Statement of the problem or situation that is being addressed - typically, one to three sentences.

Yield and reproducibility remain important issues in CuIn(Ga)Se₂ (CIGS) photovoltaic module fabrication. While small-area cells (<1 cm²) over 18% efficient have been reported, the best large-area manufactured devices (> 1 ft²) are 11% efficient with about 60% yield. If improvements in large-area manufacturing can accomplish 15% efficiency and 90% yield, the result is a doubling in throughput leading to a reduction in cost per watt of over 50%. The challenge now facing the photovoltaics industry is to bring the efficiencies of small-area cells and large-area industrial modules closer together and to raise manufacturing yields.

General statement of how this problem is being addressed. This is the overall objective of the combined Phase I and Phase II projects - typically, one to three sentences.

Materials Research Group, Inc. (MRG) is improving the manufacturability of CuIn(Ga)Se₂-based solar cells via development of real time, closed-loop control of co-sputtered CuInSe₂ (CIS) absorber layers. Co-sputtering, when used with plasma emission closed-loop control, provides good control and scalability of the fluxes to the CIS layer, and should maintain essentially the same film efficiency achieved in champion co-evaporated films while achieving high manufacturing yields.

What is planned for the Phase I project (typically, two to three sentences)?

Phase I demonstrated that co-sputtering of CIS layers using optical emission spectroscopy (OES) control is a promising absorber deposition process for manufacturable CIS-based modules. OES was demonstrated to give correct information about the metallic deposition rates under differing target conditions, allowing reproducible film compositions. Good spatial uniformity of fluxes were obtained, and the process was incorporated into a model for a large-scale deposition system. Good device results were obtained using all-dry, manufacturable processing.

COMMERCIAL APPLICATIONS AND OTHER BENEFITS as described by the applicant. (Limit to space provided).

The success of the research will lead to improvements in the energy efficiency and manufacturability and therefore lower costs for CIS-based modules. Off-grid and mobile power applications stand to benefit immediately from lower cost photovoltaic energy systems. A cleaner environment, increased national energy independence, and cheaper power are long-term benefits.

SUMMARY FOR MEMBERS OF CONGRESS: (LAYMAN’S TERMS, TWO SENTENCES MAX.)

This research aims to provide cheaper, lighter-weight, solar electric power through developing a simpler and cheaper manufacturing process for CuInSe₂ solar cells.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
# TABLE OF CONTENTS

1. PROJECT OBJECTIVES ........................................................................................................................................ 3

2. EXPERIMENTS AND RESULTS ......................................................................................................................... 6
   2.A Introduction ...................................................................................................................................................... 6
   2.B Flux Distribution ........................................................................................................................................... 7
   2.C Film Composition Measurement and Tracking ............................................................................................... 8
   2.D Method of Se Delivery .................................................................................................................................. 13
   2.E Device Results ............................................................................................................................................. 13
   2.F Effect of Temperature on Device Performance ............................................................................................ 15
   2.G Effect of Se Flux on CIS Properties ............................................................................................................. 18
   2.H Effect of In-Only Layer on Performance .................................................................................................... 20
   2.I Effect of Cu/In ratio on Device Performance ............................................................................................... 20
   2.J Investigations of Ion Bombardment Effects ................................................................................................. 21
   2.K Effects of Annealing ..................................................................................................................................... 23
   2.L XRD Results .................................................................................................................................................. 23
   2.M SEM Results ................................................................................................................................................ 26
   2.N CBD vs. Sputtered CdS ................................................................................................................................. 28
   2.O Window Issues ............................................................................................................................................. 30
   2.P OES Hardware and Software Development ............................................................................................... 31
   2.Q Large-Scale System Model ........................................................................................................................... 33
   2.R Future Work .................................................................................................................................................. 36

3. TECHNICAL FEASIBILITY .................................................................................................................................. 39

4. REFERENCES ....................................................................................................................................................... 40
1. PROJECT OBJECTIVES

Yield and reproducibility remain important issues in CuIn(Ga)Se$_2$ (CIGS) photovoltaic module fabrication. While multiple groups report champion small-area cells (<1 cm$^2$) over 15% efficient, and world-record small-area cells are over 18% efficient, the best large-area manufactured devices (> 1 ft$^2$) are 11% efficient with about 60% yield. The challenge now facing the photovoltaics industry is to bring the efficiencies of small-area cells and large-area industrial modules closer together and to raise manufacturing yields.

The most efficient small-scale CIGS cells to date have been fabricated using the four-source co-evaporation method. However, a number of factors make co-evaporated cells difficult to produce in a manufacturing environment. During four-source co-evaporation, species flux can vary; for example, due to thermocouple drift, difference in pool surface temperature as source material is depleted, temporally non-uniform source emission ("spitting"), and differences in source materials. In addition, achieving simultaneous delivery of at least three fluxes that are uniform over the intended module area is difficult. The problem is compounded by the current lack of precise multi-species flux sensors. The absorber layer, critical for device performance, is particularly sensitive to changes in deposition fluxes. Cu/In ratio, Ga content, and presence of non-CIGS phases, are important factors in device quality that can deviate due to species flux variations.

In an effort to improve the manufacturability of CIGS modules and avoid the control problems associated with co-evaporation, a number of groups have fabricated CIGS layers by sequential depositions. These efforts include sequential sputtering and evaporation of elements, and by sequential sputtering of compounds. Devices made with sequentially deposited CIGS, however, have not yet reached the efficiencies of devices made with co-evaporated absorbers. Poor through-film uniformity and crystallinity are often seen in sequentially-deposited CIGS. In addition, post-deposition reactions can be time-consuming, and controlling the Ga profile in sequentially deposited films is difficult.

Materials Research Group, Inc. (MRG) has proposed improvement of the manufacturability of CuIn(Ga)Se$_2$-based solar cells via development of co-sputtered CuInSe$_2$ (CIS) absorber layers, where metallic fluxes are controlled by optical emission spectroscopy (OES). In this research, Cu and In fluxes are simultaneously delivered to the substrate by sputtering from elemental sources rather than by co-evaporation or by sequentially sputtered layers. The fluxes are tightly controlled by monitoring the appropriate plasma emission lines, despite varying degrees of selenization of the target surfaces from the evaporative Se source. The Se flux does not need to be carefully controlled, since the incorporation of the Se into a hot CIS film is self-regulating.
therefore champion cells are made with Se fluxes ranging from 2 to 6 times the required stoichiometric flux. Additionally, fluxes to the substrate are made uniform over large areas by not co-focussing the sputtering cathodes. Large area uniformity is obtained by continuously moving the substrate and heater into positions directly over each cathode. Reproducible control of co-delivered fluxes using OES, and achievement of flux uniformity over areas comparable to the target size, are important advances achieved during the Phase I research.

The deposition technique developed during Phase I provides a number of advantages over co-evaporative CIGS fabrication methods. First, because sputtering is a plasma process, precise, inexpensive, and reproducible flux monitoring can be achieved via optical emission spectroscopy. As each species in the plasma emits at its own characteristic frequencies, the presence of multiple fluxes is easily accommodated. Corrections to sputtered deposition fluxes can be achieved instantaneously by changing cathode powers. No heating or cooling of thermal masses is necessary. Second, moving the substrate parallel to each target surface easily provides uniform large-area fluxes. Third, the sputtering process does not require high temperature sources and therefore avoids problems associated with heat transfer between sources and inaccurate thermocouple control. Finally, co-sputtering the absorber layer permits manufacture of a high-quality all-sputtered solar cell, lowering equipment costs.

Co-sputtering also promises a number of advantages over sequentially deposited layers. Co-sputtered films should avoid the problems of through-film uniformity and crystallinity, lengthy reaction times, and lack of Ga incorporation, since film growth is expected to follow the same reaction pathway during co-sputtering as during co-evaporation. Also, co-sputtering from elemental metal targets minimizes the cost of starting materials and allows higher deposition rates than sputtering from compound, less conductive targets.

Sputtering of In and Cu during Se evaporation has been performed by other groups in the past, with up to 10% active area efficiencies resulting. The innovation in the CIS growth performed in this Phase I research are the modifications that allow the process to be manufacturable in a large-scale facility. These modifications include the use of optical emission spectroscopy (OES) to improve yields and repeatability, the utilization of a moving substrate that is parallel to all target surfaces to achieve deposition flux uniform over large areas, all-dry window-layer processing, and changes in the In profile from previous work.

High deposition rates are possible for co-sputtered films. Sputter deposition rates from metallic targets are typically in the 50 Å/sec range, and can be increased even further with efficient magnetron design and good target cooling. For cathodes with the same dimensions as those in MRG's large-scale sputtering system, a 50 Å/sec maximum delivery rate for Cu, In, and Se implies that sputtered fluxes can be delivered at a rate compatible with coating 1 inch per minute of a 12 inch wide substrate with 2 μm of CIS.
This speed translates to a 200 kW/yr. production capacity if production occurs 12 hours per day and modules average 10% efficient. This calculation assumes only 1 cathode for each material is in place; production capacity scales proportionally as additional cathodes are added. Note that if yield and efficiency in manufacturing can be improved from the current state (10% efficient, 60% yield) to 15% efficiency and 90% yield, the result is a doubling in throughput leading to a reduction in cost per watt of over 50%.

During Phase I, MRG proved the feasibility of scaling up in-situ-controlled co-sputtering of CIS for large-scale manufacturing. OES was demonstrated to give correct information about the metallic deposition rates under differing target conditions, allowing reproducible film compositions. Good device results were obtained using all-dry, manufacturable processing. By using a moving substrate parallel to the target surfaces, good spatial uniformity of fluxes were obtained, and the process was incorporated into a model for a large-scale deposition system. CIS fabrication during Phase I was performed on 2” x 3” substrates in MRG’s research-scale deposition system.

MRG expects that the development of large-area co-sputtered CIS layers will lead to a number of improvements in the manufacturability and therefore cost of CIS-based photovoltaic modules. Lower product costs should result from improved yields achieved by use of inexpensive monitoring equipment and closed-loop control. Current differences between cell and module efficiencies may be decreased by the production of quality uniform material. The proposed co-sputtered absorber layers should be deposited with high throughput and have been incorporated into a structure in which all constituent layers are manufacturing-friendly. High throughput, high yield, and low equipment costs are generally recognized as key factors in the reduction of cost per watt of Cu(In,Ga)Se₂ modules.²²

Single-crystal silicon modules dominate the current 90 MW per year photovoltaics market.²³ For the sale of Cu(In,Ga)Se₂ modules to be feasible, they must at least compete in price with single-crystal silicon modules. It is currently estimated that Cu(In,Ga)Se₂ modules must be manufactured at a cost less than about $1.80 per Watt to compete with single-crystal technology.²² It is estimated that a manufacturing cost of $1 per watt can be attained for a high-efficiency, high-yield Cu(In,Ga)Se₂ deposition process.²⁴

The federal government, the commercial sector, and individual citizens all stand to benefit from the development of cost-effective Cu(In,Ga)Se₂ modules. In the long term, a cleaner environment, increased national energy independence, and cheaper grid-connected power are benefits. In the short-term, users with off-grid power requirements stand to benefit. Examples of such applications are agricultural water pumping, emergency telecommunications, mobile road signs, supplementary power in watercraft, and household power in areas that are not grid-connected or where the grid is unreliable. Foreign markets comprise a substantial portion of the current off-grid sales opportunities.²⁵,²⁶,²⁷
U.S. Department of Defense (DoD) applications are a particularly important market to consider when developing thin-film photovoltaics, as the DoD is the largest single consumer of energy in the U.S.\(^2\) The DoD spends about 3 billion dollars per year on electricity, 1 billion of which is spent on electricity for off-grid facilities.\(^2\) The development of cost-effective photovoltaics that are silent, non-polluting, and nearly maintenance free would provide a significant benefit over battery and diesel generator power. Additionally, with some tailoring of the substrate from glass to light-weight polymer, thin-film photovoltaics may provide substantial improvements in power density (power per weight) over currently available remote sources. This is a particularly important consideration for mobile and space applications.

2. EXPERIMENTS AND RESULTS

2.A Introduction

The innovation in the CIS growth performed in Phase I involves the use of optical emission spectroscopy (OES) control to regulate flux while co-delivering all necessary species, the utilization of a moving substrate that is parallel to all target surfaces to achieve deposition flux uniform over large areas, and the adaptation of high-efficiency co-evaporative recipes to co-sputtering.

The CIS growth performed in Phase I is based upon the “two-stage” recipe for CIS growth developed at the National Renewable Energy Laboratory (NREL). This process was chosen as a starting point for the Phase I research, because because the process has produced the world-record efficiency CIGS solar cells,\(^1\) requires only short reaction times, and allows profiling of flux ratios to engineer formation chemistry and band gap. The typical disadvantage to the two-stage absorber fabrication process is the difficulty of controlling all species fluxes simultaneously and achieving uniform fluxes over large areas. However, the combination of sputtered fluxes and OES-based control minimizes these difficulties for the co-sputtered films.

The two-stage absorber fabrication process for CIS involves concurrent delivery of Cu, In, and, Se to the substrate. In the first stage, Cu, In, and Sc are delivered to the substrate in a ratio causing the film to be slightly Cu-rich. The excess CuSe is thought to act as a fluxing agent that promotes grain growth.\(^1\) Most of the film thickness is grown in the first stage. In the second stage, enough In is delivered so that stoichiometric amounts of Cu and In exist in the film. Both stages are conducted with an overpressure of Se. Lack of precise deposition rate control during Se evaporation is not an issue, since incorporation of Se into the growing film is self-regulating,\(^1\) with excess Se simply evaporating from the film surface. Se fluxes for champion cells are routinely allowed to vary from 2 to 6 times the required stoichiometric rate.\(^2\)
2.B Flux Distribution

For effective deposition, fluxes must be uniform over the desired substrate area, they must arrive at the substrate in the specified ratios, and they must be deposited quickly enough to produce a reasonable film growth time.

Achieving uniform flux over the substrate area is a significant challenge that was met during the phase I research. Cu and In targets co-focused onto a stationary substrate were originally planned, as shown in Figure 1a. However it was discovered that this arrangement yields severely graded films. For example, for a 3” source to substrate distance and 12 mTorr sputtering pressure, film thickness varied by ±20% over 2” x 2”. The gradation occurs because the mean free path at sputtering pressures is less than the target-to-sample distance, and therefore more metallic atoms reach the closer edge of the substrate than the farther edge.

The uniformity problem was solved by moving the substrate over each source, parallel to each target surface. This solution is illustrated schematically in Figure 1. The diagram on the left shows how a stationary substrate position led to films with graded metal distributions. The diagram on the right shows the moving substrate configuration, with the substrate parallel to each target surface. Films uniform over approximately the target area resulted. Uniformity is about ±6.7% over 2” x 2”. The substrate passes over each target more than 50 times during a typical deposition.

![Figure 1: Schematic illustration of the flux distributions resulting from a stationary substrate (at left), and a moving substrate (at right).](image-url)

When moving the substrate and heater, special care must be taken to avoid arcing from the plasmas to the moving heater leads. This challenge was met by using a combination of ceramic sleeves over the heater leads, large distances between the heater leads and the sputtering target, and slow-blow fuses.
Delay times over each cathode were set and programmed into the deposition controls. These delay times were used to keep deposition times relatively short, even when the maximum In deposition rate with the sputtering power supplies available is significantly smaller than the maximum Cu deposition rate, in atoms/sec/cm². Deposition time is minimized when

\[
\frac{\text{delay over } Cu}{\text{delay over } In} = \frac{\text{max imum In rate}(\text{atoms/ sec/cm}^2)}{\text{max imum In rate}(\text{atoms/ sec/cm}^2)} \cdot \frac{1}{\text{Cu / In ratio desired}} = 1
\]

The above equation assumes that Se rate can be increased enough to meet the requirements of the In and Cu rates. Film depositions were performed in this arrangement over 20 to 30 minutes, following the NREL two-stage recipe.

2.C Film Composition Measurement and Tracking

Control of the sputtering fluxes by monitoring the Cu and In optical emission and adjusting the cathode powers appropriately was used to provide accurate and reproducible Cu and In deposition rates. In systems where Cu, In, and Se are delivered concurrently by methods other than evaporation, contamination of the Cu and In sources with Se, and the resulting deposition rate fluctuations, often resulted in irreproducible compositions. OES, however, provides a means to monitor the sputtering flux rates and maintain it at the correct level using cathode power adjustments, regardless of the target surface condition.

To use OES as a deposition rate control, the intensity of the characteristic lines for each element are continuously tracked. Figure 2 shows the emission spectra of the Cu and In plasmas during CIS deposition. The intensities of the Cu emission at 325 nm and the In emission at 451 nm (at constant pressure) were used to track Cu and In deposition rates. Note that no Se lines are apparent in the Cu and In plasmas, although Se is in the deposition chamber.
The intensities of the Cu and In emissions, as shown in Figure 2, are then used to provide a means to monitor the sputtering flux rates and maintain them at the correct level using cathode power adjustments, regardless of the target surface condition. For example, Figure 3 shows the thicknesses of several Cu samples made under constant deposition conditions. For each deposition, the surface started in a varying state of Se contamination. Due to Se contamination of the target surface, thickness of the samples varies by over 20%, even though deposition conditions, including the power to the cathode, was the same for each sample. The thickness of each sample, however, is correctly indicated by the OES Cu emission, shown on the y-axis. As the Cu emission increases, the thickness increases, regardless of the Se contamination on the target surface. Thus, the desired Cu flux can be obtained by adjusting Cu cathode power to produce the necessary Cu emission. An incorrect Cu flux may be obtained if only setpoint control is used.

Figure 2: Emission spectra of Cu and In plasmas during CIS deposition.
Figure 3: Relationship between the thicknesses of Cu samples and the Cu OES emission made under constant depositions conditions, with the surface of the target in varying states of Se contamination.

The successful use of OES to monitor and control the deposition of Cu and In is not limited to the single-element films shown in Figure 3, of course. Figure 4 shows a comparison of Cu/In ratio for several CIS films as measured by energy dispersive spectroscopy (EDS) versus the Cu/In ratio calculated in real time from the optical emission. EDS was performed by Rocky Mountain Laboratories, Inc. The Cu/In ratio calculated from OES tracks the actual Cu/In ratio measured by EDS. Note that the OES calculations are based on room temperature sticking coefficients: the calibration between optical emission and the various material thicknesses was performed at room temperature. Thus, since the CIS depositions were performed at high temperature, the Cu/In ratio calculated from OES differs from that measured via EDS by some constant factor. However, since the relationship is reproducible, the ratio of the Cu and In emission signals can be used to control the actual film composition by adjusting for the difference between room temperature and deposition temperature sticking coefficients.
When comparing EDS and OES measurements, the characteristics of the EDS measurement must be considered. EDS sampling depths are typically around 1 μm. An EDS sampling depth less than the ~2 μm CIS thickness is confirmed by lack of Mo signal in the measurements. Thus, EDS measurements are likely to be weighted heavily by the material within 1 μm of the film surface. So, in samples with different Cu/In profiles, yet the same average Cu/In ratio, EDS will indicate different compositions. Similarly, the presence or absence of an In-rich layer on the CIS surface may make very little difference in the total composition of the sample, but may make a large difference in the EDS measurement of the composition. Thus, the relationship between the composition indicated by OES (average composition) and that indicated by EDS (composition weighted toward top of film) is not always as clean as that shown in Figure 4. Figure 5 shows a comparison of EDS and OES compositions for all co-sputtered samples on which EDS composition was measured. Error bars on EPMA measurements represent statistical, not systematic, errors. Samples were made at different temperatures, with different Cu/In profiles, different thicknesses of the In-only layer, and different Se fluxes. Although there is loose agreement between all OES and EDS compositions measurements, the best correlation is found when samples made under similar conditions (i.e. differing amounts of Cu and In, but delivered with the same profile and all other variables held constant) are compared. It is likely that a bulk composition measurement, such as those made by inductively coupled plasma (ICP), would agree more closely with the OES comparison when different Cu/In profiles are involved.

Figure 4: Comparison of Cu/In ratio as measured by EDS versus Cu/In ratio calculated in real time from OES, based on room temperature sticking coefficients.
Figure 5: Cu/In ratio as determined by OES and EDS, for all samples.

A second characteristic of EDS measurements that should be considered is the relative nature of the calibration. Semi-empirical relationships are typically used to convert the measured x-ray signals to atomic concentration. Thus, although a percent change in an element’s concentration from one sample to the next may be very accurate, the absolute percentage composition indicated by the EDS is not necessarily accurate. Table 1 shows atomic percent composition of one sample that was measured by EDS at two facilities and ICP at a third facility. The uncertainty in the EDS measurements represents noise, not absolute uncertainty. The three measurements imply the same Cu/In ratio, but show very different amounts of Se. All composition measurements referenced in this report were performed at the facility “EDS1”.

<table>
<thead>
<tr>
<th></th>
<th>%Cu</th>
<th>%In</th>
<th>%Se</th>
<th>Cu/In Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS 1</td>
<td>33.8 ± 1</td>
<td>30.1 ± 1</td>
<td>36.0 ± 1</td>
<td>1.12 ± .07</td>
</tr>
<tr>
<td>EDS 2</td>
<td>25.3 ± 0.3</td>
<td>24.9 ± 0.2</td>
<td>49.8 ± 0.4</td>
<td>1.02 ± 0.02</td>
</tr>
<tr>
<td>ICP</td>
<td>26.8</td>
<td>24.6</td>
<td>48.5</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 1: Comparison of atomic percent composition obtained by EDS measurements at two different facilities and by ICP measurements.
2.D Method of Se Delivery

Two methods of Se delivery - pulsed DC sputtering of Se and evaporation of Se at sputtering pressures - were compared. Evaporation was shown to be more effective than sputtering in delivering Se to the growing films. Deposition rate during pulsed DC sputtering could not be increased beyond about 0.5 Å/sec, even with variations in deposition pressure, target thickness, source to substrate distance, target annealing, and target doping. Evaporation at sputtering pressures, however, easily produced deposition rates of 95 Å/sec and higher. A 30 minute CIS growth time requires a Se deposition rate at least 12 Å/sec. Even higher deposition rates are required if the substrate is not in the location of maximum flux at all times. Lack of precise deposition rate control during Se evaporation is not an issue, since incorporation of Se into the growing film is self-regulating, and fluxes for champion cells are routinely allowed to vary from 2 to 6 times the required stoichiometric rate. No Se emission lines were visible in the Se plasma, due to the combination of low Se deposition rates and the absence of strong Se emission lines in the UV-visible range.

2.E Device Results

Good device quality was demonstrated by quantum efficiency and current-voltage response. Figure 6 shows the current-voltage curve of the most efficient co-sputtered device made to date at MRG. In the inset, its parameters are compared with that of the world-record total-area efficiency CIS cell. The MRG cell was made with all dry processing, the type that will be used in large-scale manufacturing. Figure 7 shows the quantum efficiency of the highest current co-sputtered device made to date at MRG. The results were obtained after only 19 separate CIS device runs. Rapid progress can be expected as the process is optimized through additional experiments.
Figure 6: Current-voltage curve of the most efficient co-sputtered device made to date at MRG. Parameters are compared with that of the world-record total area efficiency CIS cell.

Figure 7: Quantum efficiency of highest current co-sputtered device made to date at MRG.

Efficiency losses in the co-sputtered cells are spread fairly evenly among the device parameters. Table 1 compares the device parameters for co-sputtered cells with those of record CIS cells. The fourth column of Table 1 lists the efficiency differences...
that would result from improving each co-sputtered parameter to the record value. The losses listed together account for the 8.2% efficiency difference between the 13.2% efficient record CIS cell and the 5.0% efficient co-sputtered cells. Current losses in QE data are also spread fairly evenly among the possible current loss mechanisms: deep penetration, short wavelength loss, and wavelength independent loss.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Co-Sputtered Value</th>
<th>Record Cell Value</th>
<th>Resulting Efficiency Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short-circuit current</td>
<td>27.1 mA/cm²</td>
<td>36.3 mA/cm²</td>
<td>2.8%</td>
</tr>
<tr>
<td>Open-circuit voltage</td>
<td>0.372 V</td>
<td>0.484 V</td>
<td>2.5%</td>
</tr>
<tr>
<td>Series Resistance</td>
<td>3.8 Ω-cm²</td>
<td>0.5 Ω-cm²</td>
<td>2.4%</td>
</tr>
<tr>
<td>Shunt Resistance</td>
<td>210 Ω-cm²</td>
<td>2000 Ω-cm²</td>
<td>+ 0.5%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>8.2%</td>
</tr>
</tbody>
</table>

Table 2: Table of possible efficiency improvements in co-sputtered device parameters.

2.F Effect of Temperature On Device Performance

The effect of deposition temperature on device performance was examined. Multiple samples were fabricated using the two-stage recipe under identical conditions except for the heater temperature. Figure 8 graphs the results. The hottest deposition was made first. For each succeeding sample, the temperature setpoint of both stages was adjusted downward. The x-axis shows the average temperature during deposition. The figure shows that device performance depends strongly on the CIS deposition temperature. For the temperatures shown, all parameters improve as temperature decreases. A fourth absorber was made at an average heater temperature of 403 °C, with very poor devices resulting. No devices on this fourth substrate yielded an open-circuit voltage greater than 50 mV. Thus, an optimum average heater temperature for the deposition process was found to exist between 403 and 472 °C.
Figure 8: Effect of CIS deposition temperature on co-sputtered device parameters.
High-efficiency co-evaporated cells are typically deposited at substrate temperatures exceeding 550 °C.\textsuperscript{1,2} Therefore, an optimum deposition temperature around 450 °C is somewhat surprising. Experiments were performed to determine whether or not the thermocouple indicating the heater temperature also correctly indicated the substrate temperature. Additional thermocouples were introduced into the system to compare the heater temperature (on top of the heater), the heater temperature on the bottom of the heater (where the substrate is located), and the substrate temperature. The temperature control versus time profile for the 522 °C run shown in Figure 8 was repeated. The results are shown in Figure 9. The data show that, with the heater in its original configuration, the substrate experiences a maximum temperature of 378 °C when the heater reaches its maximum temperature of 568 °C. Thus, it is likely that the unexpected performance versus temperature trend seen in Figure 8 results from the CIS unintentionally being formed in a different growth regime than that of the most efficient CIS co-evaporated cells.

![Figure 9: Substrate temperature, heater temperature, and heater temperature setpoint versus time for CIS deposition, before and after heater modifications.](image)
further improvement of the heater will be an important part of future development of the co-sputtered cells. The hypothesis that increasing the heater temperature is important to device performance is supported by the observation that the highest efficiency (and most specular) material is located on the substrate near the clip that presses the substrate against the heater. This area near the clip is expected to be warmer than the rest of the sample, since it experiences the greatest pressure between the heater and substrate, and since the clip provides another path for heat conduction from the heater to the substrate.

2.6 Effect of Se Flux on CIS Properties

The expected insensitivity of film composition, structure, and device performance to Se flux were verified. During CIS depositions, the Se flux is typically not carefully controlled, since the incorporation of the Se into a hot CIS film is self-regulating, and therefore champion cells are made with Se fluxes ranging from 2 to 6 times the required stoichiometric flux.

Se flux was controlled by the evaporation crucible temperature. Figure 10 shows Se film thickness as a function of crucible temperature. The solid points show data from the fabricated films. The line is an exponential based on the simple evaporation theory presented by Polanyi and Wigner. For each film, deposition time was 40 minutes, and the substrate was placed the same distance from the target as during CIS deposition. The crucible volume is 2 cm$^3$. The depositions shown, for thickness calibration, were made with no Ar flow in the chamber.

![Figure 10: Se film thickness as a function of crucible temperature.](image)
Source-to-substrate distance and sputtering pressure also have an effect on Se deposition rate. In traditional, low-pressure evaporation, the flux reaching the substrate shows a $1/r^2$ dependency on source-to-substrate distance. The introduction of sputtering gas into the chamber further decreases the evaporative flux reaching the substrate as source-to-substrate distance is increased. At sputtering pressures (for example, 10 mT), the mean free path of gas molecules in the chamber is less than 1 mm. Thus, for source-to-substrate distances on the order of inches, significant scattering of the evaporated flux occurs. For the chamber configuration at MRG, it was found that the introduction of 12 mT sputtering pressure reduces the amount of Se reaching the substrate by 45%.

The effect of Se flux on device performance was examined. An Se crucible temperature was chosen to deliver approximately twice the stoichiometrically required amount of Se flux at every pass of the substrate. This flux level was calculated, at sputtering pressures, to occur for a crucible temperature of 305 °C. CIS films were also made at temperatures corresponding to 37% of the original Se flux, and 23% of the original flux. No effect of the reduced Se - as judged by device performance, EDS composition, and XRD pattern – was seen at the 37% flux level. However, when the Se flux was reduced to 23%, all data indicated Se-deficient films. Devices made with the 23% Se were not electrically active. EDS measurements showed a 40% reduction in Se (relative to the Se in the normal samples). In XRD measurements, the presence of off-stoichiometric phases is evident in the 23% Se samples. (The actual diffraction pattern of the Se-deficient film can be found below, in Figure 14.) SEM micrographs show that the CIS films made with 23% Se flux have a morphology different from the other films. Figure 11 shows SEM micrographs of a stoichiometric film on the left, and of a selenium-deficient films on the right. The roughly micron-sized spheres of CIS are present in a smooth matrix in the left micrograph. The Se-deficient film, shown in the right micrograph, has faceted and striated crystallites varying from 1-5 microns in size.

Figure 11: SEM micrographs of stoichiometric (left) and selenium-deficient (right) films.
2.1 Effect of In-Only Layer on Performance

High efficiency CIS cells are typically deposited in a sequence that involves growing the majority of the film thickness in a Cu-rich state, then increasing the In deposition rate at the end of the deposition to bring the film back to a nearly stoichiometric state.\(^1\) This sequence is thought to enhance grain growth by allowing the presence of Cu-Se, which acts as a fluxing agent and promotes grain growth, throughout the majority of the deposition.\(^2\)

The importance of the Cu-rich growth phase was examined for the co-sputtered cells. The In-only final layer was suspected as possibly detrimental to device photocurrent after an error in sample handling was made. After the CIS had been deposited on one substrate, the film was mistakenly brushed with a gloved hand, and the surface of the film appeared to be removed. Then, devices were fabricated on the CIS-coated substrate, and those in the vicinity of the handling “damage” showed markedly higher photocurrents than the other devices on the substrate.

To investigate the effect of the In-only layer on photocurrent, two samples were made with roughly the same amount of Cu and In. In the first sample, 18% of the In was deposited during the In-only layer. In the second sample, all of the In was deposited concurrently with the Cu. Results are shown in Table 3. The short-circuit current increases dramatically when the In-only layer is eliminated. Open-circuit voltage and fill factor remain essentially unchanged. The increase in efficiency resulting from eliminating the In-only layer reflects only the increase in short-circuit current.

<table>
<thead>
<tr>
<th></th>
<th>Sample DOE125</th>
<th>Sample DOE126</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of In thickness</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>deposited during</td>
<td></td>
<td></td>
</tr>
<tr>
<td>second, In-only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jsc (mA/cm(^2))</td>
<td>16.8</td>
<td>23.7</td>
</tr>
<tr>
<td>Voc (mV)</td>
<td>318</td>
<td>330</td>
</tr>
<tr>
<td>Fill Factor (%)</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>2.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>

*Table 3: Device parameters comparing the effect of changing the In-only layer thickness.*

2.1 Effect of Cu/In ratio on device performance

Numerous samples were made with varying Cu/In ratios. The Cu/In ratios of the best co-sputtered cells (as measured by EDS or OES deposition rates) are significantly lower than that of the best co-evaporated cells. When co-sputtered cells are fabricated with the Cu/In ratio \(\approx 0.98\), the Cu/In ratio of champion CIS cells, the co-sputtered cells
exhibit severely shunted behavior. Several possibilities for the cause of the composition discrepancy exist. For example, the material may be "under-reacted". If, in the reaction path of the film during deposition, it is favorable for In to exist in its metallic form rather than only in CIS, excess In and a low Cu/In ratio may result. Considering the low heater temperature that was discovered, as discussed in section "2.F Effect of Temperature On Device Performance", the under-reacted scenario is particularly likely. Another possible cause of the composition discrepancy is the existence of Cu-rich and Cu-poor layers in the co-sputtered samples, resulting from the cycling motion of the substrate. Compositional measurements that profile the sample (such as secondary ion mass spectrometry) and those that measure the entire sample uniformly (such as inductively coupled plasma measurements) should be performed to verify or disprove the existence of layers in the compositional profile. If layers, or under-reacted material, exist, they must be eliminated by process variations, such as substrate temperature or motion.

Except for the tendency of devices with high Cu/In ratios to be leaky, no correlation between Cu/In ratio and other device parameters is evident.

2.1 Investigations of Ion Bombardment Effects

An investigation of the effects of ion bombardment on the growing film was planned for the Phase I research. The possible effects of ion bombardment are illustrated in Figure 12. The samples in this figure are high-quality CIGS absorber made at the National Renewable Energy Laboratory (NREL) that were subjected to various plasma treatments at MRG after fabrication. One film was exposed to an Ar plasma, another was exposed to a H plasma, and a third was left unchanged. The films were then returned to NREL to be finished into solar cells. Figure 12 shows light and dark current-voltage (IV) curves from each cell. Compared to the control sample, the H-treated cell shows somewhat reduced currents and voltages, and increased shunting. The Ar-treated cell shows a complete disappearance of zero-bias photocurrent. The absorber surface has clearly been damaged in both plasma treatments, and has been damaged most severely in the case of the heavy ion (Ar) plasma. The plateau seen in the IV curve of the Ar-treated sample is consistent with a spike in the band edges in the junction region due to surface damage.
Figure 12: Light and dark current-voltage curves from CIGS solar cells where the absorber layer was a) left unchanged, b) exposed to a H plasma, and c) exposed to an Ar plasma.

During the fabrication of co-sputtered samples, however, no effects bearing the signature of ion bombardment damage (as seen in Figure 12c) were observed at any
deposition powers. It is likely that the relatively high substrate temperatures during deposition allowed sufficient atomic mobility for recrystallization and repair of damage from ion bombardment.

2.K. Effects of Annealing

The effects of annealing on cell performance were examined. Anneals have been reported by some researchers to produce small increases in efficiency.\textsuperscript{237} In accordance with these authors' experiences, two types of anneals were performed: 1) a 200 °C anneal in air of the finished device for 15 minutes, and 2) a 200 °C, 3 minute anneal in air of the CdS/CIS/Mo/glass structure before the i-ZnO deposition. Devices were characterized both before and after the first type of anneal. The first type of anneal was performed on 5 substrates, and caused all devices to exhibit decreases in open-circuit voltages. The decreases ranged from 10 to over 200 mV. As a consequence of the voltage decrease, the first type of anneal in most cases caused device efficiencies to decrease substantially. Efficiency increases from the first type of anneal were seen only on one substrate, on which photocurrents were originally very low. On this substrate, a mild voltage decrease after annealing was offset by a photocurrent increase to result in a small efficiency increase. To evaluate the second type of anneal, one CIS/Mo/glass piece was divided into two pieces. Each piece was finished into devices, but only one piece was given the post-CdS anneal. Devices on the annealed piece exhibited open-circuit voltages and short-circuit currents comparable to the control piece, but had significantly smaller fill factors. Thus, the two types of anneals performed were detrimental to device efficiency in most cases, particularly for the most efficient cells. Small improvements in device efficiency were seen in only one case, where a substrate with very low original photocurrent showed some improvement in photocurrent after annealing. Annealing was therefore assessed to not be a promising route towards efficiency improvements.

2.L. XRD Results

XRD measurements were made on 9 CIS films. The 9 films covered a broad range of compositions and deposition conditions. Cu/In ratio, as measured by EDS, ranged from 0.35 to 2, and Se content varied by a factor of 4 over these films. A \(\Theta\)-2\(\Theta\) drive, Siemens powder x-ray diffractometer using Cu k\(\alpha\) radiation was used. In all films, CIS was evidenced to be oriented most strongly in the (112) direction, with significant contribution from the (204) or (220) orientation as well. The Mo (110) peak could be seen clearly in all films. Figure 13 shows representative XRD spectra. All peaks evident on the scale shown in Figure 13 can be indexed to CIS or Mo.
Figure 13: XRD spectra of co-sputtered CIS films.

For two films, non-CIS peaks can be seen if the baseline region of the XRD pattern is expanded. These two films were the films in which composition is farthest from stoichiometric. XRD patterns of these films are shown in Figure 14. The XRD patterns from a Cu-rich and Se-deficient film are shown. The XRD pattern of a stoichiometric film is also shown for comparison. For the Cu-rich film, the Cu/In ratio is two. For the Se-deficient film, the Se content is only about 30% of stoichiometric. In Figure 14a, the major lines from CIS and Mo are indicated. Figure 14b expands the baseline regions of the XRD patterns. On the magnified scale, differences in the diffraction patterns of the Se-deficient, Cu-rich, and stoichiometric films can be seen, particularly the manifestation of non-CIS phases in the Se-deficient material.
Figure 14: X-Ray diffraction patterns of three CIS films illustrating the effects of varying film composition. Patterns are shown a) full scale, and b) on a magnified scale.
2.M SEM Results

A variety of film characteristics were seen in SEM surface photographs. SEM photographs were taken by Rocky Mountain Laboratories, Inc. Films were observed to have average grain sizes ranging from about ¾ μm to about 2 μm. Grain size differences are illustrated in Figure 15, which shows two SEM micrographs of films of different grain size.

![Figure 15: SEM photographs at 5000x magnification, showing sample 116 (left) with ~¾ μm grain size, and sample 120 (right) with ~1 ½ μm grain size.](image)

Many of the CIS films showed appeared to have raised material on the film surface, as illustrated in Figure 16. The two leftmost SEM photographs show various shapes of raised material above the main film surface. The rightmost photograph shows no such material.

![Figure 16: SEM photographs at 2000x magnification, showing samples 102 (left) and 105 (middle) with raised material growing above the main film surface, and sample 103 (right) with no such material.](image)

SEM photographs also revealed differences in film densities. Most films on which SEM measurements were made had a density similar to that shown in Figure 17, middle. Such “average density” films exhibit a closely-packed grain structure with only small voids apparent between the grains. Other films were very dense, such as that
shown at the left in Figure 17. For the very dense films, almost no voids are visible in the SEM photographs. Finally, the least dense films showed voids in the SEM photographs on the same order as the grain size. Such a film is shown as the rightmost SEM photograph in Figure 17.

Figure 17: SEM photographs at 5000x magnification, showing samples 111 (left) with a relatively dense appearance, sample 107 (middle) of average density, and sample 118 (right) with voids on the order of the grain size.

An SEM photograph of high-efficiency co-evaporated CIGS from NREL is shown in Figure 18, as reprinted from reference 17. The figure shows both the film surface (tilted at 20° from normal), and a cross-section. Magnification is 15,000x. The film appears very dense, and no excess material can be seen raised above the film surface. The grain size is on the order of 1 μm.

Figure 18: SEM photograph of NREL co-sputtered CIGS, at 15,000x magnification. Reprinted from reference 17.

A summary of the characteristics seen in the SEM micrographs is shown in the first four columns of Table 4. Also shown in Table 4 are the Cu/In ratios as measured by EDS, the device efficiencies, and the two-point resistances made at the same location (called "location #3") on each sample. All films on which SEM measurements were made are included in the table. The highest efficiency devices shown (#'s 104, 110, 111, 113) span a wide range of grain sizes, densities, and presence or lack of raised material on the film. Thus, it appears that none of these three characteristics detectable by SEM is a
controlling factor in efficiency. Also, there is no apparent correlation between the Cu/In ratio and grain size, presence of raised material, and density. Rather, the one parameter that appears to correlate well with the device efficiency is the two-point resistance. The highest efficiency samples exhibit two-point resistances in the range from 15,000 to 200,000 Ω. All of the lower-efficiency samples exhibit two-point resistances outside of this range.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Approx. Grain Size (μm)</th>
<th>Raised Material</th>
<th>Density</th>
<th>EDS Cu/In</th>
<th>Efficiency (%)</th>
<th>Resistance 3 (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>1⅛</td>
<td>Yes</td>
<td>Average</td>
<td>2.93</td>
<td>&lt; 0.5</td>
<td>26</td>
</tr>
<tr>
<td>103</td>
<td>1</td>
<td>No</td>
<td>Average</td>
<td>1.74</td>
<td>&lt; 0.5</td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>1½</td>
<td>Yes</td>
<td>Voids</td>
<td>1.08</td>
<td>3.40</td>
<td>200,000</td>
</tr>
<tr>
<td>105</td>
<td>1⅛</td>
<td>Yes</td>
<td>Average</td>
<td>0.67</td>
<td>1.00</td>
<td>1.5 x 10⁴</td>
</tr>
<tr>
<td>107</td>
<td>1</td>
<td>No</td>
<td>Average</td>
<td>0.69</td>
<td>&lt; 0.5</td>
<td>2</td>
</tr>
<tr>
<td>109</td>
<td>2</td>
<td>No</td>
<td>Average</td>
<td>0.62</td>
<td>&lt; 0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>110</td>
<td>%4</td>
<td>Yes</td>
<td>Dense</td>
<td>0.5</td>
<td>3</td>
<td>25,000</td>
</tr>
<tr>
<td>111</td>
<td>1</td>
<td>Yes</td>
<td>Dense</td>
<td>0.35</td>
<td>4.4</td>
<td>15,000</td>
</tr>
<tr>
<td>113</td>
<td>1½</td>
<td>Yes</td>
<td>Voids</td>
<td>0.7</td>
<td>3.9</td>
<td>30,000</td>
</tr>
<tr>
<td>114</td>
<td>1½</td>
<td>No</td>
<td>Average</td>
<td>0.99</td>
<td>2.2</td>
<td>5,000</td>
</tr>
<tr>
<td>115</td>
<td>1⅛</td>
<td>No</td>
<td>Voids</td>
<td>0.96</td>
<td>&lt; 0.5</td>
<td>1,000</td>
</tr>
<tr>
<td>116</td>
<td>%4</td>
<td>No</td>
<td>Voids</td>
<td>0.93</td>
<td>&lt; 0.5</td>
<td>22</td>
</tr>
<tr>
<td>117</td>
<td>1</td>
<td>No</td>
<td>Voids</td>
<td>0.99</td>
<td>&lt; 0.5</td>
<td>8</td>
</tr>
<tr>
<td>118</td>
<td>1½</td>
<td>No</td>
<td>Voids</td>
<td>0.74</td>
<td>0.5</td>
<td>11</td>
</tr>
<tr>
<td>119</td>
<td>1⅛</td>
<td>No</td>
<td>Voids</td>
<td>0.80</td>
<td>&lt; 0.5</td>
<td>100</td>
</tr>
<tr>
<td>120</td>
<td>1½</td>
<td>No</td>
<td>Voids</td>
<td>0.94</td>
<td>&lt; 0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4: Summary of characteristics seen in SEM micrographs.

2. N CBD vs. sputtered CdS

Sputtered CdS was used as the first part of the window layer to finish all devices, except where noted otherwise. Traditional high-efficiency solar cells have been fabricated using chemical bath deposited (CBD) CdS. The CBD CdS process is considered problematic for manufacturing for a number of reasons. First, it involves the use of volatile toxic chemicals – most notably thioirea, a mutagen, and carcinogenic aqueous solutions of Cd salts. Second, the process is a batch, rather than continuous process. Third, high volumes of aqueous, volatile, toxic wastes are generated. For example, the typical laboratory setup generates about 2 gallons of such waste for each square foot coated. Sputter deposition of CdS, on the other hand, is all-dry, generates an extremely low volume of waste (~0.01 cm³ waste per ft² coated), generates only waste that is contained in the vacuum chamber, and can be performed continuously. The use of
sputtered CdS is therefore an important aspect of the manufacturability of the fabricated devices.

The performance of sputtered CdS has been compared to CBD CdS at MRG in the past. The performances of the two window layers were found to be comparable. In these preliminary experiments Absorber material was CIGS on molybdenum-coated soda-lime glass, fabricated at the Institute for Energy Conversion. The sputtered CdS sample yielded a 12.1% efficiency, and the CBD CdS sample yielded a 12.9% efficiency. The CBD CdS sample showed only slightly higher fill factor and voltage than its sputtered counterpart.

Similar experiments were repeated at MRG, using the co-sputtered absorbers. One CIS-coated substrate was cut into 4 pieces, as shown in Figure 19. One piece received CBD CdS, and the two neighboring pieces received sputtered CdS. Neighboring pieces on both sides of the piece receiving CBD CdS were chosen so that the effects of slight gradients in the CIS composition, which exist from one end of the substrate to the other, would not invalidate the CBD / sputtered comparison. Next, all three pieces received i-ZnO and indium tin oxide (ITO) in the same deposition runs. The fourth piece was set aside for other types of characterization. The three pieces that received window layers were scribed into multiple devices. Results are shown in Table 5. No difference between the performance of the sputtered and CBD CdS layers can be deduced from Table 5.

![Figure 19: Division of CIS/Mo/Glass sample #DOE113.](image)

<table>
<thead>
<tr>
<th>Piece</th>
<th>Number of devices</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (sputtered)</td>
<td>19</td>
<td>11.3 ± 4.0</td>
<td>250 ± 30</td>
<td>35 ± 4</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>2 (CBD)</td>
<td>23</td>
<td>10 ± 2.3</td>
<td>300 ± 30</td>
<td>32 ± 3</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>3 (sputtered)</td>
<td>28</td>
<td>13.6 ± 5.4</td>
<td>250 ± 50</td>
<td>32 ± 5</td>
<td>1.3 ± 0.8</td>
</tr>
</tbody>
</table>

Table 5: Device parameters for three pieces of sample #DOE113. Values are shown ± the standard deviation.
2.0 Window Issues

High-efficiency co-evaporated CIS solar cells utilize three semiconductor window layers deposited on top of the CIS absorber. These three layers are typically 500Å CdS, 500Å i-ZnO, and 0.5-1 μm transparent conducting oxide (TCO). The CdS was originally thought to form a heterojunction with the CIS, but more recent data indicate that the electrical junction may be buried in the CIS, and the CdS may facilitate the formation of defects in the near-surface CIS to create the buried junction. It has been found empirically that the most efficient CIS solar cells utilize a highly resistive ZnO layer on top of the CdS. It is hypothesized that this i-ZnO layer might prevent shunting by capping areas that are not completely covered by CdS, or that the i-ZnO layer might increase efficiency by protecting the CdS and CIS from harsh conditions encountered during the final window layer deposition. The final window layer is the highly conductive TCO, which provides photocurrent collection across the cell without substantial resistive losses. A number of window layer issues still need to be examined for the co-sputtered cells.

Evidence from Phase I exists that the transparent conducting oxide grown on a glass witness slide has different properties than that grown on the CIS devices during the same deposition. TCO grown on glass exhibits typically 20 Ω/□ and > 85% transmission averaged over the AM1.5 spectrum. The resistance between two probes placed ~0.5 mm apart on the TCO/glass structure is typically ~40 Ω. When the same probes are placed on completed devices the measured resistance ranges from 200 to 400 ohms. The described method of comparing resistances is not rigorous because it includes contact resistance and cannot be converted to sheet resistance. However, the traditional and rigorous method of sheet resistance measurements, four-point probing, is not readily performed on TCO/i-ZnO/CdS/CIS/Mo/glass. When making four-point measurements on the completed device structure, conduction can occur across the junction and then through the extremely conductive Mo, rather than just through the TCO. Measured sheet resistance is then significantly lower than the actual sheet resistance. The problem is particularly severe when a large distance exists between the probes, making flow across the junction even more favorable. The measured sheet resistance also depends on the CIS junction properties, since a leakier junction makes current flow to the Mo more favorable. Furthermore, transmission measurements of TCO on devices are also problematic, since the substrate is opaque. Consistent with the high resistance observed in the two-point measurements, cell photocurrent was observed to be dependent (reproducibly) on probe placement. Cell photocurrent should only be dependent on probe placement if extremely severe localized shunting defects exist, or if TCO resistance is so high that voltage drops across the TCO affect the short-circuit current. The cell series resistance - as extracted from IV curves - is also consistent with a resistive TCO, although multiple sources of series resistance are possible. If the series resistance of the cells is in fact due to the
TCO, the 3.8 Ω-cm² series resistance seen in the most efficient device implies a TCO resistance of approximately 130 Ω/□ for the 0.3 x 0.6 cm² devices. Note that the 130 Ω/□ sheet resistance value estimated from the IV curves is consistent with the estimation of the sheet resistance based on the two-point probes.

Strong effects of substrates on transparent conducting oxide (TCO) properties are commonly observed. It has been found that crystallinity and orientation of the ITO film are very important to its conductive and transmissive properties. It is likely that the roughness and orientation of the CIS, CdS, and i-ZnO surfaces are affecting the ITO crystallinity and orientation, and therefore its properties. Characterization of the TCO on the glass slide and on the sample must be performed to determine exactly how the two films are different. XRD will be used to examine film crystallinity and orientation both on glass and on devices. On glass, four-point probing can be used to measure sheet resistance, and traditional transmission measurements can be performed. On devices, due to the opaque and conductive Mo substrate, a combination of two-point and four-point probing, current-voltage, and quantum efficiency measurements must be used to deduce ITO sheet resistance and transmission. The two and four-point probing measurements can provide a comparison of changes from one sample to the next. Resistance information can also be obtained on finished devices by looking at the slope of the current-voltage curve in far forward bias. Quantum efficiency measurements can provide information about TCO absorption by indicating the photon loss fraction that is relatively wavelength-independent.

The crystallinity and orientation of the ITO can be controlled by a combination of Ar pressure, water vapor pressure, and cathode power. Once the correct deposition conditions have been determined, closed-loop control by OES can be used to maintain these film properties as the target ages and the deposition system becomes coated.

A second window layer issue that should be examined for the co-sputtered cells is the optimization of the i-ZnO properties. For the fabricated cells, i-ZnO was deposited with the same conductivity as that used for the highest efficiency co-evaporated cells with CBD CdS. The role of the i-ZnO in the co-sputtered cells finished with sputtered CdS may be very different than that required of the i-ZnO in a cell finished with CBD CdS. CBD CdS is known to be an agglomerated, noncontiguous, relatively porous, film. Such qualities make the hypothesized role of the i-ZnO, as described above, particularly important. It is possible that the i-ZnO may be unnecessary, or even detrimental, to devices fabricated with sputtered CdS. The effect of i-ZnO parameters on co-sputtered device performance must be investigated.

2.P OES Hardware and Software Development

Hardware for OES control consists of a dual-grating, charge-coupled device (CCD), optical emission spectrometer manufactured by Princeton Instruments, Inc. with
fiber optic input. Vacuum compatible fiber optics were placed inside the sputtering chamber and directed at each sputtering target. Coating of the fiber tip was prevented by aiming the fiber down a long, grounded tube parallel to the sputtering target surface. Since plasma emission is isotropic, but deposition is not, the fiber tips are not coated. The lack of coating has been verified previously.\textsuperscript{43}

Software was developed to process the OES data and recommend adjustments to the chamber controls. The main screen for this software is shown in Figure 20. The calibration that converts OES signal to deposition rate for each metal is built into the application code. With each run, the operator then simply enters the CIS recipe that he is using, determining the amount of materials that will be deposited in each stage. The application then tells the operator in real time, during the deposition, how to adjust the cathode powers. The algorithms used keep the Cu/In ratio as specified by the operator in the recipe, and compensate for inaccurate power supply adjustments by the operator earlier in the run. The power supplies are adjusted manually by the operator as recommended by the computer, but closed-loop control will be implemented in the future. In MRG’s ITO process, the OES output already ties directly and automatically to multiple chamber controls, and improved yield and film qualities have been demonstrated.\textsuperscript{43} The algorithms used by the OES application account for either (or both) power supplies being set at their maximum power, emission produced by arcing in the plasma, the time delay of the substrate motion over each sputtering target, and subtraction of background counts. Monochromator settings, such as grating numbers, grating positions, wavelength range for each peak of interest, and exposure times, are set at the beginning of the deposition by the operator and then are executed automatically. The application operates continuously, informing the operator of the recommended power setting for each cathode based on the OES readings, and also informs the operator when either cathode should be turned off. The Cu and In peaks are remeasured approximately every 30 seconds. The application allows graphics to be turned on or off, allowing visual presentation of spectra for troubleshooting, or maximum speed of the control during deposition. The application automatically saves to disk each OES spectrum it takes. A summary file – consisting of the time each spectrum was taken, the integrated intensity of each peak of interest at each time, and the implied thickness of each material deposited as a function of time - is also automatically saved to disk for each CIS deposition.
2.0 Large-Scale System Model

The process developed in phase I can be used to design a large-scale co-sputtered CIS system. A basic schematic of such a system is shown in Figure 21. This system is based on the deposition process researched during Phase I and the commercially-available MRG P1400 vacuum chamber. This modified "off-the-shelf" system incorporates all elements of the deposition process developed in Phase I. Sputtering is used to deliver Cu, In, and Ga, while OES in-situ controls regulate the deposition rate from these sources. The substrate is parallel to all target surfaces to maintain the materials uniformity already proven in MRG P1400 systems, and position sensors regulate the substrate motion. Note that because a moving substrate has already been incorporated into the Phase I process, it is not necessary to perform the involved modeling that is generally required to reproduce flux profiles from a stationary research-style deposition in a dynamic manufacturing deposition. Rather, the Phase I process transfers directly to the dynamic large-area system. As implemented during the phase I depositions, the process time should be less than 30 minutes of deposition per batch of substrates. Se is delivered by evaporation, as during the Phase I. Two In targets are included for each Cu target, to account for the lower In deposition rates when comparable voltages are applied to each cathode,
particularly in the presence of Se. This ratio of In to Cu targets (or delay time) for maximum deposition rate was discussed in section "2.B Flux Distribution". Provisions for Ga incorporation are also made in the large-area chamber.

![Diagram of deposition system](image)

**Figure 21:** Model of deposition system for 12" x 12" CIGS thin films based on process researched during Phase I and the commercially available MRG P1400 vacuum chamber.

Several features of the designed system warrant further description. For example, cathode design and positioning have been optimized to provide uniform and maximum deposition flux at a given deposition power. The cathodes in the P1400 system have already been shown to provide at least ±4% uniformity over the 12" substrate width, for a variety of materials, including CdS, ZnO, ITO, and Cu. Figure 22 shows deposition as a function of distance along the direction of substrate motion (substrate length) for several source-to-substrate distances. Deposition was measured via film thickness for films made under constant deposition conditions. For the shorter source-to-substrate distances, deposition is the fastest at the center of the cathode, but does not extend far beyond the substrate edges. For the largest source-to-substrate distance, deposition extends far beyond the cathode edges, but is significantly reduced directly over the cathode. (Note that for intermediate substrate distances maxima can be seen in the curve on each side of the target center, indicating the position of the target racetrack.) To maximize the deposition rate for dynamic depositions, a source-to-substrate distance must be chosen to utilize the wide-spread flux of the longer distances, without sacrificing the higher target-center flux of the shorter distances. The resulting relationship is shown in Figure 23. Deposition rate is maximized when the source-to-substrate distance is about 3". Thus the MRG P1400 systems are designed with approximately a 3" source-to-substrate distance.
Figure 22: Deposition as a function of distance from the target center along the substrate length, for MRG P1400 cathodes. The relationship is graphed for three different source-to-substrate distances.

Figure 23: Film thickness as a function of source-to-substrate distance for constant deposition conditions.
Another aspect of the proposed chamber that deserves further description is the expected throughput. During Phase I, CIS was deposited over 2" x 2" substrates in 25 minutes using 3" diameter (i.e. 7.1 in² area) sputtering targets. In the designed system, deposition will be performed using 3.5" x 18" sputtering targets, increasing the volume of material per second delivered to the substrate by approximately a factor of 9.2. In the Phase I small deposition system, the substrate spends approximately one third of the deposition time over the Cu target and two thirds of the deposition time over the In target. As mentioned in the previous paragraph, the delay times over each target were set to minimize deposition time when operating each sputtering supply at maximum voltage. Two In cathodes per Cu cathode are designed into the large-area system to simulate the delay times of the small-area system. Assuming, in the large-scale system, that a substrate transport can be implemented so that multiple substrates are loaded, and each deposition target is covered by a substrate at all times (i.e. no deposition flux is wasted), then another factor of 3 in the volume of material per second delivered to the substrate is gained. (A simple example of substrate transport that does not waste deposition flux is a roll-to-roll cartridge for flexible substrates. For rigid substrates, an example is a spinning cassette, with cathodes arranged radially around the cassette axis.) The total area coated per minute, assuming no deposition flux is wasted, is then 4.4 in². Assuming a 10% product efficiency, 90% yield, 10% machine down-time for maintenance, and 40 hour per week shifts, the throughput of one of the large-area machines is 29 kW/year/shift. As a maximum of 4.2 shifts can be run during nonstop operation, the maximum throughput of the designed machine is 121 kW/year.

2.R Future Work

A number of items exist as future work in the development of manufacturable CIS-based solar cells via co-sputtered CIS absorber layers.

Most notably, the efficiency of the co-sputtered devices must be improved. Although the devices show great promise, as efficiencies of 5.0% have been obtained using all-dry processing after only 19 CIS depositions, world-record CIS cells exceed 13% efficiency. Therefore, the CIS process sequence has to be optimized in terms of number of sublayers, deposition rates of the metals, Cu/In profile, and temperature profile. For example, world-record CIS cells exhibit a Cu/In ratio around 0.98, with nearly uniform Cu/In ratio through the thickness. The Cu/In ratio of the best co-sputtered cells (as measured by EDS) is significantly lower than that of the best co-evaporated cells. When co-sputtered cells are fabricated with the Cu/In ratio ≈ 0.98, the co-sputtered cells exhibit severely shunted behavior. An understanding of why the composition of the best co-sputtered cells is significantly different than that of the best co-evaporated cells will likely lead to efficiency improvements in the co-sputtered cells. Several possibilities for the cause of the composition discrepancy exist. For example, the material may be "under-reacted". If, in the reaction path of the film during deposition, it is favorable for In to exist in its metallic form rather than only in CIS, excess In and a low Cu/In ratio
may result. An observed difference between the actual substrate temperature and that indicated by the thermocouple controlling the heater, as discussed in section “2.F Effect of Temperature On Device Performance”, must also be investigated as a source of under-reacted material. In fact, a number of issues – such as the effect of the In-rich layer, and the impact of substrate temperature – should be re-examined once it is insured that the heater is operating properly. Another possible cause of the composition discrepancy is the existence of Cu-rich and Cu-poor layers in the co-sputtered samples, resulting from the cycling motion of the substrate. Compositional measurements that profile the sample (such as secondary ion mass spectrometry) and those that measure the entire sample uniformly (such as inductively coupled plasma measurements) should be performed to verify or disprove the existence of layers in the compositional profile. If layers, or under-reacted material, exist, they must be eliminated by process variations, such as substrate temperature or motion. It has been observed, as discussed in section “2.H Effect of In-Only Layer on Performance”, that separating the deposition into a Cu-rich and an In-only stage appears to be detrimental to co-sputtered device performance, particularly the photocurrent. Descriptions of a number of co-evaporative deposition processes that rely on starting with In-rich phases have been published. Therefore, because of the observed detrimental effect of the Cu-rich / In-only progression on co-sputtered device performance, the In-rich recipes mentioned above should be investigated for the co-sputtered deposition. Finally, several improvements in Se delivery could lead to higher efficiency co-sputtered devices. Practical improvements to the Se delivery system would likely include shattering Se sources to prevent unneeded evaporation of Se (and therefore metallic target contamination) during ramp-up and cool-down phases, larger Se crucibles to insure that Se supply is not depleted too early in the deposition, and more careful temperature control of the Se crucible by using a proportional integral derivative (PID) controller and permanently attached thermocouple.

Window layer improvements offer another avenue to increase the efficiency of co-sputtered devices. As discussed in section “2.O Window Issues”, evidence from Phase I exists that the transparent conducting oxide deposited on devices is adversely influenced by the CIS substrate, though exhibiting good properties on glass. A combination of two-point and four-point probing, current-voltage, and quantum efficiency measurements must be used to deduce ITO sheet resistance and transmission on CIS devices. As discussed earlier, deposition conditions, particularly the water content of the ITO, must be adjusted to produce good ITO properties on CIS, as well as on glass. The optimization of the i-ZnO properties in the window layer should also be examined for the co-sputtered cells. It is possible that the i-ZnO may be unnecessary, or even detrimental, to devices fabricated with sputtered CdS, as discussed in section “2.O Window Issues”. The effect of i-ZnO thickness and conductivity on co-sputtered device performance must be investigated.

The alteration of the CIS bandgap by incorporation of Ga allows the tailoring of device response to the solar spectrum, providing a third avenue for efficiency improvements in co-sputtered devices. Such bandgap adjustments have allowed champion cells, which have yielded 13.2% efficiencies for pure CIS, to reach 18.8% efficiency. The
incorporation of Ga during the co-sputtering process by the use of a third sputtering target should be performed. Since Ga is a liquid at room temperature, a pure Ga target cannot be used. Rather, Ga should be poured into the racetrack of a severely eroded In target. The correct deposition conditions - including temperature, composition, and profile - must be investigated for Ga incorporation. Otherwise, Ga may be poorly incorporated, preventing the full possible increase voltage from being utilized. High-efficiency co-evaporated CIGS is deposited under deposition conditions very similar to those under which CIS is deposited, except that Ga flux supplements the In flux. The high-temperature (>550 °C) portion of the deposition appears to be critical for gainful Ga incorporation. The most successful efficiency improvements from Ga incorporation have resulted from average Ga/(In+Ga) ratios around 0.25, resulting in an effective bandgap of about 1.15 eV. High efficiency CIGS often use Ga profiles within the CIGS layer. The highest Ga/(In+Ga) ratio is introduced at the back of the CIGS film, creating a bandgap graded toward the space-charge region. Electrons are thereby drawn toward the space charge region, and recombination at the back contact is reduced.

A substantial amount of future work exists in scaling the small-area process developed in Phase I to large (manufacturing-size) areas. Such a scale-up would be based upon the large-area system described in section “2.4 Large-Scale System Model”. The described modifications to the MRG P1400 chamber must be made, and the process performed in the small-area chamber must be transferred to the large-area chamber. Particularly of concern is management of thermal loads and implementation of the high-temperature transport system. Expected improvements in the co-sputtering process, as described in the preceding paragraphs, should also be incorporated into the large-area system. Eventually, optimizations to the process in the large-area chamber, to maximize materials utilization and throughput, should be performed.

Evaluation of yield is a significant aspect of determining whether or not a given process is manufacturable. If yield and efficiency in manufacturing can be improved from the current state (10% efficient, 60% yield) to 15% efficiency and 90% yield, the result is a doubling in throughput leading to a reduction in cost per watt of over 50%. Thus, several important questions regarding yield must be answered. First, the amount of yield improvement provided by using OES control, rather than setpoint control, must be assessed. It was demonstrated during phase I that OES can be used to give correct information about the metallic deposition rates under differing target conditions. Enough data points must be taken under the same deposition conditions to make statistically valid conclusions about how much OES improves yield. Such data points should include a comparison of both single-element layers and CIGS samples made under OES and setpoint control. Second, the yield of the co-sputtered process must be compared with published yield data describing current manufacturing processes.\textsuperscript{5,6}
3. TECHNICAL FEASIBILITY

During Phase I, MRG has proven the feasibility of scaling up in-situ-controlled co-sputtering of CIS for large-scale manufacturing. This has been accomplished by meeting each of the technical objectives set at the beginning of the research effort. A table showing each task as described in the work plan and how it was accomplished is shown below. Each task, as laid out in the Phase I proposal, is listed in the left column. The result obtained during the Phase I research and described in this final report is listed in the right column.

<table>
<thead>
<tr>
<th>TASK</th>
<th>RESULT</th>
</tr>
</thead>
</table>
| 1. Establish reliable film composition and quality | • OES was used to monitor and control the deposition of Cu and In.  
• OES was shown to compensate for the contamination of the Cu and In sources due to reaction with Se.  
• Good device quality was demonstrated by quantum efficiency and current-voltage response. |
| 2. Evaluate film structure | • X-ray diffraction (XRD) was used to verify the formation of the CIS phase and composition.  
• Scanning electron microscopy (SEM) micrographs show that the non-stoichiometric films have a morphology different from the stoichiometric materials. |
| 3. Determine optimal Se delivery method | • Evaporation was shown to be more effective than sputtering in delivering Se to the growing films. |
| 4. Optimize sputtered flux deposition | • Moving the substrate over each of the sources was shown to produce far greater uniformity than was possible with a fixed substrate position. |
| 5. Investigation of ion bombardment effects | • The effects of ion bombardment were found to be negligible. |
| 6. Modeling of large-scale deposition system | • A large-area deposition system suitable to in-situ controlled deposition of CIS has been modeled. |

Table 6: Tasks and results from Phase I research.

Thus, Phase I has demonstrated that co-sputtering of CIS layers using OES control is a promising absorber deposition process for manufacturable CIS-based modules. OES has been demonstrated to give correct information about the metallic
deposition rates under differing target conditions, allowing reproducible film compositions. Good device results were obtained using all-dry, manufacturable processing. By using a moving substrate parallel to the target surfaces, good spatial uniformity of fluxes were be obtained, and the process was incorporated into a model for a large-scale deposition system.

4. References


37 J. Keane, NREL, private communication, 1998.


40 K. Ramanathan, H. Wiesner, S. Asher, R.N. Bhattacharya, J. Keane, M.A. Contreras, R. Noufi, "Junction Formation in CuInSe2-Based Thin-Film Devices“, *AIP Conference Proceedings* 462, pp. 9-16.


