned with voltage pulses for module fabrication. Reducing the density of the shunt paths through changes in the process and locating and burning the remaining ones has resolved the issue for the project. However this process of shunt burning may be problematic in a manufacturing environment.

On vapor deposited films of Cu(InGa)Se₂, small area cell efficiency of more than 15% has been obtained with Cu(InGa)Se₂ thickness as small as 1.2 μm. For Cu(InGa)(SSe)₂ films obtained by precursor selenization, efficiencies of more than 12% were demonstrated. However, in this process, transitioning from glass substrate to an SS based one is believed to require a different and robust approach.

Uniformity of the device performance was shown on a 6 feet roll-to-roll PVD deposited Cu(InGa)Se₂. The central 4 ft of the web, when sampled every foot, provided devices with high efficiencies of more than 12% with Cu(InGa)Se₂ thickness of 1.4 μm.

Throughput up to 3 and 6 inches/min web speeds resulted in efficiencies in the range of 9 to 11% with an absorber thickness of around 1 μm.

The work on module fabrication was challenging in some respects. All laser monolithic integration has been a difficult problem that requires further work and more innovative solutions.
INTRODUCTION

The project has two objectives. First is to validate the use of low-cost stainless steel (SS) flexible substrate coated with silicone-based resin (SBR) dielectric, developed by Dow Corning Corporation (DCC), for Cu(InGa)Se₂ based photovoltaics. The second is to develop a monolithic integration technology for the fabrication of Cu(InGa)Se₂ based modules on this type of substrate.

The first objective overcomes many of the drawbacks of SS substrate. The SBR coating that can resist temperatures as high as 600°C will allow deposition of Cu(InGa)Se₂ films at optimum temperatures while at the same time makes possible monolithic integration of the modules. In addition, the dielectric coating will smooth the surface of the standard commercially available SS foils and may act, to a certain degree, as a diffusion barrier. As such the use of low cost, commercially available standard SS foils will become possible. The development and proof of concept of the monolithic integration scheme on such a substrate coupled with the roll-to-roll (R2R) manufacturing will demonstrate the feasibility of high throughput, fully automated commercial Cu(InGa)Se₂ based module fabrication. It will provide a strong driving force towards Solar Energy Technology Program’s major goals of reducing cost of energy and scaling up the manufacturing capacity.

The project will consist of two tasks corresponding to the two program objectives described above. Under Task 1, an SBR coated SS flexible substrate will be developed and validated for its applicability to the Cu(InGa)Se₂ based photovoltaics. The task will first develop the optimal SS/SBR substrates in terms of their thermo-mechanical properties both before and after Cu(InGa)Se₂ film processing. Later PV devices will be fabricated on Na doped Cu(InGa)Se₂ films deposited on coupons and on rolls. Task 2 focuses on developing scribing technologies to fabricate mini-modules on the material systems developed under Task 1. Initially scribing techniques for different layers will be investigated and developed and later applied to the fabrication of functional mini-modules.

BACKGROUND

Cu(InGa)Se₂ based photovoltaics has demonstrated the highest efficiency thin film solar cells and modules\(^{1,2}\). At the present time the technology is developing in two different fronts based on the type of substrate used: glass and stainless steel (SS) and polyimide foil web. Even though the highest efficiencies have been demonstrated on soda lime glass (SLG) substrates and being an electrical insulator allows monolithically interconnected module fabrication, it does present certain challenges as a substrate material in commercial manufacturing. Due to its softening below the 500 to 550 °C required for the high efficiency they must be supported from underneath, thereby requiring downward evaporation. This configuration raises the possibility of particulate contamination of the absorber layer surface, as well. In addition, given the significant quantities of fragile glass mass being transported in a commercial scale production the processing equipment is limited in throughput and quite complicated and expensive.
Thin flexible web substrates, allowing roll-to-roll manufacturing, reduce the capex cost and can reach very high throughputs. However polyimide films can not be used at temperatures above 450 °C(3), they require an extrinsic source of Na, and are relatively expensive. SS substrates are inexpensive and can be used at temperatures as high as 600 °C, but they won’t allow monolithic interconnection construction (being electrically conducting), they are a source of contaminants and their surface roughness is a major source of shunt losses in the devices.

In principle high temperature Silicone Based Resin (SBR) coated SS web will remove the disadvantages of the bare steel substrate mentioned above. As such, SBR coated SS foil web could be an attractive candidate as a substrate for Cu(InGa)Se₂ photovoltaics. The present project will validate the SBR coated SS foils as a substrate for Cu(InGa)Se₂ photovoltaics both in terms of its effect on the performance of single devices and of monolithically interconnected mini-modules.

**DEPOSITION OF Cu(InGa)Se₂ ON SBR COATED STAINLESS STEEL**

**SUBSTRATE DEVELOPMENT**

Initially, two types of 4 mil SS foils coated with SBR were evaluated to provide a baseline for the program. The foils were respectively 304 SS BR finish, which is a medium surface finish, and 430 SS #2 mil finish, which is the surface as it comes from the mill. These two types of steel, besides their surface finish, differ from each other in other ways as well. They are both low carbon steel but their composition is quite different as can be seen in Table I, provided by the supplier.

<table>
<thead>
<tr>
<th>Element</th>
<th>430 SS</th>
<th>304 SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.042</td>
<td>0.061</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.33</td>
<td>1.713</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.27</td>
<td>0.317</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.025</td>
<td>0.029</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Chromium</td>
<td>16.10</td>
<td>18.169</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.22</td>
<td>8.665</td>
</tr>
<tr>
<td>Molybdenium</td>
<td>0.02</td>
<td>0.372</td>
</tr>
<tr>
<td>Copper</td>
<td>n/a</td>
<td>0.399</td>
</tr>
<tr>
<td>Cobalt</td>
<td>n/a</td>
<td>0.186</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.045</td>
<td>0.033</td>
</tr>
</tbody>
</table>

The major difference is that 430 SS is nickel free. Micro-structurally they are substantially different in that 430 SS is martensitic while 304 is austenitic as Ni stabilizes the austenitic phase. It is also known that 430 SS is harder and less corrosion resistant.
than 304 SS. In addition martensitic SS is magnetic while austenitic is not. Perhaps more relevant to the present project is their respective Coefficient of Thermal Expansion (CTE): 430 SS is $11 \times 10^{-6}$ °C/°C while 304 SS is $18 \times 10^{-6}$ °C/°C. For comparison CTE of SLG, Mo, and Cu(InGa)Se$_2$ are respectively $9 \times 10^{-6}$ °C/°C, $5 \times 10^{-6}$ °C/°C, and $9 \times 10^{-6}$ °C/°C.

These SS foils have been SBR coated by Dow Corning Corporation (DCC). The coating thicknesses were measured in an SEM looking at the cryogenically prepared cross sections. Figure 1 gives thicknesses of 5.3 μm and 4.7 μm for SBR coatings applied respectively on 304 and 430 SS foils.

Fig. 1. Cross section SEM micrographs of the SBR coatings on 304 SS (left) and on 430 SS (right).

Surfaces of the uncoated and SBR coated SS foils were characterized by AFM tool. In all cases 3 randomly selected regions on a 1”x1” coupon were examined and the average RMS and Rmax (maximum observed elevation) were taken. Table II gives these averages. As expected 304 SS sample shows smoother surface than 430 SS.
Table II. Surface Rms and Maximum elevation, Rmax, observed by AFM on coated and uncoated samples (average of 3 measurements.)

<table>
<thead>
<tr>
<th>SS</th>
<th>SS &lt;Rms&gt; (nm)</th>
<th>SS/SBR &lt;Rms&gt; (nm)</th>
<th>SS &lt;Rmax&gt; (nm)</th>
<th>SS/SBR &lt;Rmax&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>24.3</td>
<td>6.1</td>
<td>204.1</td>
<td>108.7</td>
</tr>
<tr>
<td>304</td>
<td>16.1</td>
<td>3.3</td>
<td>173.9</td>
<td>65.0</td>
</tr>
</tbody>
</table>

The Table also shows, convincingly, that SBR coating smoothes out the surface as both Rms and Rmax parameter are reduced substantially. For purposes of information, actual AFM data for SBR coated 304 SS and 430 SS samples are given in Fig. 2.

![AFM micrographs](image_url)

Fig. 2. AFM micrographs of the SBR coatings on 304 SS BR finish (right) and on 430 SS #2 finish (left).

The above substrates in the form of 1”x1” coupons were sputter coated with 0.5 μm Mo for the purpose of evaluating the Mo films on SBR coated SS samples.

First adhesion testing was performed on the Mo coated samples using tape testing method utilizing 3M’s #600 tape rated at 40 oz/inch. The result for both 304 and 430 SS base resulted in glue failure. The test indicates that adhesion of SBR to SS and Mo film to SBR is quite adequate. The adhesion testing was continued for some time early in the project until convincing statistics were obtained.

Electrical tests on these samples consisted on measuring the sheet resistance (4-point probe) and comparing them to the sheet resistance of the Mo film deposited on the glass witness slide. The witness slide and both 304 and 430 SS based samples, probed at different locations, all gave a value of 0.3 Ω/sqr. This seems to indicate the SBR coating seems to provide a benign base for the Mo coating.

The surface topography of the 430 SS CB as characterized by AFM presented an average (3-points) surface Rms and maximum elevation, Rmax, of 10 nm and 78 nm respectively. These values were 3 nm and 54 nm respectively on samples coated with
SBR. By comparison to 430 SS #2 (mil finish) the CB finish showed a lower surface roughness by a factor of 2. Mo coating of the SBR coated 430 SS CB samples were found to have high adhesion based on the tape test performed by 3M’s #600 tape rated at 40 oz/inch. The test resulted in glue failure.

The two type of SS substrates behaved dramatically differently when coated with Cu(InGa)Se$_2$ by physical vapor deposition (PVD). While Cu(InGa)Se$_2$ deposited on the 304SS/SBR/Mo substrate was heavily cracked and partially lifted, there were no observable defects on the film deposited on 430SS/SBR/Mo the film. This can be seen in Figure 3. The tape test performed on the latter sample showed glue failure rather than any delamination. Even though the sample 430SS substrate wasn’t suitable for the device,

Fig. 3. Secondary electron micrographs (SEM) of the Cu(InGa)Se$_2$ films deposited on 304SS/SBR/Mo substrate (A) and on 430SS/SBR/Mo substrate (B).

Fig. 4. SEM image (A) and the Si K$\alpha$ image (B) showing the lifting off of the Cu(InGa)Se$_2$ and Mo films over large areas on 304 SS based substrate.
it was nevertheless put through the CdS bath deposition process to give an idea of the extent of the adhesive failure besides film cracking. The process removed both Mo and Cu(InGa)Se₂ film over large areas as can be observed in Figure 4.

The difference in the physical damage observed is directly related to the CTE differences of the two types of steel. In view of these observations only 430SS/SBR substrates were subsequently used in the project.

Subsequent to the substrate selection, shunting through the SBR coatings has been investigated. Initial experiments consisted of depositing 5 µm Mo through a square mask, smaller than 1”x1” on 1”x1” SBR coated 4 mil 430SS CB finish. The resistance was measured between the Mo square and the back-side SS of the sample. For samples where there was a measurable resistance a gradually increasing DC voltage was applied while measuring the current to find out if the current burns the shunt. Table III summarizes the results.

As the table shows almost 50% of the samples do show some level of shunting, and all but one of the shunts are burned at applied voltages of less then 6 V.

Similar results were obtained with:

- 0.2 µm Mo on 5 µm SBR coated 4 mil 430SS CB finish,
- 0.2 µm Mo on 5 µm SBR coated 4 mil 430SS #2 finish, and
- 0.2 µm Mo on 5 µm SBR coated 2 mil 430SS # finish

Thermal radiance measurement using a low-cost Bolometer Camera helped visualize the shunts very clearly. Figure 5 is such an image captured from the SS side of a typical sample.

The cause and the nature of these shunting paths could not be determined with certainty. These shunts did not present any problem for small area single devices. However, for the evaluation of 4”x4” interconnected modules they would present a problem and needed to be burned as will be discussed later in the report. Such an approach is feasible in a research program but for commercial scale applications a more robust solution is needed.

Based on these findings, DCC organized and completed another coating trial using an alternate coating method to generate SBR coated 1.5 mil 430 SS foil samples with reduced coating defects. Out of 46 samples tested, only 7 showed shunting. They were all burned with a voltage less than 3 V.
Table III. Shunt resistance thru SBR and the maximum voltage to burn them.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R (Ω)</th>
<th>Max Applied Voltage (V)</th>
<th>R (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33A9-1</td>
<td>2</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>33A9-3</td>
<td>&gt; 20 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33A9-4</td>
<td>&gt; 20 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33A9-5</td>
<td>&gt; 20 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33A9-6</td>
<td>&gt; 20 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30B6-1</td>
<td>3.2</td>
<td>5</td>
<td>1.5 M</td>
</tr>
<tr>
<td>30B6-2</td>
<td>82.8</td>
<td>6</td>
<td>6 M</td>
</tr>
<tr>
<td>30B6-3</td>
<td>64.9</td>
<td>6</td>
<td>&gt; 20 M</td>
</tr>
<tr>
<td>30B6-4</td>
<td>109.5</td>
<td>3</td>
<td>&gt; 20 M</td>
</tr>
<tr>
<td>30B6-5</td>
<td>8.3</td>
<td>3</td>
<td>&gt; 20 M</td>
</tr>
<tr>
<td>30B2-1</td>
<td>85.8</td>
<td>4</td>
<td>&gt; 20 M</td>
</tr>
<tr>
<td>30B2-2</td>
<td>4.1</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>30B2-3</td>
<td>&gt; 20 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30B5-1</td>
<td>1.9</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. The picture of the SS side of a sample captured by a bolometer camera with 2V applied between SS surface and the Mo film at the back (in the picture). Two hot spots are clearly visible.
As a result of these improvements on batch coating and annealing DCC put in service roll-to-roll equipment for coating (3 μm standard) and annealing 8” wide SS web. The SS rolls were Mo coated at our outside vendor, TechniMet at a thickness of 0.2 μm giving sheet resistances in the range of 0.8 to 1.3 Ω/sqr.

SMALL AREA SUBSTRATE VALIDATION

Small area substrate validation consists of depositing Cu(InGa)Se₂ films on the SS/SBR/Mo structure to evaluate the resistance of the structure to the Cu(InGa)Se₂ deposition environment and to determine the device performance of small area cells fabricated on them. Cu(InGa)Se₂ deposition is performed by either elemental evaporation or by selenization of the precursor films.

Elemental Evaporation: In-Line Deposition

Elemental evaporation is performed in two different reactors. The first is the roll-to-roll reactor modified into an in-line system for 1”x1” coupon type samples, Figure 6. The second is a bell-jar type multi-source evaporation system.

Fig. 6. Roll-to-roll Cu(InGa)Se₂ deposition system configured for in-line deposition on multiple coupon substrates.
Initial experiments were performed in the in-line system where various substrates were loaded onto the carrier that was translated over the effusing sources. Source effusion rates are controlled by thermocouples imbedded into the source. The reactor is controlled through LabView software developed in-house. The web/carrier transport is controlled by a commercial PLC. Initially the carrier is translated from the pickup roller side to the payout side with the Cu source turned off so as to deposit a thin layer, approximately 0.2 to 0.3 μm Ga2-xInxSe3 film that acts as an adhesion layer. This is our standard operating procedure for polymide web substrate. After the substrate temperatures are raised to 550 °C, and the sources stabilized to their respective temperatures the carrier is moved through the deposition zone to have Cu(InGa)Se2 deposited. Initially Na source was not turned on.

Initial experiments in the in-line system, with Na source was turned off, gave a comparison of device results on soda-lime-glass (SLG) / Mo and 430SS / SBR / Mo substrates processed during the same run. Figure 7 gives examples of the results obtained from devices fabricated from each substrate.

The device data on SBR coated 430SS give efficiency of 11% that is encouraging for initial tries. The data when compared to the SL glass substrate reference (B) shows a decrease of 100 mV in Voc and 10 points in FF. These are generally associated with the lack of Na in the absorber.

Similar experiments were performed in the stationary evaporation system using the same type of substrates. In this case, in addition to the device performances, the composition of the absorbers has been measured (Table IV). It should be pointed out that Cu(InGa)Se2 films deposited in the stationary system have uniform depth composition while the ones deposited in the in-line system always show a gradient in Ga and In through the depth(3,4,6). As such compositions measured by energy
dispersive spectroscopy (EDS) are generally more accurate for films deposited in the stationary system via single stage process.

Table IV. Composition of Cu(InGa)Se$_2$ film on 430 SS / SBR and SLG from the same Cu(InGa)Se$_2$ run in the stationary system.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu (at%)</th>
<th>Ga (at%)</th>
<th>In (at%)</th>
<th>Se (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430 SS</td>
<td>25.8</td>
<td>6.3</td>
<td>16.5</td>
<td>51.4</td>
</tr>
<tr>
<td>SLG</td>
<td>24.0</td>
<td>6.9</td>
<td>18.4</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Fig. 8. Cu(InGa)Se$_2$ device characteristics deposited on 430 SS/SBR/Mo (A) and on SLG/Mo (B) in the same stationary run.

Again comparison of the samples show lower performance of the device on SS/SBR/Mo most likely associated with the lack of Na.

More precise characterization of the chemistry and of the interdiffusion of trace amounts of impurities from SLG and SS/SBR substrates were characterized by the secondary ion mass spectroscopy (SIMS) at NREL.

Figures 9 and 10 compare the SIMS profiles for Na, and all the matrix elements (i.e., Cu, In, Ga, Se and Mo) and for the impurities for CIGS films fabricated by in-line co-evaporation on SLG and SS/SBR substrates. It should be pointed out that in these profile counts, rates of the elements were normalized to that of Se to be able to make proper relative comparison.

In Figure 9 SIMS profiles of SLG/Mo/CIGS and of SS/SBR/Mo/CIGS were found to be similar except for Na. The Na concentration in SLG/Mo/CIGS was almost two orders of magnitude higher than in SS/SBR/Mo/CIGS in the absence of external Na dosing.
In Figure 10 where all the counts were again normalized to that of Se, the concentration of Si detected in the CIGS layer of a SS/SBR/Mo/CIGS sample was negligible and much smaller than that of SLG/Mo/CIGS. Therefore, it is reasonable to conclude that no Si is diffused out of SBR layer but did diffuse out of SLG during in-line co-evaporation of CIGS. This was an unexpected observation and needs further verification within the context of other research projects.

Next step was to introduce Na into the films by co-evaporating NaF in the in-line system from a source identical to other metallic sources. Initially the NaF evaporation from a powdered source was evaluated in a bell-jar vacuum system. Using the vapor pressure data from literature(5) and the film deposition modeling previously developed in our laboratories(6) the amount of NaF impinging on the substrate was estimated as shown in Figure 11. The red line in the figure gives the amount of Cu impinging at the same location. If it is assumed that 0.1% atomic Na should be adequate, the Na source temperature of less than 500°C must be sufficient. However, a number of runs made at 550°C showed no effect of Na incorporated into the Cu(InGa)Se2 films. This probably is due to the fact that the original effusion data was obtained from unheated samples while the deposition of Cu(InGa)Se2 films are performed at a 550°C substrate temperature. Sticking coefficient had to be dramatically different in these two cases. As a result, a series of Cu(InGa)Se2 depositions were made with NaF source temperature varying from 775°C to 875°C in order to find the appropriate range. All the films were deposited at nominally identical conditions except for NaF source temperature. Each run had two SLG/Mo and 430SS/SBR/Mo substrates.

Table V gives the composition of the Cu(InGa)Se2 films deposited on SLG/Mo and 430SS/SBR/Mo of the substrates in each run along with the normalized Na contents. The latter were obtained by SIMS analysis as explained earlier. In run number 7530 Na source was not used and the data from this run was included as a reference.
Fig. 9. SIMS profiles of in-line co-evaporated CIGS samples on SLG (A) and on SS/SBR (B) substrates for Na, Al and major elements.
Fig. 10. SIMS profiles of in-line co-evaporated CIGS samples on SLG (A) and on SS/SBR (B) substrates for impurities Mg, Si, Cr, Fe.

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Fig. 11. Amount of NaF as a function its source temperature; Cu arrival rate in red.

Figure 12 gives the best device data on SS/SBR/Mo and on its companion (in the same run) SLG/Mo substrates. Even though there is considerable scatter in the performance of the devices, the effect of Na can be seen even at 775°C by the $V_{oc}$ and FF values that are similar to what is observed on SLG substrates and are considerably improved from devices produced without Na. It should be pointed out that Cu(InGa)Se$_2$ films on SLG substrates get Na from the glass, by diffusion, as well as from the NaF evaporation. Na content in the films follow the Na source temperature up to 850°C. At higher temperature a drop in Na content is observed. It is believed that this may be the result of the powder NaF in the source getting sintered and thus changing the evaporation characteristics.

Table V. Composition of Cu(InGa)Se$_2$ films for different NaF source temperature.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Substrate</th>
<th>$T_{Na}$ (°C)</th>
<th>EDS composition (at%)</th>
<th>[Na/Se] (SIMS)</th>
<th>Cu/III</th>
<th>Ga/III</th>
</tr>
</thead>
<tbody>
<tr>
<td>70530</td>
<td>SS/SBR</td>
<td>21.5</td>
<td>6.5</td>
<td>17.4</td>
<td>50.4</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>SLG</td>
<td>21.4</td>
<td>7.0</td>
<td>18.0</td>
<td>51.0</td>
<td>200</td>
</tr>
<tr>
<td>70513</td>
<td>SS/SBR</td>
<td>22.3</td>
<td>8.0</td>
<td>17.0</td>
<td>52.3</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>SLG</td>
<td>22.4</td>
<td>4.7</td>
<td>16.7</td>
<td>53.2</td>
<td>1.05</td>
</tr>
<tr>
<td>70511</td>
<td>SS/SBR</td>
<td>21.4</td>
<td>7.4</td>
<td>18.0</td>
<td>53.2</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>SLG</td>
<td>21.4</td>
<td>7.5</td>
<td>17.6</td>
<td>53.5</td>
<td>0.85</td>
</tr>
<tr>
<td>70510</td>
<td>SS/SBR</td>
<td>21.6</td>
<td>8.2</td>
<td>16.2</td>
<td>54.1</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>SLG</td>
<td>20.4</td>
<td>8.7</td>
<td>15.7</td>
<td>55.2</td>
<td>0.89</td>
</tr>
<tr>
<td>70512</td>
<td>SS/SBR</td>
<td>21.7</td>
<td>7.0</td>
<td>17.2</td>
<td>54.1</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td>SLG</td>
<td>22.3</td>
<td>7.3</td>
<td>16.6</td>
<td>53.8</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Fig. 12. Best devices on SS/SBR/Mo and on its companion SLG/Mo substrates for different NaF source temperature.
The best efficiency among the devices fabricated on SS/SBR/Mo substrates of Figure 12 was obtained for NaF temperature of 775°C. Furthermore, 775°C NaF gives a Na content quite close to that from SLG substrate. Consequently, in the present work, 775°C was used as the baseline NaF source temperature.

**Precursor Selenization /Sulfization**

Metallic precursors were deposited from targets of Cu$_{0.8}$Ga$_{0.2}$ alloy and In forming a bi-layer structure or from single target of Cu0.5In.4Ga.1. Figure 13 shows schematically 2-target precursor deposition. Sample trays were designed to rotate over the sputtering targets at 5 RPM during the process for either case depositing a total precursor layer of 700 nm.

![Schematic diagram of sputtering system for metal precursor deposition.](image)

Fig. 13. Schematic diagram of sputtering system for metal precursor deposition.

![SEM micrographs of Cu-In-Ga metal precursors on (A) Mo/SLG and, (B) Mo/SBR/SS.](image)

Fig. 14. SEM micrographs of Cu-In-Ga metal precursors on (A) Mo/SLG and, (B) Mo/SBR/SS.
The SEM micrographs of metal precursors on SLG/Mo and SS/SBR/Mo are shown in Fig. 14. EDS analysis revealed that the white islands exhibit In-rich composition while the background matrix is Cu-rich. There is no significant difference in average composition, although on the SS substrate the In-rich islands are linked together forming larger structures. Compositional data are given in Table VI.

Table VI. Compositional data of samples in Figure 14, obtained by spot and wide-area EDS measurements.

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Ga (at%)</th>
<th>Mo (at%)</th>
<th>Cu/III</th>
<th>Ga/III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>38.4</td>
<td>37.9</td>
<td>8.7</td>
<td>15.1</td>
<td>0.82</td>
<td>0.19</td>
</tr>
<tr>
<td>Island</td>
<td>35.6</td>
<td>43.6</td>
<td>8.1</td>
<td>12.6</td>
<td>0.69</td>
<td>0.16</td>
</tr>
<tr>
<td>Matrix</td>
<td>41.2</td>
<td>25.2</td>
<td>9.7</td>
<td>23.0</td>
<td>1.18</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Various phases in the films were determined by Grazing-Incidence X-Ray Diffraction (GIXRD.) Figure 15 shows the spectra taken at 0.5° and 4° incidence for precursors deposited on SLG substrate. The spectra shows the presence of In, Cu₃Ga, Cu₄In, and Cu₉(In₁₋ₓ,Gax)₄, phases. It can be seen that the intensity of the In phase was higher in the surface region than the bulk due to the contribution from the islands. It is observed that both precursor deposition processes give similar morphology and composition.

Fig. 15. GIXRD patterns taken from incident angles of 0.5°(black) and 4° (Red). Symbols of ■, ●, ▲, and ▼ are indicating In, Cu₃Ga, Cu₄In, Cu₉(In₁₋ₓ,Gax)₄, respectively.
Initial effort was concentrated on developing 3-step reaction process on SLG substrate. Once the process is successfully developed it was transitioned to SS/SBR substrate.

The reaction process, in terms of temperature v. time, is shown schematically in Figure 16. All the reactions were conducted at a total flow of 1.3 sLm under 1 atm pressure.

![Diagram of reaction process](image)

**Fig. 16.** 3-step reaction for metal precursor involving selenization, annealing and sulfization.

During the 1st step, precursor coated samples are inserted into the preheated hot zone of the 2" diameter quartz reaction tube after establishing the flow of the reaction gases. The reaction takes place at 400°C or 450°C for 60 or 15 min respectively in a gas mixture of:

- 0.35% H₂Se
- 0.0035% O₂
- Balance Ar

2nd step involves removing the samples from the heat zone, raising the temperature to 550°C and establishing Ar only flow and reinserting the sample back to the heat zone for 20 min.

In the third step, the sample was kept at the heat zone at 550°C for 10 min with gas flows as in the 1st step.

SEM images of the reacted films with associated EDS data are shown in Figure 17. The transition between the 1st step and the 2nd step exhibited a significant change in the morphology while the transition from 2nd to 3rd step did not. The EDS analysis revealed that the ratio of Ga/III also have a considerable change through the 1st step and the 2nd step. The Ga grading toward the Mo back contact by selenization is a well-known phenomenon and is also observed here after the 1st step.(7-9) However, It was found
that during 2nd step there is a significant Ga redistribution through the films. The 3rd step did not involve any significant change in composition except for S incorporation into the film at the surface.

Fig. 17. SEM images after each reaction step and the associated composition as measured by EDS.

Cross sectional SEM images of reacted films after each step are shown in Figure 18. The 1st step of selenization resulted in fine microstructure and a continuous void between Cu(InGa)Se2 films and Mo back contact as shown in Figure 18(a). The bottom of the film in contact with Mo shows a particularly fine structure of about 500 nm thick. It is the region where the well-known Ga accumulation occurs at the end of the selenization step. After the 2nd step of annealing in Ar at 550°C for 20 min, a significant grain growth along with an agglomeration of voids at the Mo interface as shown is observed (Figure 18(b).) Even though there are still voids between Cu(InGa)Se2 and Mo films, there are few in numbers substantially increasing the contact area. As shown in Figure 18(c) the 3rd step of sulfization did not bring any significant changes except for a slight increase of grain boundaries.

Further insight to the selenization / sulfization process is obtained by the Auger electron spectroscopy depth profiles (Figure 19) taken after each process step. The profile after the 1st step clearly shows Ga and Cu accumulation at the back of the structure. It is believed that this is the indication of Cu-Ga intermetallic compound moving to the back of the structure due to the preferential selenization of In over the intermetallic Cu-Ga compound. During the 2nd step, a significant Ga distribution through films is observed. The sulfization step did not accompany a significant change in composition except for S incorporation into the film surface.

Figure 20 and Table VII show the SEM images and the EDS data of Mo surface after Cu(InGa)Se2 film were lifted off after the 1st step. The spot EDS analysis identified the nodules as Cu9Ga4 intermetallic and the background as Mo thus confirming the Cu-Ga accumulation at the back of the film. Figure 20 also shows that Cu9Ga4 is largely dissolved into the film as a result of Ar annealing step.
Fig. 18. Cross sectional SEM images showing the structure of reacted films after each step.

Fig. 19. AES depth profiles of reacted films following each reaction step.
Fig. 20. SEM micrograph of the surface after removal of the film structure following the 1st step.

Table VII. Compositional data of the samples in Figure 20 obtained by spot analysis EDS measurements.

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Ga (at%)</th>
<th>Mo (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nodule</td>
<td>10.6</td>
<td>5</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Matrix</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>99.4</td>
<td></td>
</tr>
</tbody>
</table>

In order to evaluate absorber formation on SS/SBR foil substrate, Cu(InGa)(SeS)$_2$ thin films were prepared by the above described method on three kinds of substrate as shown in Table VIII. Two different variants of the 1st step were used: process 1 was 60 min at 400°C and process 2 was 10 min at 450°C.

Table VIII. Samples used for 3-step H$_2$Se/Ar/H$_2$S reactions utilizing two different selenization process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Process</th>
<th>Substrate</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1305.21F</td>
<td>1</td>
<td>SS/SBR</td>
<td>Na-free</td>
</tr>
<tr>
<td>L1305.11B</td>
<td>1</td>
<td>SLG</td>
<td>Na</td>
</tr>
<tr>
<td>L1308.11A</td>
<td>1</td>
<td>Ti</td>
<td>Na-free</td>
</tr>
<tr>
<td>L1305.13F</td>
<td>2</td>
<td>SS/SBR</td>
<td>Na-free</td>
</tr>
<tr>
<td>L1305.12B</td>
<td>2</td>
<td>SLG</td>
<td>Na</td>
</tr>
<tr>
<td>L1308.12A</td>
<td>2</td>
<td>Ti</td>
<td>Na-free</td>
</tr>
</tbody>
</table>
The films obtained using Process 1 had morphology and composition that depended on the type of substrate. Figure 21, where samples’ surface microstructure and their compositions obtained by SEM and EDS respectively are shown, highlights this difference. Macroscopic view of the samples, obtained through an optical scanner, are also shown to display differences over the entire 1”x1” surface. In particular, the SS/SBR sample, found to have non-uniform S incorporation, showed spots on the surface. On the other hand, the Ti sample, though visually uniform, showed low S incorporation overall. The two Na-free samples, L1305.21F (SS/SBR) and L1308.11A (Ti), showed different morphology and composition suggesting that surface structure of the substrates might be influencing the reaction.

Contrary to Process 1, Process 2 provided more homogeneous films on all of the substrates as shown in Figure 22. Although the two samples on SS/SBR formed by this variant still had faint in-homogeneities in surface color and S incorporation.

JV characteristics of Cu(InGa)(SeS)2 solar cells fabricated on different substrates are listed in Table IX. The SLG sample obtained by Process 1 demonstrated the best efficiency of 14.2 %. However, the SS/SBR and Ti samples fabricated with Process 2 showed better performance than the ones from Process 1. In both cases, the Na-free
Fig. 22. Optical scanning images of complete 1”x1” sample (1st row) and SEM images (2nd row) of films formed by Process 2; see text for explanation.

Table IX. Light JV characteristics of Cu(InGa)(SeS)2 solar cells on different substrate using Processes 1 and 2.

<table>
<thead>
<tr>
<th>Process</th>
<th>Substrate</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SS/SBR, Na-free</td>
<td>0.370</td>
<td>14.0</td>
<td>43.5</td>
<td>2.3</td>
</tr>
<tr>
<td>1</td>
<td>SLG</td>
<td>0.600</td>
<td>32.4</td>
<td>72.3</td>
<td>14.2</td>
</tr>
<tr>
<td>1</td>
<td>Ti, Na-free</td>
<td>0.437</td>
<td>30.3</td>
<td>49.7</td>
<td>6.6</td>
</tr>
<tr>
<td>2</td>
<td>SS/SBR, Na-free</td>
<td>0.471</td>
<td>26.7</td>
<td>44.2</td>
<td>5.6</td>
</tr>
<tr>
<td>2</td>
<td>SLG</td>
<td>0.603</td>
<td>32.0</td>
<td>68.6</td>
<td>13.2</td>
</tr>
<tr>
<td>2</td>
<td>Ti, Na-free</td>
<td>0.446</td>
<td>31.8</td>
<td>60.6</td>
<td>9.0</td>
</tr>
</tbody>
</table>

samples were found to have significantly lower \(V_{oc}\) than that of the SLG sample, which has been typically observed in a previous study\(^{10}\). Since Process 2 has shown better device performance with the flexible SS/SBR substrates, it has been employed as the baseline process for the rest of the present work.
The incorporation of Na into the Cu(InGa)(SeS)$_2$ film was the next step. For this purpose, NaF films with various thicknesses were deposited onto the Mo back contact, followed by metal precursor layers deposited from single target.

NaF thicknesses used and corresponding substrates are listed in Table X. Using the single CuInGa target, about 7500 Å-thick metal precursors have been prepared for Cu/III and Ga/III of 0.86 and 0.19, respectively. As stated earlier Process 2 has been used to convert Cu(InGa)(SeS)$_2$ films from the metal precursors.

Table X. NaF thickness and the substrates used for the conversion of the metal precursors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>NaF thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS031.31A</td>
<td>Mo/SBR/SS</td>
<td>0</td>
</tr>
<tr>
<td>NS031.12B</td>
<td>NaF/Mo/SBR/SS</td>
<td>5</td>
</tr>
<tr>
<td>NS031.13C</td>
<td>NaF/Mo/SBR/SS</td>
<td>10</td>
</tr>
<tr>
<td>NS031.12C</td>
<td>NaF/Mo/SBR/SS</td>
<td>30</td>
</tr>
<tr>
<td>NS033.23</td>
<td>Mo/SLG</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 23 shows SEM images with the associated composition values determined by EDS, for samples converted to Cu(InGa)(SeS)$_2$ on Mo/SBR/SS substrates. Mo/SLG substrate was used as reference in comparing device performances and SIMS profiles. Surface morphologies in every case exhibited strongly faceted structure. The Cu(InGa)(SeS)$_2$ film with 30 nm NaF appears to have slightly finer grain structure, but other than that no significant difference in the morphology was observed as a function of NaF thickness. This fact was also confirmed in the cross-sectional SEM images of Figure 24. It should be noted that Cu to group III ratios shown in Figure 23 are very close to or above one. However, since devices fabricated on these samples didn’t show any significant shunting, EDS measurements might slightly overestimate the Cu content.

The SEM examination of the Cu(InGa)(SeS)$_2$ films on Mo/SBR/SS at low magnification (i.e. large area) showed peculiar dome shaped features in the case of 10 nm NaF on Mo, and Cu(InGa)(SeS)$_2$ film delamination in the case of 30 nm NaF on Mo (Figure 25.) The cause of the dome shaped features is not well understood. However, it did not negatively affect the performance of the devices fabricated on such samples. On the other hand the lack of adhesion associated with the sample on 30 nm NaF did not allow it to further processing. It seems that 10 nm NaF on Mo/SBR/SS is the upper limit of the thickness of NaF for this method of introducing Na into the Cu(InGa)(SeS)$_2$ film.
Fig. 23. SEM surface morphology and EDS composition of reacted Cu(InGa)(SeS)$_2$ films on Mo/SBR/SS with various NaF thicknesses.

Fig. 24. SEM cross-sectional morphology reacted Cu(InGa)(SeS)$_2$ films on Mo/SBR/SS with various NaF thicknesses.
SIMS analysis of the Cu(InGa)(SeS)$_2$ films can be summarized as follows:

- All the films exhibit surface accumulation of Na,
- Na content in the bulk follows the thickness of the NaF with approximately:
  - $3 \times 10^{16}$ cm$^{-3}$ for no NaF
  - $2 \times 10^{18}$ cm$^{-3}$ for 5 nm NaF
  - $1 \times 10^{19}$ cm$^{-3}$ for 10 nm NaF and for SLG substrate with no NaF
- There is a linear gradient of 0.1 in Ga/III decreasing from 0.2 at the back to 0.1 at the surface, independent of NaF thickness.
- S/VI decreases from 0.7 at the surface to 0 within 0.6 $\mu$m for all NaF thicknesses. In the case of SLG substrate and 10 nm NaF the ratio decreases to around 0.1 within the same distance and stay constant throughout the film.

Figure 26 and Table XI show dark and light JV characteristics of a finished device with various NaF thicknesses. The data is shown right after device fabrication and following the heat treatment at 200$^\circ$C for 2 min in air. Na incorporation into the Cu(InGa)(SeS)$_2$ film is found to affect device performances in two ways. Firstly, higher Na incorporation significantly promoted $V_{oc}$ and consequently the conversion efficiency. Previous analysis of Na free Cu(InGa)Se$_2$ devices do not operate through the recombination in the absorber space charge region via SRH mechanism and may be controlled through interface recombination resulting in lower $V_{oc}$ (10). The same explanation could be applied to the Cu(InGa)(SeS)$_2$ devices with various NaF thicknesses. Second aspect of Na incorporation is its effect on the result of the heat treatment of the devices. There is some indication, not very strong, that devices with Na benefit from the heat treatment but in the absence of Na heat treatment actually reduces the performance.
Fig. 26. Initial / heat treated light / dark JV curves of Cu(InGa)(SeS)₂ solar cells on SBR/SS and SLG substrates with various NaF thicknesses: (a) 0 nm NaF, (b) 5 nm NaF, (c) 10 nm NaF, and (d) SLG.

Table XI. Initial and heat treated light / dark JV characteristics of Cu(InGa)(SeS)₂ solar cells on SBR/SS and SLG substrates with various NaF thicknesses.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>HT</th>
<th>NaF thickness (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS/SBR</td>
<td></td>
<td>0</td>
<td>0.452</td>
<td>34.1</td>
<td>61.4</td>
<td>9.5</td>
</tr>
<tr>
<td>SS/SBR</td>
<td>Y</td>
<td>0</td>
<td>0.443</td>
<td>34.8</td>
<td>56.6</td>
<td>8.7</td>
</tr>
<tr>
<td>SS/SBR</td>
<td></td>
<td>5</td>
<td>0.494</td>
<td>35.0</td>
<td>64.1</td>
<td>11.4</td>
</tr>
<tr>
<td>SS/SBR</td>
<td>Y</td>
<td>5</td>
<td>0.513</td>
<td>35.1</td>
<td>62.0</td>
<td>11.2</td>
</tr>
<tr>
<td>SS/SBR</td>
<td></td>
<td>10</td>
<td>0.522</td>
<td>34.0</td>
<td>66.3</td>
<td>11.8</td>
</tr>
<tr>
<td>SS/SBR</td>
<td>Y</td>
<td>10</td>
<td>0.529</td>
<td>33.7</td>
<td>69.8</td>
<td>12.5</td>
</tr>
<tr>
<td>SLG</td>
<td></td>
<td>0</td>
<td>0.546</td>
<td>30.4</td>
<td>68.9</td>
<td>11.4</td>
</tr>
<tr>
<td>SLG</td>
<td>Y</td>
<td>0</td>
<td>0.552</td>
<td>30.4</td>
<td>72.2</td>
<td>12.1</td>
</tr>
</tbody>
</table>
Figure 27 displays external quantum efficiencies (EQE) and their first derivatives of the devices. Low Na-incorporated samples showed better collection efficiency for wavelength over 600 nm, which has been already reported by other groups. Caballero et al. reported that Na incorporation affected Ga grading\(^{11}\) and hence it could change the band gap of absorber. However, it is worthwhile to note that the first derivatives of the EQE do not seem to be affected by Na incorporation. The local minima of all the samples are found at nearly identical places giving an estimate of the band gaps which in this case is around 1.05 eV (marked with arrow in the Figure) and therefore Na does not greatly affect the Ga grading in the absorber.

![Graph showing external quantum efficiency (EQE) and their first derivatives for Cu(InGa)(SeS)\(_2\) solar cells with various NaF content.](image-url)

**Fig. 27.** External QE curves for Cu(InGa)(SeS)\(_2\) solar cells with various NaF content. dQE/d\(\lambda\) plots for each cell are also presented right Y scale. Arrow points to a band gap of 1.05 eV.

Temperature dependence of \(V_{OC}\) measurements were carried out to understand this effect. Figure 28 shows \(V_{OC}-T\) plots for each device after the heat treatment.

The relationship between \(J_{SC}\) and \(V_{OC}\) is given by

\[
J_{sc} = J_0 \exp \left( \frac{qV_{oc}}{AKT} \right) = J_{00} \exp \left( \frac{qV_{oc}}{AKT} \right) \exp \left( -\frac{E_a}{AKT} \right) \tag{1}
\]

where, A and \(J_0\) are the diode ideality factor and the saturation current density of the
diode, $kT/q$ is the thermal voltage, $J_{00}$ is a temperature-dependent prefactor, and $E_a$ is the activation energy of recombination. Rearranging Eq. (1) yields the following,

$$V_{oc} = \frac{E_a}{q} - \frac{A k T}{q} \ln \left( \frac{J_{00}}{J_{sc}} \right)$$  (2)

By measuring $V_{OC}$, as a function of temperature one can estimate the activation energy of recombination (Figure 28). Typically, Cu(InGa)(SeS)$_2$ solar cells show an activation energy similar to its band gap. However, in these selenized/sulfized films the activation energies are found to be larger than the band gap as obtained from QE measurements. The complete explanation for this behavior has not yet been made especially in the case of S containing cells. Nevertheless, Figure 28 shows that Na incorporation seems to be the cause of this increase in the recombination activation energy.

![Fig. 28. $V_{OC}$-T plots of Cu(InGa)(SeS)$_2$ solar cells on SBR/SS substrate described in Table XI. Generally, Na-incorporated cells have higher activation energy of recombination.](image)

Na incorporation into the Cu(InGa)(SeS)$_2$ films by depositing NaF onto the SBR prior to Mo deposition and also onto the precursors after their deposition were also investigated. In these cases, precursors were deposited by the 2-target sputtering, and only 10 and 30 nm thick NaF films were used. However, thicker NaF on SBR showed loss of adhesion and on metal precursors resulted in incomplete reaction. Table XII gives the light JV characteristics of the representative devices.
Table XII. Light JV characteristics of Cu(InGa)(SeS)2 solar cells on SBR/SS and SLG substrates with various NaF thicknesses at different interface.

<table>
<thead>
<tr>
<th>NaF deposited on</th>
<th>NaF (nm)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS/SBR</td>
<td>10</td>
<td>0.567</td>
<td>33.9</td>
<td>63.2</td>
<td>12.2</td>
</tr>
<tr>
<td>SS/SBR</td>
<td>30</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precursor</td>
<td>10</td>
<td>0.563</td>
<td>33.3</td>
<td>69.8</td>
<td>12.5</td>
</tr>
<tr>
<td>Precursor</td>
<td>30</td>
<td>0.429</td>
<td>14.4</td>
<td>63.5</td>
<td>2.6</td>
</tr>
<tr>
<td>SLG</td>
<td>0</td>
<td>0.603</td>
<td>32.1</td>
<td>68.8</td>
<td>13.3</td>
</tr>
</tbody>
</table>

The results seem to indicate that, within this set, the interface NaF deposited does not make significant difference in the performance of the devices. In terms of process reliability, however, it would be advisable to deposit NaF on metal precursors since the adhesion would not be an issue. However, if thicker NaF is found to be necessary, the process would need to be re-optimized to allow selenization to proceed unimpeded by NaF.

In order to be able to produce mini-modules based on precursor selenization, a 6” diameter tube reactor placed in a triple heating zone box furnace was put in service. The process is similar to the one used in the 2” furnace (i.e. 3-step process) but for a different time-temperature profile. In bringing up the process, issues with adhesion, incomplete reaction, and surface morphology had to be dealt with. Figure 29 gives the modified 3-step developed in the 6” reactor.

Fig. 29. Modified 3-step reaction for the 6” reactor.
Figure 30 shows the SEM surface morphology and EDS data of Cu(InGa)(SeS)$_2$ films on SLG/Mo and SS/SBR/Mo substrates obtained through the modified 3-step reaction of Figure 29. In order to add Na to the SS/SBR sample, 10 nm-thick NaF film was deposited onto the top of the metal precursor prior to the 3-step reaction. There is no significant difference in the surface morphology but S incorporation in the SS substrate is higher than that of the SLG substrate sample. The reason for different S incorporation is unclear. However, it is presumed that NaF on the film surface might retard selenization resulting in over-sulfization.

Fig. 30. Surface morphology (SEM) and composition (EDS) of Cu(InGa)(SeS)$_2$ films from 6” reactor: (a) SLG/Mo and (b) SS/SBR/Mo substrates.

Fig. 31. XRD patterns of Cu(InGa)(SeS)$_2$ films on SLG and SBR/SS substrates: (a) wide scan and (b) (112) fine scan.
Figure 31 gives the XRD patterns of Cu(InGa)(SeS)_2 films on SLG and SBR/SS substrates. Intermediate species such as InSe were not shown in the broad scan and it indicates that the metal precursors were completely converted to chalcopyrite phase. However, (112) fine scans reveals that the SBR/SS substrate sample still has slight Ga grading based on the slightly lower angle position of the (112) as compared to that of the SLG substrate sample.

Figure 32 shows light JV curves for devices fabricated on Cu(InGa)(SeS)_2 deposited in 6” reactor on SLG and SS/SBR substrates. Device characteristics are listed in Table XIII. The SS/SBR sample shows poorer device performance compared to the SLG substrate sample. It seems that undesirable high S incorporation near the surface impedes carrier transport through the junction. Such JV behavior is commonly observed when S incorporation is not well controlled.

![Light JV curves for devices fabricated on Cu(InGa)(SeS)_2 deposited in 6” reactor on SLG and SS/SBR substrates.](image)

Fig. 32. Light JV curves for devices fabricated on Cu(InGa)(SeS)_2 deposited in 6” reactor on SLG and SS/SBR substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm^2)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS/SBR</td>
<td>0.585</td>
<td>31.5</td>
<td>64.4</td>
<td>11.9</td>
</tr>
<tr>
<td>SLG</td>
<td>0.612</td>
<td>33.2</td>
<td>72.9</td>
<td>14.8</td>
</tr>
</tbody>
</table>

Table XIII. Light JV characteristics of Cu(InGa)(SeS)_2 solar cells on SBR/SS and SLG substrates from the 6” reactor.
ROLL-TO-ROLL DEPOSITION

The performance and uniformity of small area Cu(InGa)Se$_2$ films deposited on SS web in roll-to-roll configuration traveling at 1 inch/min were investigated on rolls of SS/SBR Mo coated at 0.2 $\mu$m at our outside vendor Techni-Met. Na was provided by co-evaporation of NaF at 775°C. Table XIV gives the Cu(InGa)Se$_2$ film composition (as measured by EDS) and the characteristics of the highest efficiency obtained from devices fabricated on it. The thickness of the film was measured by SEM cross-sectional analysis to be 1.2 $\mu$m.

<table>
<thead>
<tr>
<th>Run #</th>
<th>EDS composition (at%)</th>
<th>Device Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ga</td>
</tr>
<tr>
<td>70592</td>
<td>23.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Average device results based on 8 cells over 2 samples are given in Table XV.

<table>
<thead>
<tr>
<th>Dist. From LE* (in)</th>
<th>Voc (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.633</td>
<td>30.1</td>
<td>69.6</td>
<td>13.3</td>
</tr>
<tr>
<td>SD</td>
<td>0.004</td>
<td>0.2</td>
<td>5.3</td>
<td>1.1</td>
</tr>
<tr>
<td>8</td>
<td>0.634</td>
<td>29.9</td>
<td>71.2</td>
<td>13.5</td>
</tr>
<tr>
<td>SD</td>
<td>0.003</td>
<td>0.3</td>
<td>2.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Overall</td>
<td>Avg</td>
<td>0.634</td>
<td>30.0</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>0.004</td>
<td>0.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

* LE: leading edge

Highest efficiency device, was AR coated with MgF$_2$ and sent to NREL for performance verification. Figure 33 present the results of the J-V and QE measurements performed at NREL giving an efficiency of 15.2%.
Fig. 33. JV and QE data of the Cu(InGa)Se$_2$ based device of 15.2% efficiency. Cu(InGa)Se$_2$ was deposited in a R2R reactor on insulated coated SS web.
The uniformity of the Cu(InGa)Se$_2$ film deposited in the R2R reactor on SS/SBR/Mo web was evaluated by coating webs of 9ft and 30ft length and evaluating the Cu(InGa)Se$_2$ coating and small area devices fabricated on it. Figure 34 is the picture of the coated webs laid out on a table.

![SS/SBR/Mo webs, 9ft and 30ft respectively, deposited in the R2R reactor.](image)

In the case of 9 ft web the materials characteristics of the Cu(InGa)Se$_2$ film were analyzed every 2 ft along the center line of the web. The composition of the samples, as measured by EDS, and the thickness of the film, as measured by SEM cross section analysis are given in Table XVI. Samples 1” x1” in size were removed adjacent to these analyzed locations for device fabrication and characterization. The data is summarized in Table XVII.

In the case of the 30ft run, the same material and device analysis were performed but at only two points, 2 ft and 29 ft from the leading edge. The results are given in Tables XVIII and XIX. In this case only the best device results are given.

### Table XVI. Composition and thickness of 9ft Cu(InGa)Se$_2$ film of run No.: 70593.

<table>
<thead>
<tr>
<th>Dist From LE* (ft)</th>
<th>Cu (at%)</th>
<th>Ga (at%)</th>
<th>Se (at%)</th>
<th>In (at%)</th>
<th>Cu/(Ga+In)</th>
<th>Ga/(Ga+In)</th>
<th>t (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23.1</td>
<td>10.1</td>
<td>50.0</td>
<td>16.8</td>
<td>0.86</td>
<td>0.38</td>
<td>1.4</td>
</tr>
<tr>
<td>4</td>
<td>23.9</td>
<td>10.4</td>
<td>48.4</td>
<td>17.3</td>
<td>0.86</td>
<td>0.38</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>22.9</td>
<td>9.9</td>
<td>50.2</td>
<td>17.0</td>
<td>0.85</td>
<td>0.37</td>
<td>1.4</td>
</tr>
<tr>
<td>8</td>
<td>22.9</td>
<td>10.6</td>
<td>49.5</td>
<td>17.0</td>
<td>0.83</td>
<td>0.39</td>
<td>1.3</td>
</tr>
<tr>
<td>Average</td>
<td>23.2</td>
<td>10.3</td>
<td>49.5</td>
<td>17.0</td>
<td>0.85</td>
<td>0.38</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* LE: leading edge
Table XVII. Device results from the Cu(InGa)Se₂ film of run No.: 70593 along the length of the web.

<table>
<thead>
<tr>
<th>Dist. From LE (ft)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Best</td>
<td>0.621</td>
<td>28.4</td>
<td>65.6</td>
<td>11.6</td>
</tr>
<tr>
<td>Avg</td>
<td>0.608</td>
<td>28.3</td>
<td>59.9</td>
<td>10.3</td>
</tr>
<tr>
<td>SD</td>
<td>0.009</td>
<td>0.3</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>4 Best</td>
<td>0.618</td>
<td>29.2</td>
<td>59.4</td>
<td>10.7</td>
</tr>
<tr>
<td>Avg</td>
<td>0.615</td>
<td>28.8</td>
<td>55.4</td>
<td>9.8</td>
</tr>
<tr>
<td>SD</td>
<td>0.007</td>
<td>0.3</td>
<td>2.9</td>
<td>0.7</td>
</tr>
<tr>
<td>6 Best</td>
<td>0.620</td>
<td>30.1</td>
<td>66.9</td>
<td>12.5</td>
</tr>
<tr>
<td>Avg</td>
<td>0.612</td>
<td>29.2</td>
<td>64.9</td>
<td>11.6</td>
</tr>
<tr>
<td>SD</td>
<td>0.010</td>
<td>0.5</td>
<td>5.7</td>
<td>1.2</td>
</tr>
<tr>
<td>8 Best</td>
<td>0.637</td>
<td>29.2</td>
<td>70.9</td>
<td>13.2</td>
</tr>
<tr>
<td>Avg</td>
<td>0.607</td>
<td>30.1</td>
<td>63.4</td>
<td>11.6</td>
</tr>
<tr>
<td>SD</td>
<td>0.035</td>
<td>1.0</td>
<td>7.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Overall Avg</td>
<td>0.610</td>
<td>29.1</td>
<td>60.9</td>
<td>10.8</td>
</tr>
<tr>
<td>SD</td>
<td>0.020</td>
<td>0.9</td>
<td>6.4</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table XVIII. Composition and thickness of 30ft Cu(InGa)Se₂ film of run No.: 70594.

<table>
<thead>
<tr>
<th>Dist From LE* (ft)</th>
<th>Cu (at%)</th>
<th>Ga (at%)</th>
<th>Se (at%)</th>
<th>In (at%)</th>
<th>Cu/(Ga+In)</th>
<th>Ga/(Ga+In)</th>
<th>t (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22.2</td>
<td>10.4</td>
<td>49.6</td>
<td>17.8</td>
<td>0.79</td>
<td>0.37</td>
<td>1.3</td>
</tr>
<tr>
<td>29</td>
<td>21.9</td>
<td>10.5</td>
<td>50.6</td>
<td>17.0</td>
<td>0.80</td>
<td>0.38</td>
<td>1.3</td>
</tr>
<tr>
<td>Average</td>
<td>22.1</td>
<td>10.5</td>
<td>50.1</td>
<td>17.4</td>
<td>0.80</td>
<td>0.38</td>
<td>1.3</td>
</tr>
</tbody>
</table>

* LE: leading edge

Table XIX. Best device results from the Cu(InGa)Se₂ film of run No.: 70594.

<table>
<thead>
<tr>
<th>Dist. From LE (ft)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.615</td>
<td>29.9</td>
<td>64.4</td>
<td>11.9</td>
</tr>
<tr>
<td>4</td>
<td>0.628</td>
<td>28.0</td>
<td>65.3</td>
<td>11.5</td>
</tr>
</tbody>
</table>

* LE: leading edge
In order to improve on these results it was decided to make two changes on the system. The first change involved NaF evaporation from solid rather than powder form. Evaporation from solid NaF is expected to be more reproducible from run to run since gradual sintering of NaF powder would be eliminated. The second modification was made in the substrate heater. Careful web temperature measurement indicated that during Cu(InGa)Se$_2$ deposition zone the web was going through a temperature drop by as much as 75°C. To avoid this situation a third heater was built and placed into the system at a location where the temperature drop was the largest. The heater set points were then optimized resulting in web temperature fluctuations of no more than 20°C within the critical section of the web path.

The new NaF source was calibrated by measuring Na content in the Cu(InGa)Se$_2$ films deposited at different NaF source temperature. The samples were analyzed at Evans Analytical by quantitative SIMS depth profiling. The data, showing simply Na and K concentration as a function of depth at different NaF source temperatures are shown in Figure 35. The source of K is presently unknown. However, it correlates quite well with Na. Furthermore, sodium profile corresponding to NaF source temperature of 820°C is rather inexplicable. But, in summary, within the range of NaF source temperature used there is Na incorporation into the Cu(InGa)Se$_2$ between $4 \times 10^{19}$ to $2 \times 10^{20}$ at/cm$^3$. The Na levels in the CIGS films scale well with source temperatures. The exception is for 725°C and 750°C where, the measured level of incorporation is reversed.

![SIMS concentration profile for Na and K at various NaF temperatures.](image)
On the basis of these results a NaF source temperature of 775°C was chosen. A 6’ web was coated in the R2R reactor, and from the central 4’, two samples were removed every foot for device fabrication. Each sample had 4 devices on it. Typical composition and thickness of the Cu(InGa)Se₂ film on web are given in Table XX.

Table XX. Composition and thickness of Cu(InGa)Se₂ film on 6’ web.

<table>
<thead>
<tr>
<th>Cu (at%)</th>
<th>Ga (at%)</th>
<th>Se (at%)</th>
<th>In (at%)</th>
<th>Cu/(Ga+In)</th>
<th>Ga/(Ga+In)</th>
<th>t (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.9</td>
<td>9.3</td>
<td>48.0</td>
<td>17.8</td>
<td>0.92</td>
<td>0.34</td>
<td>1.4</td>
</tr>
</tbody>
</table>

After the initial measurements, it was found that on most of the devices J_{sc} were abnormally high. This was traced to the placement of masking during ITO deposition, which allowed ITO to deposit under the mask. In order to correct for that, the devices were mechanically scribed and J_{sc}’s were measured utilizing the new area. These values then used to compute the efficiencies utilizing other parameters measured originally. This was necessary because scribing introduced shunting, sometimes severe. Figure 36 shows the average and best efficiencies along the web. Best efficiencies are all above 12% except for the data at 12” from leading edge where the value is 11.5%. Table XXI below gives the characteristics of the cells where best cell efficiencies are shown in red.

Fig. 36. Best and average efficiencies along the center 4’ of 6’ SBR/SS web foil.
The throughput of the R2R was tested by depositing Cu(InGa)Se₂ films on SS/SBR web moving at speeds of 3 and 6 inches/min. In order to achieve that, the source temperatures had to be increased; at 6"/min Cu source was running at 1525°C. However, the NaF source temperature was not increased for reasons of simplicity.

Tables XXII gives typical composition of the Cu(InGa)Se₂ films for the web moving at the above speed. Table XXIII gives the characteristics of the best devices in runs where web speed was increased. Clearly, lack of Na is evidence by low open circuit voltages observed. Also to note is the fact that even at 6"/min efficiencies of 9 to 10% were obtained. However, a source temperature of 1525°C was excessive for the reactor. Post mortem examination of the Cu source showed that it was bent under the heat load probably due to the non-symmetric heater design. In order to achieve
commercial speed with the present reactor it is necessary to modify the source heater and probably the source design itself. Low $V_{oc}$ on high throughput devices is probably due to the fact that the NaF source temperature was not increased during these first tries. Consequently Na incorporation was substantially lower than what it should be.

Table XXII. Typical composition and thickness of Cu(InGa)Se$_2$ films deposited on SS/SBR web moving at 3 and 6 "$/\text{min}$. 

<table>
<thead>
<tr>
<th>Web Speed (&quot;$/\text{min}$)</th>
<th>Cu (at%)</th>
<th>Ga (at%)</th>
<th>In (at%)</th>
<th>Se (at%)</th>
<th>Cu/(Ga+In)</th>
<th>Ga/(Ga+In)</th>
<th>t (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>22.0</td>
<td>9.3</td>
<td>17.4</td>
<td>51.3</td>
<td>0.82</td>
<td>0.35</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>21.1</td>
<td>8.3</td>
<td>18.5</td>
<td>52.2</td>
<td>0.79</td>
<td>0.31</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table XXIII. Best device results from the Cu(InGa)Se$_2$ films deposited on SS/SBR web moving at 3 and 6 "$/\text{min}$. 

<table>
<thead>
<tr>
<th>Run #</th>
<th>Web Speed (&quot;$/\text{min}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Eff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70784.11</td>
<td>3</td>
<td>0.543</td>
<td>31.2</td>
<td>69.5</td>
<td>11.3</td>
</tr>
<tr>
<td>70784.12</td>
<td></td>
<td>0.544</td>
<td>29.8</td>
<td>66.6</td>
<td>11.3</td>
</tr>
<tr>
<td>70794.11</td>
<td></td>
<td>0.491</td>
<td>30.5</td>
<td>63.9</td>
<td>9.6</td>
</tr>
<tr>
<td>70794.12</td>
<td></td>
<td>0.466</td>
<td>31.3</td>
<td>54.5</td>
<td>8.0</td>
</tr>
<tr>
<td>70795.11</td>
<td>6</td>
<td>0.417</td>
<td>31.0</td>
<td>64.5</td>
<td>8.4</td>
</tr>
<tr>
<td>70795.12</td>
<td></td>
<td>0.422</td>
<td>31.3</td>
<td>64.6</td>
<td>8.5</td>
</tr>
<tr>
<td>70797.11</td>
<td></td>
<td>0.499</td>
<td>30.1</td>
<td>67.9</td>
<td>10.2</td>
</tr>
<tr>
<td>70797.12</td>
<td></td>
<td>0.518</td>
<td>30.3</td>
<td>68.5</td>
<td>10.7</td>
</tr>
<tr>
<td>70798.11</td>
<td></td>
<td>0.510</td>
<td>29.8</td>
<td>58.8</td>
<td>9.0</td>
</tr>
<tr>
<td>70798.12</td>
<td></td>
<td>0.508</td>
<td>28.6</td>
<td>55.9</td>
<td>8.1</td>
</tr>
</tbody>
</table>
MONOLITHIC INTEGRATION

Monolithic integration scheme chosen for the present work has to take account of the special nature of the substrate. The substrate being 2 mil SS foil coated with 3 to 4 $\mu$m silicone resin would not allow mechanical scribing without being creased. Starting with this condition, the scribing had to be done by laser. Since the substrate and the back contact are opaque the scribing had to be performed from the top. As a result an integration scheme, shown schematically in Figure 37 was chosen.

![Fig. 37. Schematics of the monolithic integration chosen for module fabrication.](image)

Note that except for P2 this is the standard cascade type integration in wide use. For the P2 scribe it was decided to partially laser melt/transform the i-ZnO / CdS / Cu(InGa)Se$_2$ structure over Mo rather than laser etch the cut. It is believed that in view of the uncertainties over the thickness (knowingly or not) it was impossible to ablate the structure without damaging Mo or silicone resin.

Once the general scheme has been decided, scribe parameters were individually developed and then brought together to fabricate mini-modules of 3”x3” in size.

Figure 38 shows schematically the laser system used for scribing modules. The laser
Fig. 38. Laser system used for scribing monolithic mini-modules.

is a Q-switched double wavelength (1064 and 532 nm) YAG laser with a maximum power of 2 W. A laser beam is stationary and the work piece is mounted on a X-Y table with a motional accuracy of ± 1 μm. The flexible foil is held in place with a vacuum chuck attached to the X-Y table.

In order to achieve an operational scribe one needs to find the optimum point in the parameter space defined by the wavelength $\lambda$, frequency (repetition rate) $f$, table feed rate $F$ and power $P$.

P1 Scribe

The difficulty with the P1 cut was that the Mo removal had to be gentle enough so that the SBR layer is not damaged causing the absorber to contact the SS base layer. Furthermore P1 cut should be electrically isolating Mo sections over distances of several inches in the present study, and over feet in commercial production. The parameters that gave satisfactory results were:

- $\lambda = 532$ nm
- $f = 8$ kHz
- $F = 60$ mm/s
- $P = 60$ mW

Figure 39 gives the typical high magnification SEM view of one of these P1 cuts and also the EDS spot spectrum taken at the center of the cut. Some damage in the form of cracks on the edge of Mo film and dimpling of the SBR are visible. On the other hand
no breech in the SBR is observed. EDS data show that SBR seems to be intact (Si peak height). A small amount of Fe and Cr is expected due to the fact that SBR’s density is relatively low, 1.68 g/cm\(^3\), making the X-ray escape depth as large as 5 \(\mu\)m.

![SEM micrograph of the P1 scribe](image)

Fig. 39. SEM micrograph of the P1 scribe (30 \(\mu\)m) and the spot EDS spectrum taken from the middle of the cut.

Figure 40 is a 4”x8” Mo coated SBR/SS sample with the laser cuts 7 mm apart to be used as substrate for module fabrication. For preparing substrates for module fabrication it was necessary to burn any shunts that might exit in each of the cell strips as well as burn any Mo bridges or contacts shorting each cut. The actual useful area for module fabrication is from segment 1 to 12 since segments 0 and 13 are in contact with SS base along the edges. Table XXIV gives the results of shunting before and after burning them with an applied voltage pulse of 15V. In this case there was no need to burn any shorts across the scribe lines.
Fig. 40. 4"x8" Mo coated SBR/SS sample with horizontal isolation and vertical P1 laser cuts; see text for details.

Table XXIV. Shunts between Mo and SS before and after burning and scribe line isolation.

<table>
<thead>
<tr>
<th>Segment</th>
<th>R_{SH} Before (Ω)</th>
<th>R_{SH} After (Ω)</th>
<th>Scribe Line</th>
<th>R_{SL} (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>0,1</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>&gt;20M</td>
<td>1,2</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>2</td>
<td>78K</td>
<td>&gt;20M</td>
<td>2,3</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>3</td>
<td>274K</td>
<td>&gt;20M</td>
<td>3,4</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>4</td>
<td>&gt;20M</td>
<td>&gt;20M</td>
<td>4,5</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>5</td>
<td>5K</td>
<td>&gt;20M</td>
<td>5,6</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>1M</td>
<td>6,7</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>&gt;20M</td>
<td>7,8</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>8</td>
<td>&gt;20M</td>
<td>&gt;20M</td>
<td>8,9</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>81K</td>
<td>9,10</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>10</td>
<td>3M</td>
<td>&gt;20M</td>
<td>10,11</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>11</td>
<td>136</td>
<td>&gt;20M</td>
<td>11,12</td>
<td>&gt;20M</td>
</tr>
<tr>
<td>12</td>
<td>474</td>
<td>3M</td>
<td>12,13</td>
<td>&gt;20M</td>
</tr>
</tbody>
</table>
P2 Scribe

In the scheme explained earlier for the P2 cut laser beam melt/transform the i-ZnO / CdS / Cu(InGa)Se$_2$ structure over Mo to render it conductive. The laser parameters used to partially melt the structure were:

- $\lambda = 1064$ nm
- $f = 10$ kHz
- $F = 125$ mm/s
- $P = 58$ mW

In this case a wavelength of 1064 nm ($= 1.16$ eV) was chosen in order to get uniform a relatively weak absorption in the Cu(InGa)Se$_2$. Figure 41 is the SEM image of such a scribe, and Figure 42 compares spot EDS spectrum on the scribe and on the untouched surface of the sample. Melting of the material along the scribe line is evident from Figure 41. Comparing the spectra in Figure 42 by referencing to the respective Se peaks, one will see an increase in metal content and consequently Se loss in the P2 scribe region. It is, however, impossible to evaluate electrical characteristics since the junction is already formed on the sample, rather they need to be evaluated in the finished modules.

Fig. 41. SEM micrograph of the P2 scribe.
P3 SCRIBE

In this case, laser wavelength of 532 nm was used as ITO, CdS and ZnO are transparent at this wavelength while Cu(InGa)Se$_2$ is strongly absorbing. As a result, the top layer of the Cu(InGa)Se$_2$ film would be ablated and vapors generated would break up the ITO layer.

The laser parameters used for the P3 scribe were:

- $\lambda = 532$ nm
- $f = 20$ kHz
- $F = 125$ mm/s
- $P = 25$ mW
Figure 43 gives the SEM image of the scribe thus obtained along with the spot EDS spectrum from its center.

Fig. 43. ITO scribe of Mo/Cu(InGa)Se₂/CdS/i-ZnO/ITO stack on SS/SBR substrate (top), EDS spectrum taken from the middle of the cut (bottom).
Again, it is impossible to evaluate electrical characteristics of the scribe since each side of the cut is a solar cell, the measured resistance values can not be properly interpreted. In this case, the evaluation should also be performed in the finished modules.

MODULE FABRICATION AND RESULTS

Following the P1 scribing of 4”x8” blanks, as described earlier, the samples were PVD coated by Cu(InGa)Se$_2$ in the R2R system or trimmed to 4”x4” size for Cu(InGa)(SeS)$_2$ coating by precursor selenization.

Fig. 44. P1 scribed foils in the R2R reactor before (top) and after (bottom) coating.
During deposition in the R2R system, samples are stapled onto a carrier over an opening on the web. Figure 44 shows the sample in the system before and after the coating.

After the Cu(InGa)Se₂ deposition, the samples are coated by CdS by chemical bath deposition, by i-ZnO by sputtering. Following that they receive P2 scribe, then they are coated with ITO and finished with the P3 scribe. The last two cuts produce on the samples a 3"x3" module. After all the processes are complete the samples are trimmed to 4"x4" size and contacts were applied. Figure 45 shows a typical finished mini-module.

Fig. 45. Finished 3"x3" mini-module with PVD Cu(InGa)Se₂.

Five mini-modules, each consisting of 10 cells, were fabricated. However measured efficiencies ranged between 2.5% to 4% showing substantial series resistance and shunt conductance. The I-V characteristics of the best mini-module produced is shown in Figure 46. It is believed that module design in general and P2 scribe in particular require further work.
In the case of precursor selenization, P1 scribed blanks were trimmed to 4”x4” size before any processes. Selenization/sulfization of the precursors was conducted in the 6” tube reactor according to the protocol developed for 1”x1” samples. However, severe problems such as weak adhesion, excessive selenization and temperature uniformity were encountered during scale up. Even though, substantial effort was spent to solve these issues, a mini-module could not be produced by precursor selenization method.

![Fig. 46. Light and dark I-V curves for 10 cell mini-module fabricated on PVD deposited Cu(InGa)Se₂.](image)

**CONCLUSION**

The use of SS foil coated with silicone resin insulator as a substrate for CuInSe₂ based photovoltaics has been demonstrated. On vapor deposited films of Cu(InGa)Se₂ small area efficiency of more than 15% have been obtained. Cu(InGa)(SSe)₂ films obtained by precursor selenization gave efficiencies of more than 12%. Uniformity in a PVD roll-to-roll reactor has been demonstrated. Throughput up to 6 inches/min was achieved.

The work was challenging in some respects. The issue of random shunts through the resin has been solved but may be problematic in a manufacturing environment. All laser monolithic integration has been a difficult problem that requires further work and more innovative solutions. In the precursor selenization process, transitioning from glass substrate to SS based, one would require a different approach.
REFERENCES


