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CIS-Based Thin Film PV Technology

Phase I Annual Technical Report
September 1995 - September 1996

D.E. Tarrant and R.R. Gay
Siemens Solar Industries
Camarillo, California

NREL technical monitor: H.S. Ullal

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
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Preface

Siemens Solar Industries (SSI) has pursued the research and development of $CuInSe_2$-based thin film PV technology since 1980. SSI began a 3-year, 3 phase cost-shared subcontract (No. ZN-1-19019-5) on May 1, 1991 with the overall project goal of fabricating a large area, stable, 12.5% aperture efficient encapsulated CIS module by scaleable, low-cost techniques on inexpensive substrates. At the start of that subcontract SSI had demonstrated a 14.1% efficient 3.4 cm^2 active-area cell, unencapsulated integrated modules with aperture efficiencies of 11.2% on 940 cm^2 and 9.1% on 3900 cm^2 and an encapsulated module with 8.7% on 3883 cm^2 (verified by NREL). Accomplishments of that subcontract included demonstration of encapsulated module efficiencies that were at that time the highest reported mini-module efficiencies for any thin film technology (encapsulated 12.8% efficient mini-module on 68.9 cm^2 and an NREL-verified 12.7% efficient unencapsulated circuit on 69 cm^2 with a prismatic cover), demonstration of a champion large area (3860 cm^2) encapsulated module efficiency of 10.3% (verified by NREL) that was the first thin film module of its size to exceed the 10% efficiency level, and delivery to NREL of a one kilowatt array of large area (~3890 cm^2) approximately 30 watt modules.

The primary objective of this subcontract (#ZAF-5-14142-03) is to establish reliable high-throughput, high-yield thin film deposition processes in order to make CIS a viable option for the next generation of photovoltaics. The primary goals for the project are to deliver a champion prototype 13% efficient large area module and to deliver sets of modules in 1-kW arrays composed of steadily increasing efficiency, reaching 1 kW of 12% efficient large-area modules by the end of the third year, demonstrating performance as well as commercial viability. The focus of the deliverables on large sets of high-performance modules reflects SSI's commitment to demonstrating a reliable low-cost product. This document reports on progress from September 1995 through September 1996.

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The Siemens Solar Industries CIS Team:
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Summary

Alloys of copper indium diselenide are promising candidates for reducing the cost of photovoltaics well below the cost of crystalline silicon. The calculated cost of CIS-based modules is about $1.00/Wp based on the measured efficiency of small-area mini-modules and projections of the processing used today to large areas and high volumes. The availability of natural resources and the effect upon the environment both appear to be acceptable. Long-term outdoor stability has been demonstrated at NREL.

Challenges remain to scale the process to larger area and to pass accelerated environmental testing. The SSI 10x10 baseline process needs to be reproduced on larger areas. The origins of thermal transient behavior needs to be identified and eliminated if possible. A package design needs to be developed which can enable the completed modules to pass standard environmental qualification testing. From today's perspective, it appears that these issues can be resolved.

From an industrial perspective, the full process sequence anticipated for use in the final product must be mastered and demonstrated rigorously. The SSI approach to developing a reliable, high-throughput, high-yield, large area thin film deposition processes is to first demonstrate process capability on small area laminated mini-modules. Following statistical process control methodologies, this baseline process has been repeatedly executed to demonstrate the potential of the technology and in support of scale up efforts. A reproducible low variation baseline has been demonstrated for over two thousand mini-modules. Laminated mini-module efficiencies after outdoor exposure typical of in-service conditions average 12.4% and a 13.6% aperture area efficient mini-module has been verified by NREL.

Process scale-up is proceeding from the foundation of this reproducible low variation baseline process. For each step in the process, the impact of the larger part size has been tested in the baseline. Such experiments indicate that the larger-area parts should be able to achieve the same level of performance as the smaller parts. However, the performance of large-area circuits processed in the SSI large area reactor has not yet reached the same level as the performance of the baseline process. The difference between the two processes has been isolated to the formation of the absorber and is the subject of current development.

Although long-term outdoor stability has been demonstrated, SSI fabricated CIS-based devices have failed standard environmental stress tests. Thermally induced losses recover with outdoor exposure while water vapor ingress during damp heat testing permanently degrades performance. Edge seal options that significantly decrease water vapor ingress have been demonstrated and are the subject of current development.

The foundations have been laid for process scale up. Future plans include reproduction of baseline process conditions in the large reactor, demonstration of large area process capability, development of a module design to pass accelerated environmental tests, and proceeding with commercialization tasks.

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Introduction

Alloys of copper indium diselenide are promising candidates for reducing the cost of photovoltaics well below the cost of crystalline silicon. Efficiencies have continually improved over the past 20 years, recently culminating in the demonstration of efficiencies over 17% for thin-film $CuInSe_2$ based solar cells fabricated by NREL [1]. Small area, fully integrated modules exceeding 13% in efficiency have been demonstrated by four groups [2, 3]. SSI has fabricated a 13.6% aperture area efficiency (NREL verified) encapsulated mini-module. Long-term outdoor stability has been demonstrated at NREL where 1x1-foot and 1x4-foot modules have undergone testing for as long as seven years [2, 3]. The availability of natural resources and the effect upon the environment both appear to be acceptable [2, 3]. Based on the measured efficiency of small-area mini-modules and projections of the processing used today to large areas and high volumes the calculated cost of CIS-based modules is about $1.00/Wp [2, 3].

However, a number of significant issues have been identified as challenges to the near-term commercialization of CIS. The SSI 10x10 baseline process needs to be reproduced on larger areas. The origins of the thermal transient behavior needs to be identified and eliminated if possible. A package design needs to be developed which can enable the completed modules to pass standard environmental qualification testing. From today's perspective, it appears that these issues can be resolved, and that CIS will play an important role in the near term future of photovoltaics.

The primary objective of this subcontract is to establish reliable high-throughput, high-yield thin film deposition processes that will utilize large-scale processing equipment, developed for existing non-PV industrial thin film production, in order to make CIS a viable option for the next generation of photovoltaics. The primary goals for the proposed project are to deliver a champion prototype 13% efficient large area module and to deliver sets of modules in 1-kW arrays composed of steadily increasing efficiency, reaching 1 kW of 12% efficient large-area modules by the end of the third year, thereby demonstrating performance as well as commercial viability. The focus of the deliverables on large sets of high-performance modules reflects SSI's commitment to demonstrating a reliable low-cost product.

From an industrial perspective, the full process sequence anticipated for use in the final product must be mastered and demonstrated rigorously. The SSI approach to developing a reliable, high-throughput, high-yield, large area thin film deposition processes is to first demonstrate process capability and the achievement of initial product requirements on small areas laminated mini-modules. Scaling to larger areas is under way based on this small area mini-module baseline foundation. Scale up efforts will include demonstration of reliability on large areas and definition and execution of cost minimization strategies. These efforts will be leveraged by participation in the Thin Film Photovoltaic Partnership Program team activities and interactions with NREL.

Milestones for this subcontract are described in Table 1. Results of accelerated testing of mini-modules delivered for M1 will be discussed in the "Module Reliability and Packaging" section of this report. Four mini-modules with an average aperture area efficiency of 13.9% have been delivered for M2.

Table 1. Milestones

Due Date	Champion Module (0.4 m^2)	Representative Samples for IQT	One Kilowatt Module Sets
Beginning of Contract		10 [M1]	n/a
End of Phase I	13% [M2]	10 [M3]	10% @ min. 0.09 m^2 [M4]
End of Phase II		10 [M5]	11% @ min. 0.09 m^2 [M6]
End of Phase III		10 [M7]	12% @ min. 0.38 m^2 [M8]

The main headings in the body of this report correspond with the main tasks for this subcontract: Safety, Health and Environment, Device Structure and Design, Process Development and Optimization, and Module Reliability and Packaging. An additional aspect of this subcontract is involvement in Thin Film Photovoltaic Partnership Program teaming activities. SSI has been involved with the "Absorber Team" and "Junction Team" and the principal investigator for this subcontract is the coordinator for the newly formed "Transient Effects Group."

Phase 1 Review

Safety, Health, and Environment

SSI emphasizes a safe working environment and works with the photovoltaic community through the Thin Film Photovoltaic Partnership Program ES&H team to promote safety throughout the industry. Safety is a key ingredient of business success. The basic principle of safety is that all personal injuries are avoidable. Effective Safety programs requires constant attention and concentration for success. To this end, SSI has established internal safety and monitoring programs including:

- Safety centers to review safety equipment and the status of facilities on a monthly basis
- Monthly department meetings to review the findings of the safety centers and promote safety through presentation of safety related news and topical training
- An equipment safety review committee to perform a safety audit on proposals for new or modified equipment
- An incident review committee review of accidents or near misses and recommend methods to avoid reoccurrence of such incidents
- Training programs on specific equipment and general safety related topics
- Regular testing of personnel for Se and Cd

SSI is a member of the Thin Film Photovoltaic Partnership Program ES&H team. SSI has participated in toxicology studies, waste determination studies, recycling evaluations and has shared information on the SSI safety program and general safety information with the photovoltaics community.

Device Structure and Design

The majority of device structure and design activities have been in support of demonstrating reproducibility and yield of the baseline mini-module process and scale up activities rather than in pursuit of improved efficiency. This emphasis is based on present status of CIS-based technology and the commercialization based objectives of this subcontract. The performance of champion thin film CIS cells and modules has climbed steadily over the past 20 years. World record efficiencies over 17% have been achieved at NREL, and cell efficiencies over 15% have been achieved by a number of groups. The use of small area cells is appropriate for initial research and process development. Characterization of cells provides detailed insights into the underlying mechanisms within the cells. However, cell efficiencies can be difficult to compare since they generally represent a small area (1 cm^2 or smaller) and are very sensitive to the details of the device design, such as the contact grid design, anti-reflection coatings and the thickness and sheet resistance of the window layer.

It is even more difficult to extrapolate from cell results to the performance to be expected for a module made from such absorbers. For example, for a small area cell, the total current is small, so the ZnO window layer can be made very thin, with high optical transmission, to boost the current generation while the associated high sheet resistance ($>15\ \Omega/\square$) does not harm the cell efficiency. However, in a typical module with larger cells and higher currents, such a high sheet resistance would result in unacceptably large resistive losses and lower efficiency.

From an industrial perspective, the full process sequence anticipated for use in the final product must be mastered and demonstrated rigorously. To this end, SSI has abandoned the use of individual cells in favor of the laminated "mini-module". A sketch of a baseline 10 cm by 10 cm, twelve cell circuit plate (unlaminated mini-module) is shown in Figure 1.

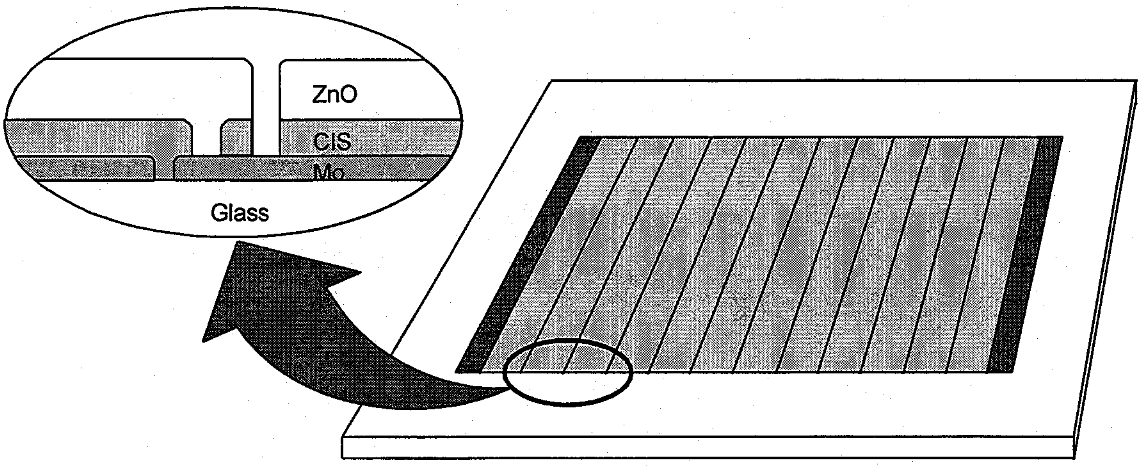


Figure 1. 10x10-cm mini-module circuit structure. Cells are interconnected monolithically, as shown in the inset.

Scale up during this phase of the subcontract is to 46 cell, 30 cm by 30 cm size circuit plates. The structure of the mini-module is essentially a subsection of larger modules incorporating all aspects of the larger module and demonstrating the full deposition, patterning, etc., process required for fabrication of larger modules. The module fabrication process including precursor deposition, absorber formation, patterning, etc. steps is represented schematically in Figure 2.

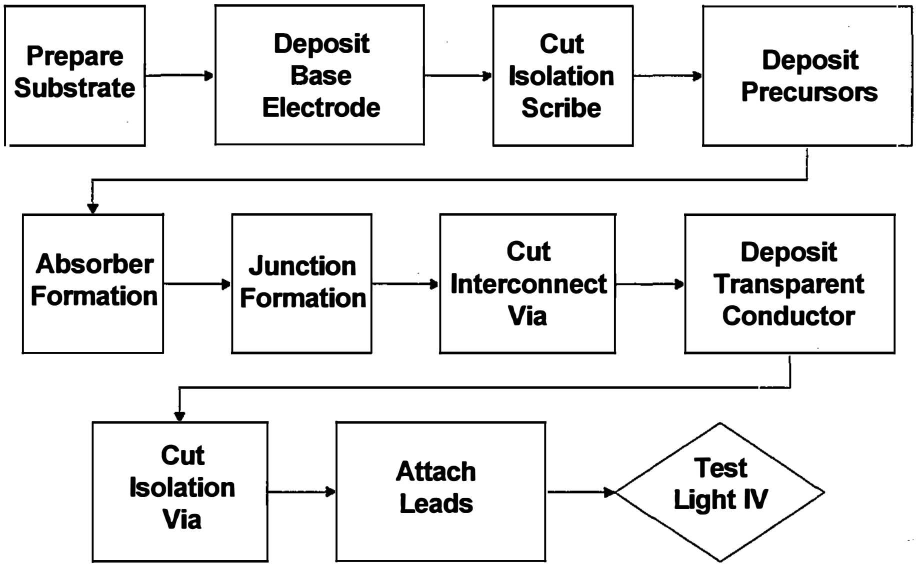


Figure 2. SSI CIS Circuit Processing Sequence

The reactor used to form the absorber from precursors for the 30 cm by 30 cm part size is the only process distinction between baseline and large circuit plates; baseline and large area modules share all other equipment and processes.

The baseline process has been repeatedly executed to demonstrate the potential of the technology through rigorous demonstration of reproducibility and yield of the process. As discussed further in a later section (Baseline Process Development), SSI has utilized statistical process control (SPC) techniques as the measure of and the tool for demonstrating process reproducibility. This baseline process has also proven invaluable in scale up efforts. The predictable baseline has allowed comparison of large area and baseline results allowing separation of effects from multiple processing steps and permitting confidence in the outcome of experiments related to scale up. These scale up experiments have included: demonstrated scaling of the CdS deposition process, demonstrated incremental improvement of substrate preparation techniques, process condition variations to demonstrate their impact on absorber properties, and mimicking proposed and/or observed large reactor conditions in the baseline reactor. For example, the culmination of surface preparation studies has resulted in the definition of an in-house surface preparation process equivalent to or slightly better than the previous baseline process. Data in the Figure 3 indicates that the new baseline process yields an approximately 3 point improvement in efficiency over the previous baseline process.

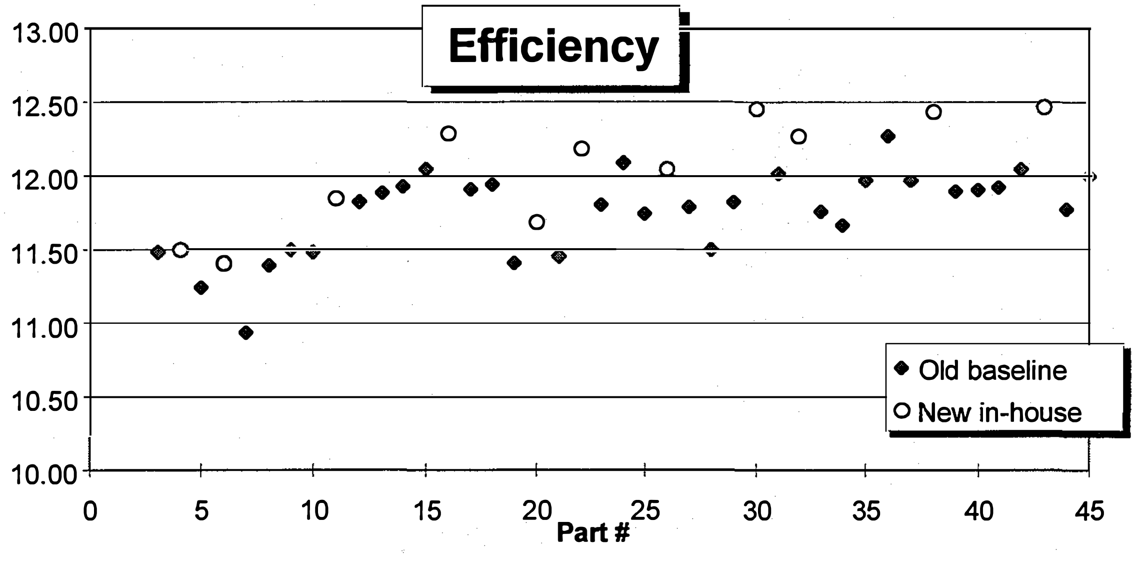


Figure 3. Comparison of in-house surface preparation process and previous baseline process.

In addition to efforts related to baseline reproducibility and scale up, improvements in absorber structures have been pursued with emphasis on improvements in module performance. Efficiency gains are feasible by adjusting the relative amounts and/or elemental profiles - grading - of the constituent elements in absorber layers composed of $Cu(In,Ga)(Se,S)_2$. Efficiency, voltage and adhesion improvements have been reported for the SSI graded absorber structure [4, 5, 6]. This structure is a graded $Cu(In,Ga)(Se,S)_2$ absorber with higher sulfur concentration at the front and back and higher Ga concentration at the back. As with the dependence of theoretical efficiency on bandgap for absorber layers with a uniform composition, counter variation of open circuit voltage and short circuit current are typical for changes in graded absorber structures to improve open circuit voltage. Higher voltages per cell for the same or somewhat lower photocurrents are advantages for integration of cells into modules. Higher voltages allow more latitude in the tradeoff between the number of cells in a module and the power losses in the thin conducting oxide (TCO). Losses due to plasma absorption in the front TCO at relatively long wavelengths may be less significant. Decreasing the current density decreases the resistive power loss in the TCO. Wider cells with fewer interconnects lead to higher active area by decreasing the total interconnect area. For the same module voltage, the temperature dependence of module voltage is lower for fewer higher voltage cells.

Improvements in absolute efficiency and the advantages for integration of cells into modules from the counter variation of open circuit voltage with short circuit current have been predicted for increases in the overall bandgap of the absorber or depth of the front sulfur doped high bandgap section of the SSI graded absorber structure [4]. These alterations are achievable by modifying the sulfur or gallium profiles in the graded $Cu(In,Ga)(Se,S)_2$ structure. During this phase of the subcontract, voltages somewhat above baseline values were achieved with minimal improvement in efficiency by changes in reaction conditions to increasing the total sulfur content in the absorber and alter the grading of the sulfur. Increases in the gallium content have also increased the open circuit voltage however, with no improvement in efficiency. Gallium was deposited on baseline precursors at the Institute of Energy Conversion (IEC) and Showa Shell Seikyu, K.K. Baseline conditions were used to react the precursors to form graded absorbers. Device parameters are plotted in Figure 4 as a function of the bandgap derived from spectral response measurements (discussed further in "Process Scale Up"). Measured bandgap increases with increasing gallium content. Improvements in open circuit voltage are observed with the accompanying counter variation in short circuit current; however, efficiency is not improved. Open circuit voltage correlates with gallium content near the front of the absorber as determined by SIMS analysis from NREL. Voltage nonuniformities were observed which are believed to be related to nonuniformity of gallium deposition. Defects in the absorber film were observed in SEM (IEC) and optical micrographs which are not observed for the baseline process. These observable nonuniformities and defects are assumed to be responsible for the lower fill factor and efficiency for the higher gallium concentrations.

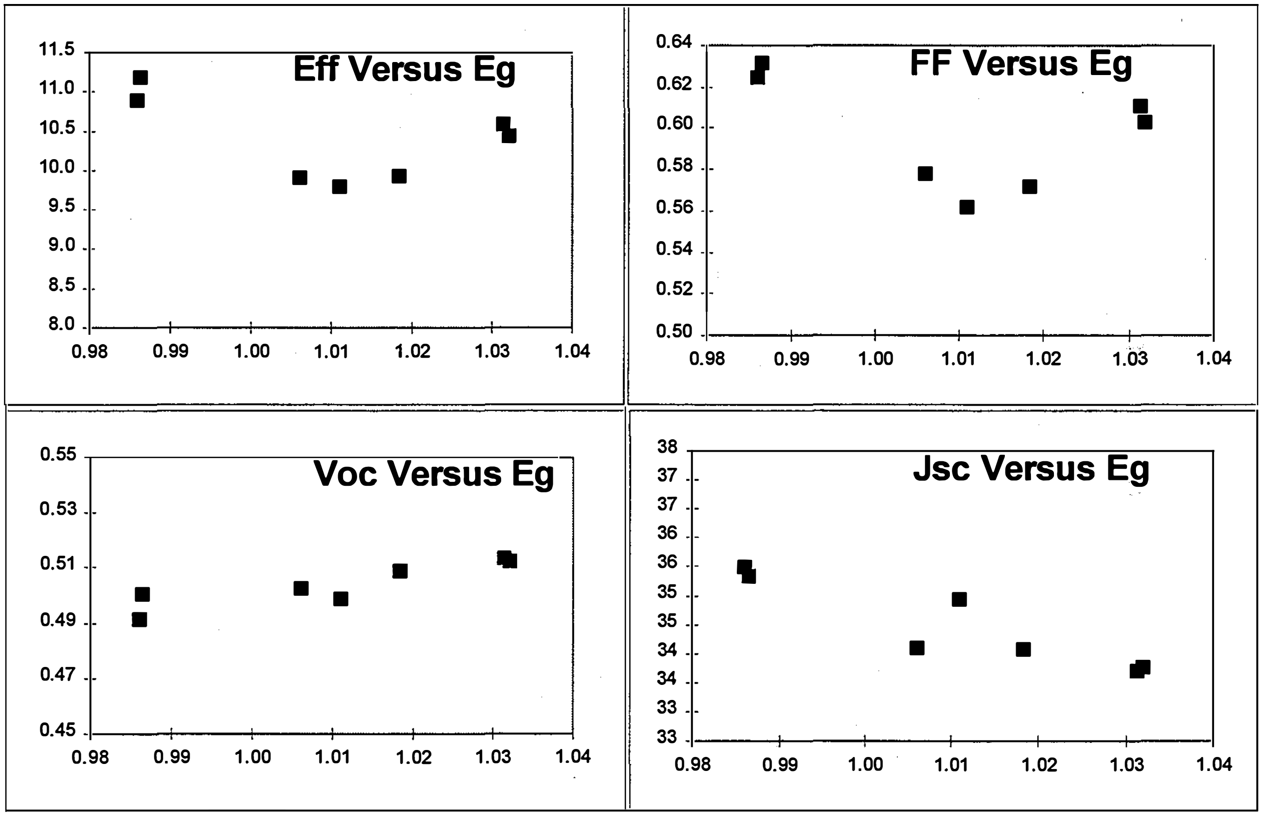


Figure 4. Device parameters as a function of bandgap for absorber structure with varied gallium content.

Baseline Process Development

SSI and a number of other groups have achieved mini-module efficiencies over 13% [2]. These high efficiency champions provide an "existence proof" for a high efficiency thin-film process. While these circuits demonstrate the potential of the technology, a rigorous measure of the reproducibility and yield of the process must also be made. Statistical process control (SPC) is a tool which can provide this rigorous measure of process reproducibility; its application to CIS module development at SSI has been described previously [7]. SPC provides a statistical foundation for judging the reproducibility of a process through charting the processing results and the definition of upper and lower control limits (UCL and LCL in figures). Results which fall within these control limits are essentially equivalent, differing only because of the random or "common cause" variation inherent in any stable, controlled process. Results which fall outside these limits can only be explained by "special causes" which reveal an error in executing the baseline process. This data presentation format emphasizes and focuses attention on eliminating the special causes of process instability, and then on continually reducing the sources of common-cause variation inherent in the stabilized process.

The baseline process has been repeatedly executed to demonstrate the potential of the technology and in support of scale up efforts. A reproducible low variation baseline is demonstrated for over two thousand mini-modules as seen in Figure 5. Efficiency versus time is plotted with separations between groups of data

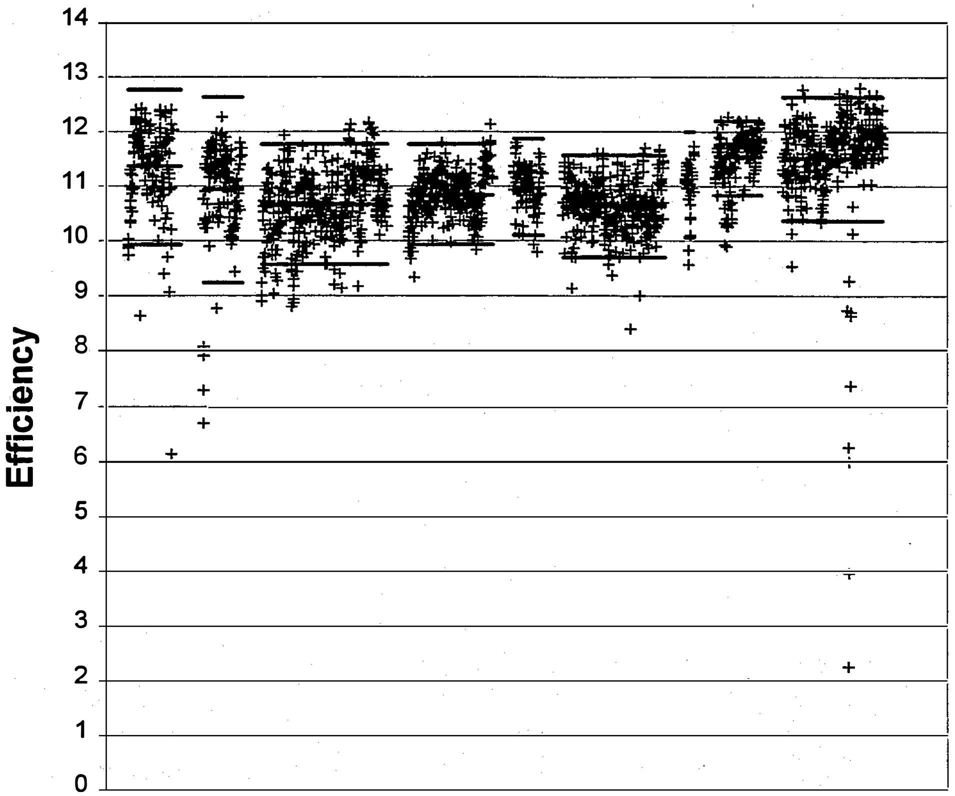


Figure 5. Control chart showing efficiency of more than two thousand mini-modules.

indicating deliberate changes in the baseline process. Experimental data is not included and identified special causes have been removed. Results due to special causes which have not been associated with a particular process error are not eliminated from the data set. Average circuit plate efficiency are typically 11.5% demonstrating a reproducible low variation baseline process as a foundation for scale up efforts.

Laminated mini-module efficiencies after outdoor exposure typical of in-service conditions average 12.4% (Figure 6).

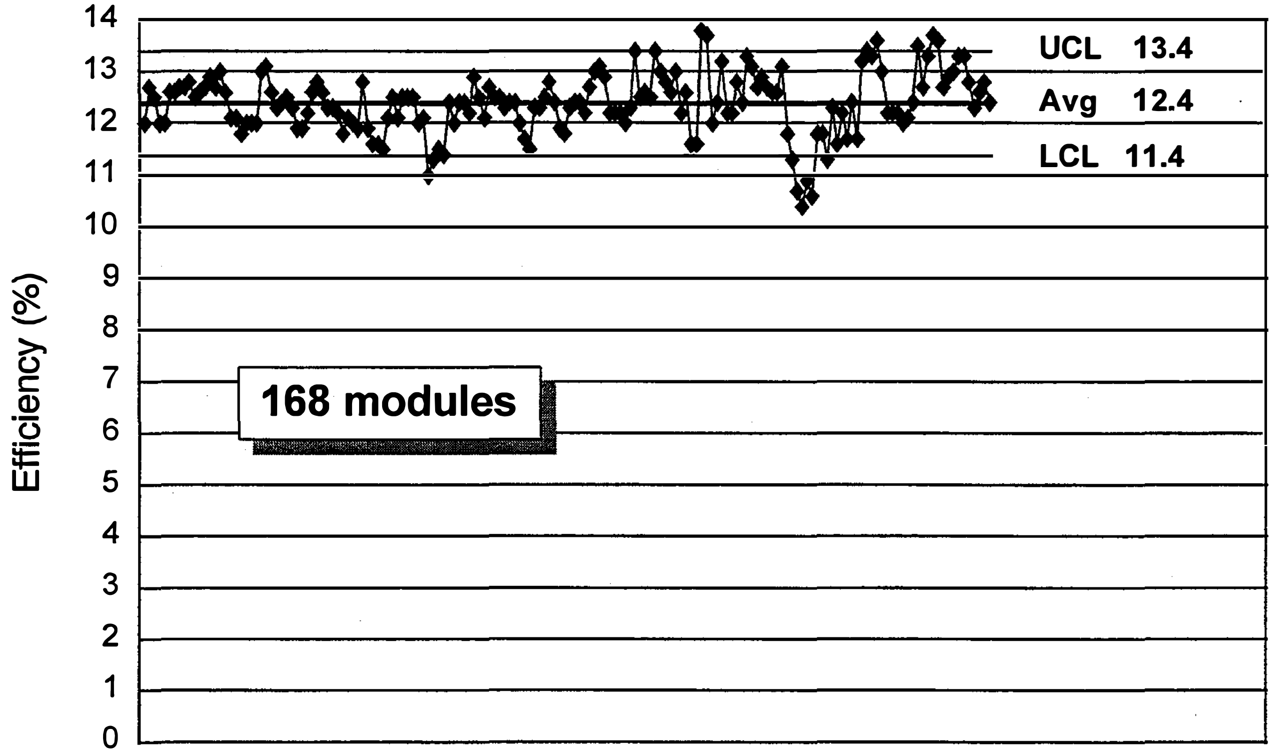
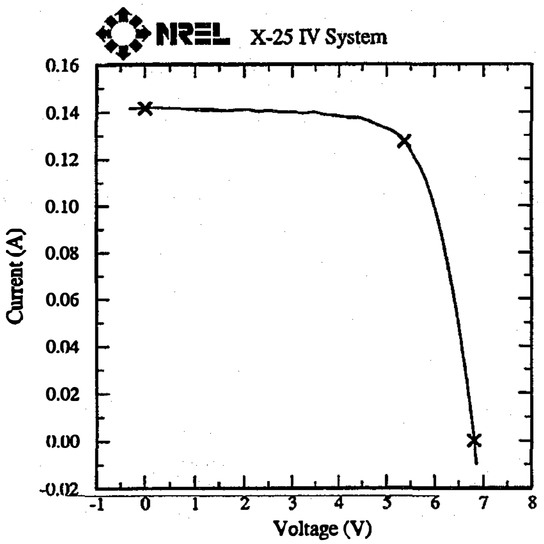


Figure 6. Control chart showing laminated mini-modules averaging 12.4% efficiency after a minimum of two weeks of outdoor exposure.

The current versus voltage curve and device parameters measured by NREL for a 13.6% aperture area efficient mini-module are displayed in Figure 7.



	Module	per Cell	
Eff	13.6		%
Voc	6.81	0.567	V
Isc	0.142		mA
Jsc		33.8	mA/cm^2
FF	71.0		%
Area	50.3	4.19	cm^2

Figure 7. 13.6% aperture area efficiency mini-module as measured by NREL.

Module and average cell parameters are listed in Table 2 for four laminated mini-modules with efficiencies averaging 13.9% which were delivered to NREL as M2 deliverables.

Table 2. Laminated mini-module averaging 13.9% efficient as M2 deliverables.

ID #	Eff	Module Voc (V)	Cell Voc (V)	Module Isc (mA)	Cell Jsc (ma/cm^2)	FF	Area cm^2
216-62	13.8	6.77	564	0.148	34.9	0.701	50.9
216-38	13.8	6.79	566	0.143	34.3	0.708	50.0
214-32	13.8	6.89	574	0.144	33.9	0.708	51.1
214-30	14.1	6.91	576	0.144	34.6	0.711	49.9

Process Scale-up

Process scale-up has proceeded from the foundation of the reproducible low variation baseline process. Transfer of the mini-module process to a 30 cm by 30 cm part size has included the tasks of calibration and transfer of baseline process to a larger reactor, evaluation of the large reactor process, and evaluation of uniformity. Characterization of the large area process and process development to isolate the sources of performance differences between the baseline process and the large area process have been greatly aided by comparison with a stable and therefore predictable baseline process. For each step in the process, the impact of the larger part size has been tested in the baseline. For example, by cutting the 30x30 parts into nine 10x10 parts, the uniformity of the performance of the larger part was measured using the baseline process. Such experiments indicate that the larger-area parts should be able to achieve the same level of performance as the smaller parts.

However, the performance of large-area circuits has not yet reached the same level as the performance of the 10x10 mini-module baseline. The difference between the baseline and large area processes has been isolated to the formation of the absorber in the larger reactor. The following will discuss the isolation of the difference between the reactors and the status of scale up efforts.

Baseline and 30 cm X 30 cm efficiency results are plotted in Figure 8. The performance of the larger parts is inferior to baseline performance; baseline circuit plate efficiencies are about 11.5% whereas 30 cm X 30 cm performance is about at 8%.

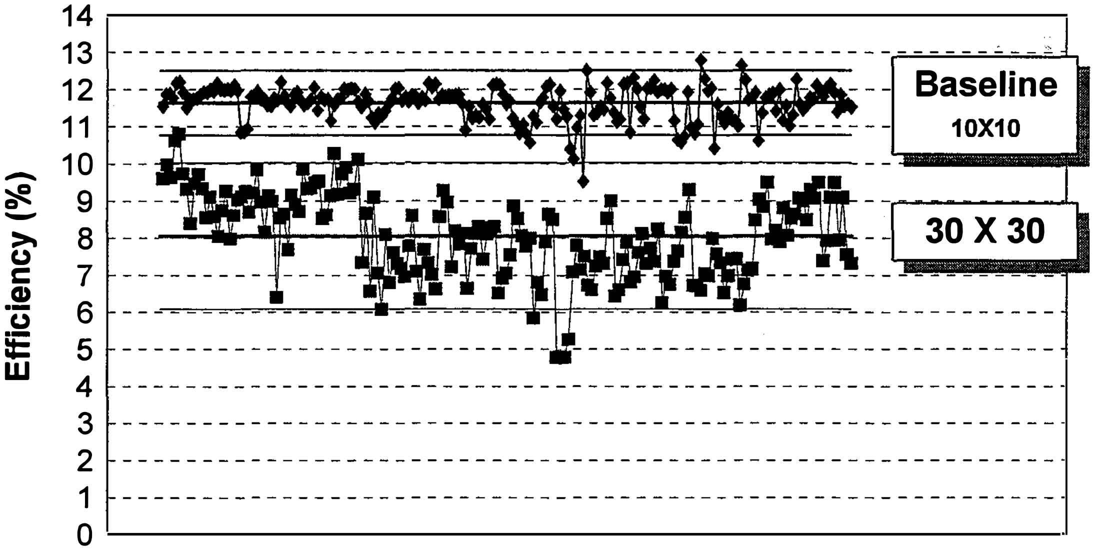


Figure 8. Comparison of the 10X10 baseline and 30X30 circuits.

Formation of the absorber on 10 cm X 10 cm circuit plates in the large reactor yields the same performance as for 30 cm X 30 cm circuits plates fabricated in the large reactor (Figure 9). This indicates that the part size itself is not the cause of the performance differences.

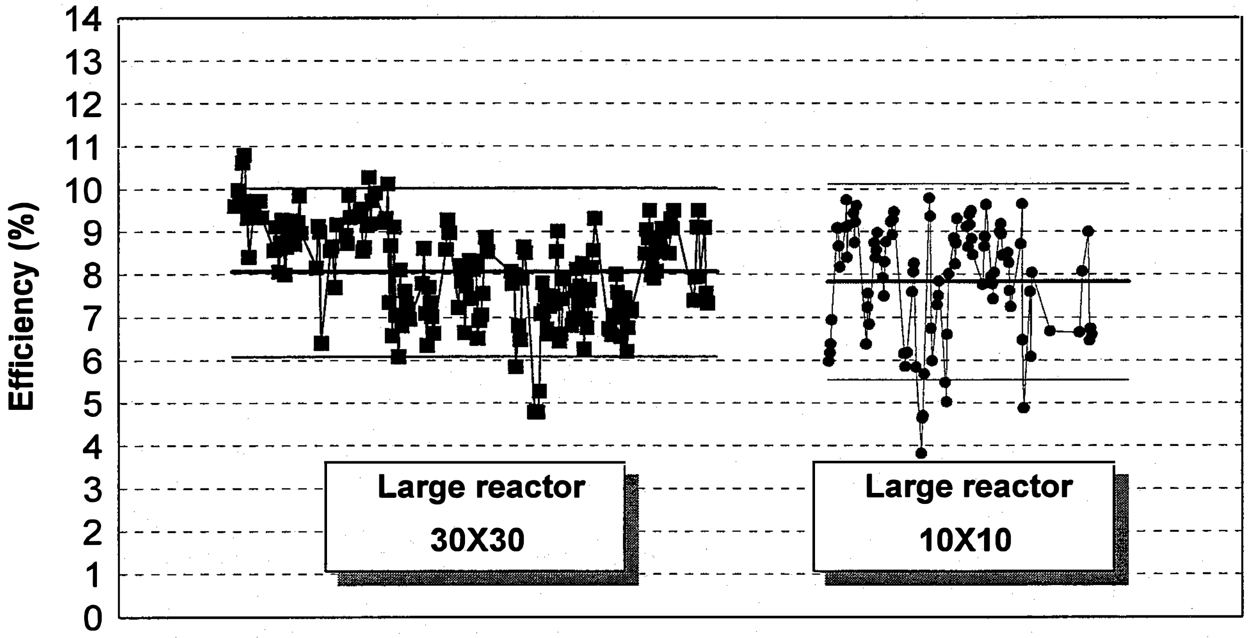


Figure 9. Comparison of 10X10 and 30X30 circuits from the large reactor.

The absorbers obtained from the baseline process and the large reactor have been compared using bandgap measurements and SIMS. Bandgap determined from spectral response measurements indicates a difference in the absorber structures for absorbers from the baseline and large area reactors. Figure 10 is a plot of the square of quantum efficiency versus photon energy for multiple devices from both the baseline and large area reactors. The intercept on the energy axis is taken as a measure of optical bandgap which is actually a convolution of the affects on absorption and collection through the varying bandgap structure of these absorbers [4, 6]. Differences in this measure of bandgap, ~0.99 eV for baseline and ~1.02 eV for absorbers from the large reactor, imply a difference in the bandgap structure of the absorbers.

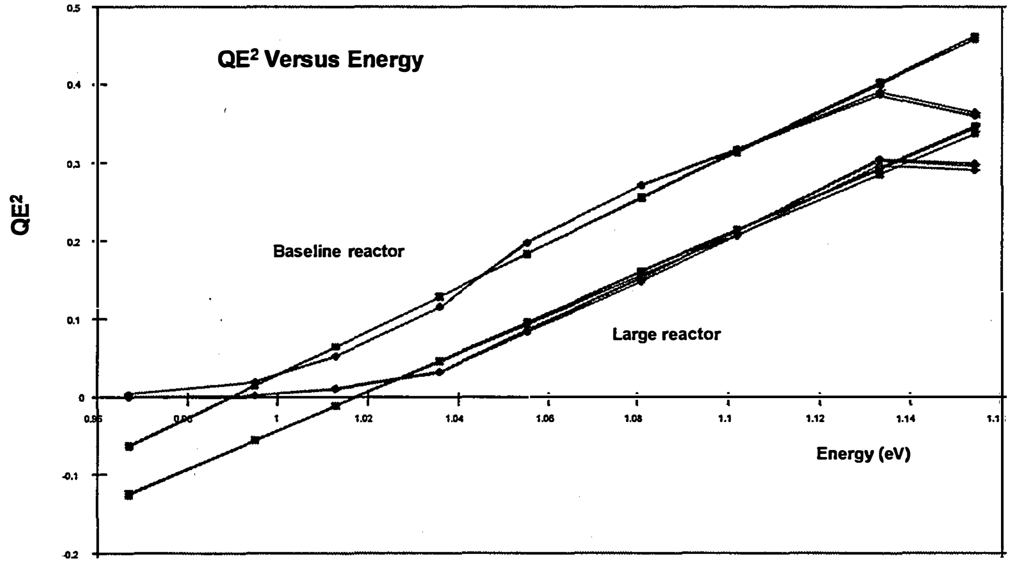


Figure 10. Comparison of bandgaps for absorbers from different reactors.

SIMS analysis of baseline absorbers and absorbers from the large reactor identify the differences in absorber structure. The profile of sulfur concentration is the primary difference between absorbers from the two reactors (Figure 11). The concentration of sulfur is highest at the front of the absorber and decreases toward the center of the absorber for both reactors. The sulfur profile for baseline absorbers is "sharper"; the sulfur profiles have a higher gradient from the front to the center of the absorber. The concentration of sulfur at the front is higher and the concentration near the middle of the absorber is lower for baseline absorbers.

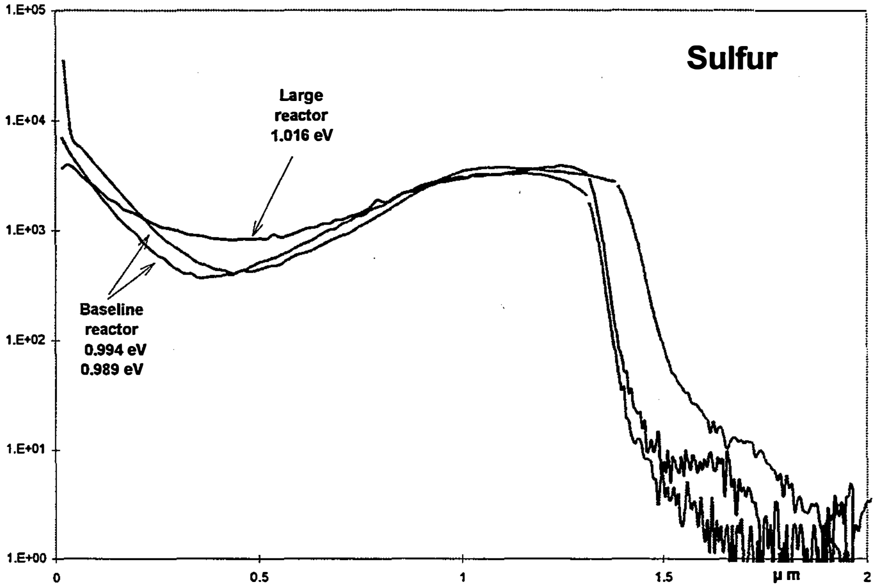


Figure 11. Comparison of SIMS sulfur profiles for absorbers from different reactors.

Comparison of circuit plates from the baseline and large reactor has identified additional differences between devices from the two reactors. Bandgap and SIMS results are summarized in Table 3 along with contact resistance measurements, relative adhesion above the interconnect scribe in the molybdenum, the visual appearance of the molybdenum after scraping off the absorber, and ICP analysis of the relative amount of sulfur and selenium in the molybdenum.

Table 3. Differences between devices processed in different reactors.

		Reactor used for absorber formation	
		Baseline	Large
Efficiency	(%)	11.6	7.8
Contact Resistance	(m Ω cm^2)	2.9	9.2
Bandgap	(eV)	0.99	1.02
SIMS sulfur profile		Sharp	Flat
Adhesion over P1		Good	Unreliable
Mo appearance		Shiny	Discolored
Se/Mo in Mo	(%)	4.0	7.5
S /Mo in Mo	(%)	1.5	3.5

These observed differences between circuit plates from the two reactors have been related to the design of the large reactor through variations in process condition to demonstrate their impact on absorber properties and mimicking large reactor conditions in the baseline reactor. Hardware changes in the large reactor to mitigate these differences are underway.

Module Reliability and Packaging

Long-term Outdoor Stability

Long-term outdoor stability has been demonstrated at NREL where 1x1-foot and 1x4-foot modules have undergone testing for as long as seven years. These measurements, shown in Figure 12, were made by bringing the modules indoors, performing the measurements under standard test conditions, then returning the modules to their outdoor test location.

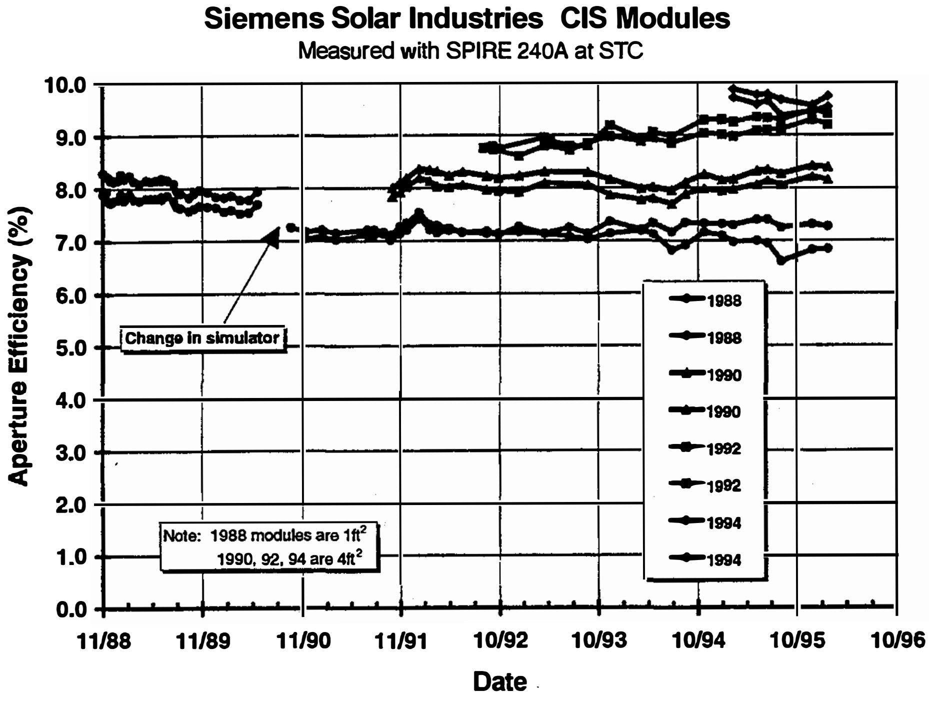


Figure 12. Results of outdoor exposure testing at NREL showing excellent long-term stability.

Additional outdoor testing is underway, as previously described [8]. In these tests, NREL is monitoring an SSI provided 1-kW array of CIS modules with measurements in the field; the modules are not brought indoors for IV measurements. They are kept under load, and measured every half-hour. The data for both the module and the array show good stability over time, with minimal or no seasonal variation in performance corrected to standard conditions (Figure 13). Therefore, thermally induced changes in efficiency are not observed in field measurements..

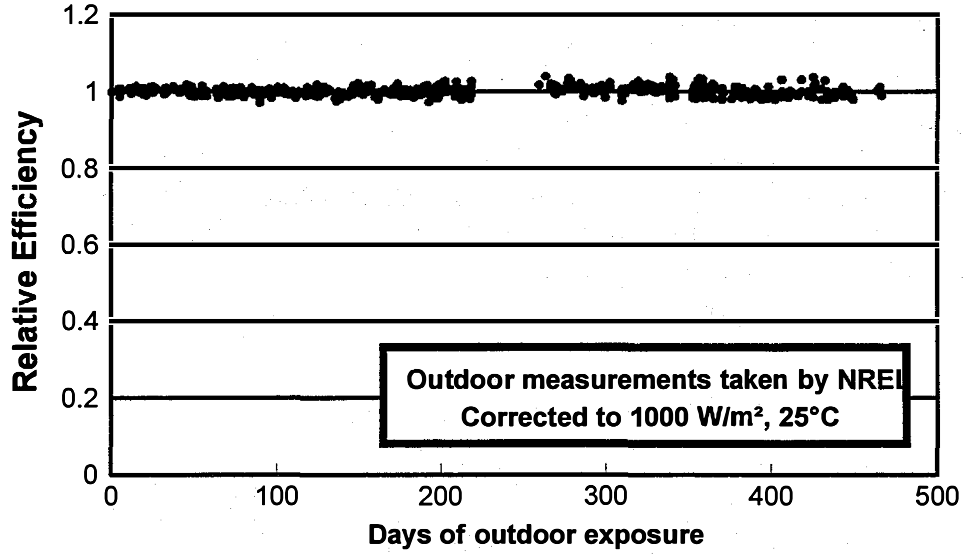


Figure 13. Field measurements of a CIS module at NREL. No thermally induced instability is observed.

Accelerated Environmental Testing

SSI fabricated CIS-based devices have failed standard environmental stress tests. Accelerated environmental testing highlights an issue regarding the sensitivity of these devices to heat and light. The efficiency of some cells and modules is seen to increase with light exposure [9]. Exposure of the modules to heat can cause the efficiency to fall, which then fully recovers with light soaking [4]. Because the standard environmental qualification tests involve exposure to 85°C [10], many modules show a loss of performance through the tests [11]. Post-test sun-soaking of the modules results in full recovery from such thermal exposures. Changes in the performance of CIS modules induced by light-soaking also represent a challenge to the proper testing and rating of these modules because the sun-soaking time required to stabilize the efficiency can be very long, from days to many weeks. Since not all modules exhibit this behavior, it should be possible to correlate the behavior with the circuit processing and reduce or eliminate it altogether.

Additional difficulties have been observed for the 1000-hour damp heat test [10] where moisture penetration into the package can cause irreversible loss of performance. Improved package designs are being pursued along with efforts to identify the origin of moisture sensitivity in the circuits.

As part of the efforts to first characterize and separate the influence of accelerated environmental testing on devices structures, interconnect test structures [4] were exposed to damp heat (85 °C 85% relative humidity). Interconnect test structures are essentially module plates with double back-to-back interconnects configured to allow independent measurement of ZnO to Mo contact resistance and ZnO sheet resistance. Figure 14 illustrates the effects of damp heat on contact resistance and sheet resistance for four laminated 10 cm X 10 cm interconnect test structures. Both parameters increase and the increase correlates with the observation of water penetration into the laminate as indicated by fogging of the EVA.

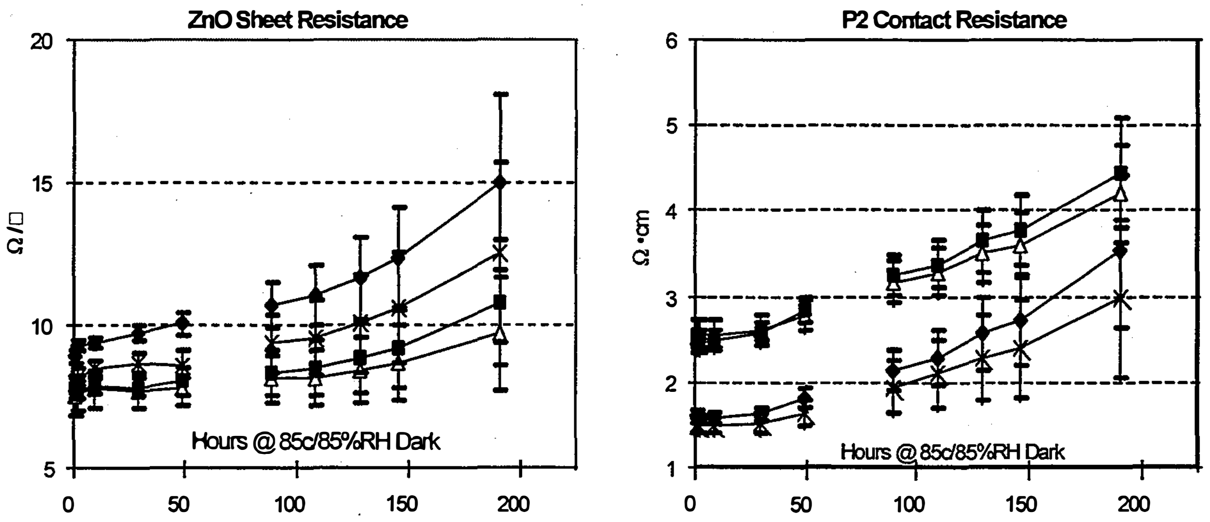


Figure 14. Effects of damp heat testing on contact resistance and sheet resistance.

Additional characterization of the effects of water ingress into laminates, combined with exploration of edge seal options to prevent this water vapor ingress, was performed using laminated 30 cm X 30 cm ZnO coated plates. These laminates mimic lamination of a large area module but with leads to measure ZnO sheet resistance and, since the package is clear, the ability to observe differences in water vapor ingress for various edge seal options. Relative sheet resistance versus time of exposure to damp heat conditions is plotted in Figure 15. Edge seal options that significantly decrease water vapor ingress have been

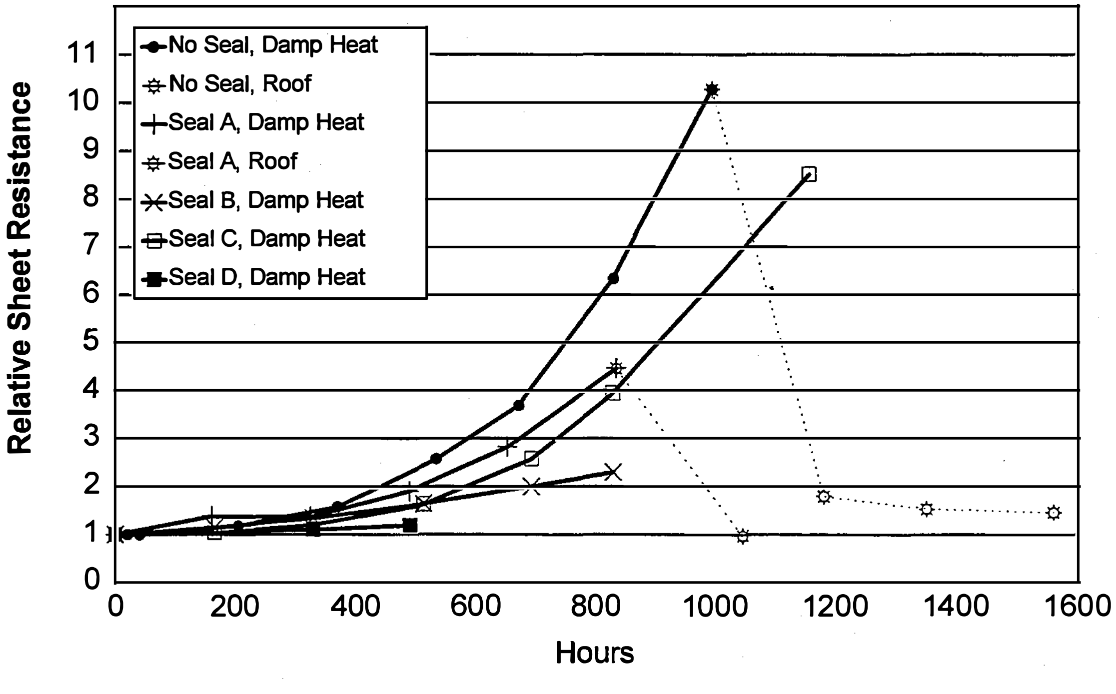


Figure 15. Increases in ZnO sheet resistance with exposure to water vapor and decreases in ZnO sheet resistance with outdoor exposure.

demonstrated. Observations indicate that improvements in the adhesion between the edge seals and the laminates will further improve resistance to water vapor ingress.

Two of these experimental laminates were exposed to outdoor light and the ZnO sheet resistance decreased to nominally the values prior to exposure to damp heat. This improvement in ZnO sheet resistance was not accompanied by a significant decrease in fogging of the EVA. These results indicate that the effect of water vapor on ZnO sheet resistance is reversible.

Laminated mini-modules (Ml deliverables), were subjected to standard thermal cycling (TC), humidity-freeze cycling (HF), and damp heat exposure at NREL. The sequence of testing and measurements was arranged to gain information on the effects of light exposure before, after and during accelerated environmental testing. All modules were placed outdoors for at least two weeks prior to accelerated environmental testing and half of the modules went through the accelerated environmental exposure with light exposure of about one sun. Results for thermal cycling are displayed in Figure 16 (testing and measurements by Ben Kropowski, NREL). Efficiencies improve with two weeks of outdoor exposure relative to measurements after shipping. Thermal cycling degraded performance by between 10 and 30 points. Less degradation is observed for the group with light exposure during thermal cycling. Performance after subsequent outdoor exposure recovers and is similar for both groups; with and without

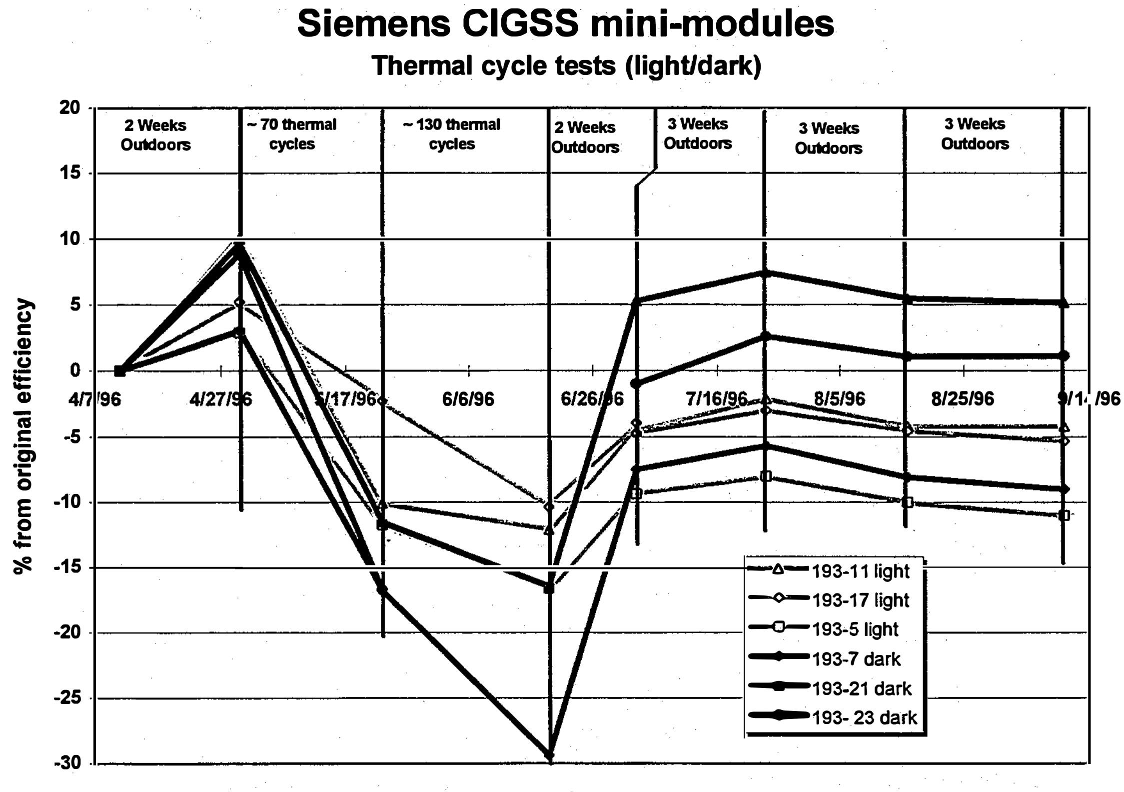


Figure 16. Results of accelerated environmental testing; temporary losses with thermal cycling and recovery with outdoor exposure (NREL testing and measurement).

light exposure during thermal cycling. Two of the three mini-modules in each group recover to within five points of initial performance.

Results of humidity-freeze cycling are similar to the results for thermal cycling; performance degrades by between 10 and 30 points during accelerated testing, less degradation during cycling is observed for the group with light exposure, and two of the three mini-modules in each group recover to within five points of initial performance. Damp heat testing was conducted in the dark only and with only two mini-modules. Losses were about seventy points with less recovery than for either thermal cycling or humidity-freeze cycling. These mini-modules exhibited a fogging around the outside edge that did not disappear with outdoor exposure.

In summary:

- Long term outdoor stability has been demonstrated
- Thermally induced losses recover with outdoor exposure
- Water vapor ingress during damp heat testing permanently degrades performance
- Light exposure during accelerated environmental testing reduces losses although subsequent outdoor exposure induces recovery independent of light exposure during the accelerated environmental testing
- Degradation of ZnO to Mo contact resistance and ZnO sheet resistance due to water vapor ingress has been demonstrated
- Light induced recovery of ZnO sheet resistance has been demonstrated
- Progress has been made on identifying an edge seal that will limit water vapor ingress.
- Edge seal development is expected to protect laminates from water vapor ingress during damp heat testing and allow modules to pass all accelerated environmental tests after subsequent outdoor exposure.

Conclusions

Device design and structure activities have demonstrated improvements in open circuit voltage with changes in sulfur and Ga profiles. Efficiency gains are feasible by adjusting the relative amounts and/or elemental profiles - grading - of the constituent elements in absorber layers composed of Cu(In,Ga)(Se,S)2.

The baseline process has been repeatedly executed to demonstrate the potential of the technology and to support scale up efforts. A reproducible low variation baseline is demonstrated for over two thousand mini-modules. Laminated mini-module efficiencies after outdoor exposure typical of in-service conditions average 12.4% and a 13.6% aperture area efficient mini-module has been verified by NREL.

Process scale-up has proceeded from the foundation of the reproducible low variation baseline process. For each step in the process, the impact of the larger part size has been tested in the baseline. Such experiments indicate that the larger-area parts should be able to achieve the same level of performance as the smaller parts. However, the performance of large-area circuits has not yet reached the same level as the performance of the 10x10 mini-module baseline. The difference between the two processes has been isolated to the formation of the absorber and is the subject of current development.

Long-term outdoor stability has been demonstrated at NREL. However, SSI fabricated CIS-based devices have failed standard environmental stress tests. Thermally induced losses recover with outdoor exposure while water vapor ingress during damp heat testing permanently degrades performance. As part of the efforts to first characterize and separate the influence of accelerated environmental testing on devices structures, humidity induced degradation of ZnO sheet resistance and the contact resistance between ZnO and Mo have been identified. The effect on ZnO sheet resistance was found to be reversible with outdoor exposure. Edge seal options that significantly decrease water vapor ingress have been demonstrated. Observations indicate that improvements in the adhesion between the edge seals and the laminates will further improve resistance to water vapor ingress.

The foundations have been laid for process scale up. Future plans include reproduction of baseline process conditions in the large reactor, demonstration of large area process capability, development of a module design to pass accelerated environmental tests, and proceeding with commercialization tasks.

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D.E. Tarrant and R.R. Gay

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Siemens Solar Industries
4150 Adohr Lane
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13. ABSTRACT *(Maximum 200 words)*

Alloys of copper indium diselenide are promising candidates for reducing the cost of photovoltaics well below the cost of crystalline silicon. The availability of natural resources and the effect on the environment both appear to be acceptable, and long-term outdoor stability has been demonstrated at NREL. The Siemens Solar Industries (SSI) approach to developing a reliable, high-throughput, high-yield, large-area thin-film deposition process is to first demonstrate process capability on small-area laminated minimodules. A reproducible low-variation baseline has been demonstrated for over 2000 minimodules. Laminated minimodule efficiencies after outdoor exposure typical of in-service conditions average 12.4%, and a 13.6% aperture-area efficient minimodule has been verified by NREL. Process scale-up is proceeding from the foundation of this reproducible low-variation baseline process. However, the performance of large-area circuits processed in the SSI large-area reactor has not yet reached the same level as the performance of the baseline process, and SSI-fabricated CIS-based devices have failed standard environmental stress tests. Future plans include reproduction of baseline process conditions in the large reactor, demonstration of large-area process capability, development of a module design to pass accelerated environmental tests, and proceeding with commercialization tasks.

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