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CIS-Based Thin Film PV Technology

Phase 2 Technical Report, October 1996 - October 1997

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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 this 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% efficiency on 3883 cm^2 (verified by NREL). Subcontract accomplishments 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 toward these objectives and goals through approximately the second year of this three year contract; October 1996 through October 1997.

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The Siemens Solar Industries CIS Team:

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Summary

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 are to demonstrate performance as well as commercial viability via the milestones of a champion prototype 13% efficient large area module and sets of modules in 1-kW arrays of steadily increasing efficiency, culminating in delivery of a 1 kW array of 12% efficient large-area modules by the end of the subcontract.

During Phase 1 of this contract, SSI repeatedly executed a baseline 10x10-cm mini-module process rigorously demonstrating process reproducibility and yield for over two thousand CIS-based mini-modules. Large-area circuit performance did not achieved the same level as the baseline process and this performance difference was related to design differences between baseline and large area absorber formation reactors. Studies of the differences between reactors continued during Phase 2 resulting in adjustment of most but not all of the process conditions to more closely mimic process conditions in the baseline reactor and thereby mitigate most but not all of the process differences. Remaining differences were isolated to differences in the materials of construction and the physical design of the large reactor. Therefore, SSI designed and built a new large area reactor which is a more direct scale-up of the baseline reactor. This reactor became operational during Phase 2 and success with this reactor was demonstrated by initial circuit performance for 28x30-cm circuits averaging 10.6% which compares very favorably to the 10x10-cm baseline

Long-term outdoor stability with no seasonal variation in performance has been demonstrated at NREL where 1x1 ft and 1x4 ft modules have undergone testing for as long as eight years. Package development continued during Phase 2 with the definition of a package for introductory products and in support of the DOE long-term goal of systems that last at least 30 years. Although long-term outdoor stability has been demonstrated at NREL and thermally induced losses from accelerated testing stress tests recover with outdoor exposure (one of several observed transient effects), water vapor ingress resulting from accelerated testing permanently degrades performance for glass/EVA/circuit laminate structures. Transient effects are not observed for in-service conditions but confound accelerated testing; understanding of these effects has been advanced during this subcontract phase.

SSI has introduced two new CIS-based products during this subcontract phase. The product designations are ST5 and ST10 which are 21x33 cm, 5 watt and 39x33 cm, 10 watt modules designed for use in 12 V systems. SSI delivered product samples to NREL as contract deliverables and NREL reports 9.6% aperture area efficiency (11.2 % circuit plate aperture area) which is the highest efficiency of any commercial non-crystalline module.

SSI delivered a set of modules to NREL for a 1 kW array replacing an existing 1 kW array based on an older absorber formation technology. NREL reports stable performance and an unprecedented average efficiency of over nine percent. A champion module was confirmed by NREL to produce 40.6 watts for a new confirmed world-record efficiency of 11.1 percent on 3665 cm^2. This demonstrated efficiency exceeds the 1995 DOE efficiency goal for CIS prototype modules and exceeds the year 2000 DOE efficiency goals for amorphous silicon and cadmium telluride technologies.

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Introduction

Multinary $Cu(In,Ga)(Se,S)_2$ absorbers (CIS-based absorbers) are promising candidates for reducing the cost of photovoltaics well below the cost of crystalline silicon. CIS champion solar cell efficiencies have reached over 17% efficiency for devices fabricated at NREL (1). Small area, fully integrated modules exceeding 13% in efficiency have been demonstrated (2). Long-term outdoor stability has been demonstrated at NREL by 1x1 ft and 1x4 ft SSI modules which have been in field testing for as long as eight years (3). Cost projections indicate about $1.00/Wp based on projection of present processing to large area and high volumes (4).

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.

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 are to demonstrate performance as well as commercial viability via the milestones of a champion prototype 13% efficient large area module and sets of modules in 1-kW arrays of steadily increasing efficiency, culminating in delivery of a 1 kW array of 12% efficient large-area modules by the end of the subcontract. This Phase 2 Technical Report presents progress toward these objectives and goals through approximately the second year of this three year contract, October 1996 through October 1997.

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 was demonstrated during the first phase of this subcontract for over two thousand mini-modules.

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, during Phase 1 of this subcontract the performance of large-area circuits processed in the SSI large area reactor (Phase 1 large area reactor) had not yet reached the same level as the performance of the baseline process. The difference between the two processes was isolated to the formation of the absorber. Investigations indicated differences between the Phase 1 large area reactor and the baseline reactor including:

- Temperature uniformity
- Reaction kinetics
- Substrate orientation
- Reactor substrate capacity
- Reaction process time

Studies of the differences between reactors continued during Phase 2 resulting in adjustment of most but not all of the process conditions to more closely mimic process conditions in the baseline reactor and thereby mitigate most but not all of the process differences. Remaining differences were isolated to differences in the materials of construction and the physical design of the large reactor. Therefore, SSI designed and built a new large area reactor (Phase 2 large area reactor) which is a more direct scale-up of the baseline reactor. This reactor became operational during Phase 2 and success with this reactor was demonstrated by initial circuit performance for 28x30-cm circuits averaging 10.6% which compares very favorably to the 10x10-cm baseline.

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. Current efforts and 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.

Milestones for this subcontract are described in Table 1.

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 "Transient Effects Group."

Phase 2 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 chartered to review the safety of SSI 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 chartered to review safety considerations regarding the installation of new equipment, definition of experiments, or modification of existing equipment
- A General Emergency Response Team which trains for emergencies throughout SSI
- An Incident Review Committee to review actual or potential incidents and recommend improvements for safe operations
- Training programs on specific equipment and general safety related topics
- Monitoring of personnel for exposure to potentially hazardous materials

SSI is a member of the Thin Film Photovoltaic Partnership Program ES&H team and has participated in the following activities in conjunction with the TFPPP ES&H Team:

- Periodic team meetings
- Toxicology studies and environmental impact studies
- Exploration of technical approaches for removing and recycling module components

As a prerequisite to implementing a new large area reactor (discussed below), SSI collaborated with the TFPPP ES&H group headed by Paul Moskowitz and supported by his associates at Brookhaven National Laboratories to avoid hazards resulting from system failure. These efforts included estimation of the potential fire or explosion hazards and definition of methods to avoid fire or explosion. The system was implemented with a nitrogen reservoir to insure safety by limiting oxygen availability in the event of system failure.

Device Structure and Design

From an industrial perspective, the full process sequence anticipated for use in the final product must be mastered and rigorously demonstrated. The use of small area cells is appropriate for initial research; however, processes and the process sequence are different for cell and module fabrication and it is also difficult to extrapolate from cell results to module performance. Therefore, SSI has abandoned the use of individual cells in favor of the "mini-module." A sketch of a baseline 10 cm by 10 cm, twelve cell circuit plate (unlaminated mini-module) is shown in Figure 1. The structure of the mini-module is essentially a subsection of larger modules therefore fabrication of mini-modules demonstrates the full process and the process sequence required for fabrication of larger modules. The module fabrication process including precursor deposition, absorber formation, and patterning steps is represented schematically in Figure 2.

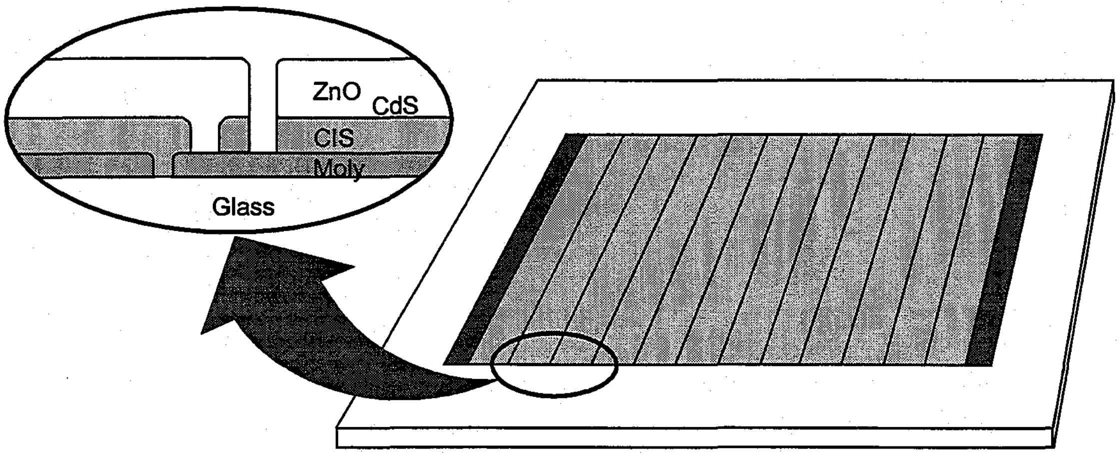


Figure 1. 10x10-cm mini-module circuit structure. Cells are interconnected monolithically, as shown in the inset.

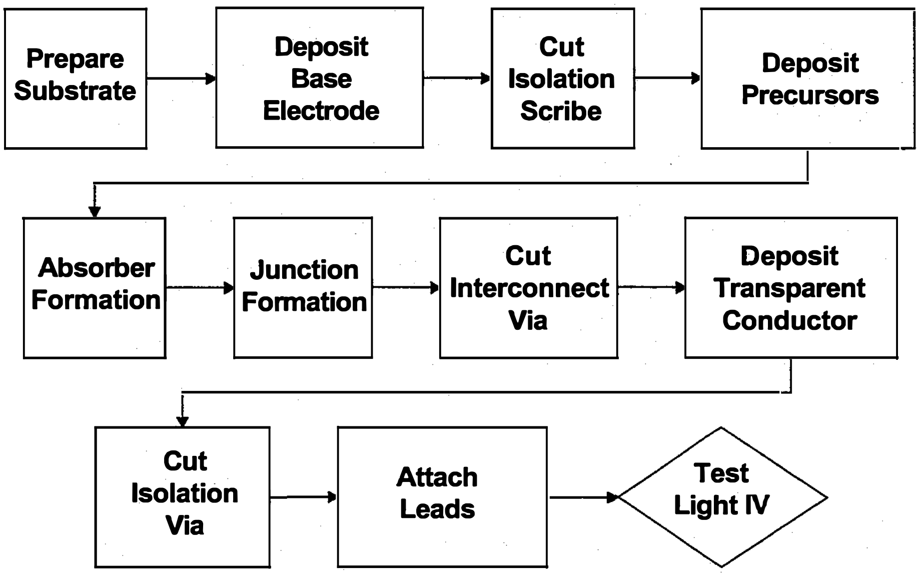


Figure 2. SSI CIS Circuit Processing Sequence.

During Phase 1 of this subcontract the majority of device structure and design activities supported demonstration of reproducibility and yield for the baseline mini-module process. The baseline process was repeatedly executed to rigorous demonstrate reproducibility and yield and device structure and design activities included varying process conditions to demonstrate their impact on reproducibility and yield. In addition, activities such as mimicking observed Phase 1 large reactor conditions in the baseline reactor supported scale up efforts. These efforts have continued through this phase of the subcontract with emphasis on understanding the transfer of the baseline process to large area reactors. Some examples of these efforts are discussed in the remainder of this section.

Device performance for an alternative method of sulfur introduction was explored. Open circuit voltage increases were achieved at the expense of lower short circuit current with minimal effect on efficiency except for the highest sulfur contents which exhibited lower fill factors. The following figure depicts the changes in open circuit voltage and short circuit current as a function of the ratio of sulfur to selenium in the absorber as determined by ICP analysis.

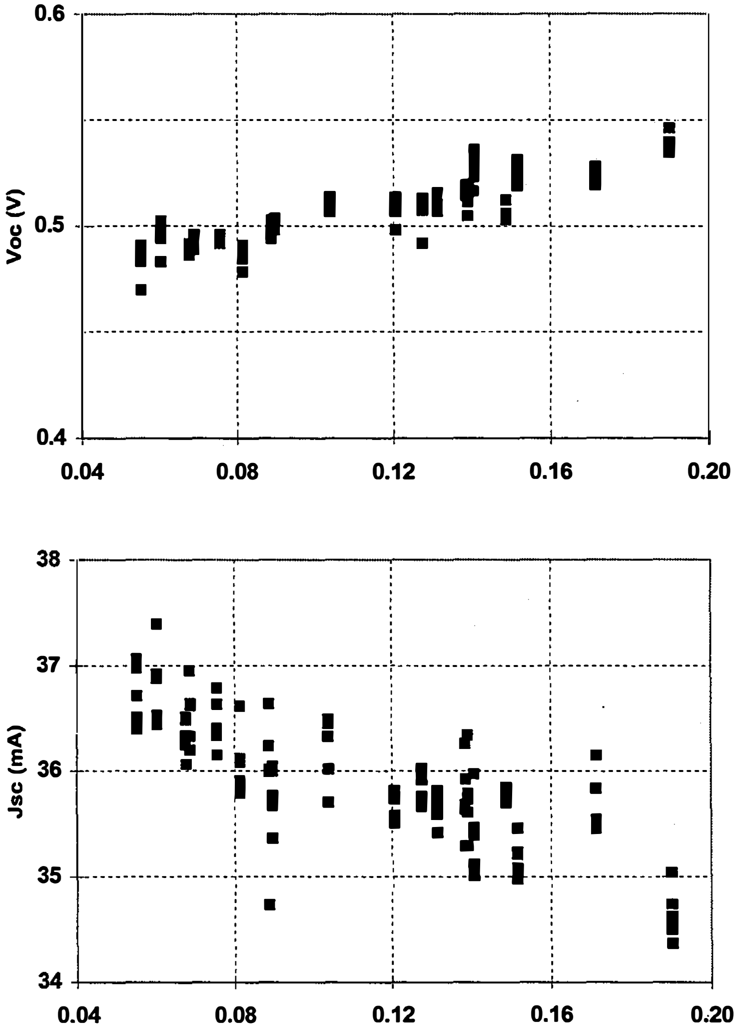


Figure 3. Open circuit voltage and short circuit current as a function of the ratio of sulfur to selenium.

Absorber formation runs designed to simulate the Phase 2 large area reactor process using the baseline reactor were pursued to gain a better understanding of the impact of reaction process parameters on adhesion. Poor adhesion was a problem for initial runs using the Phase 2 large area reactor. Nearly 50% of the parts from these runs were rejected after ZnO deposition due to peeling and tape pull tests indicated poor adhesion. Further experiments varying the selenium and sulfur introduction sections of the absorber formation process were performed in the baseline reactor to determine which section of the large area reaction process is responsible for poor adhesion. Spontaneous adhesion failure after ZnO occurred only for simulation of both the selenium and sulfur introduction sections of the large area reactor process. Intermediate adhesion was obtained for the combinations of the baseline and large area reactor selenium and sulfur introduction sections of the process as summarized in the following table. An adhesion scale from 1 to 10 is used with 1 denoting poor adhesion and 10 denoting adhesion of the baseline process.

Table 2. Dependence of relative adhesion on absorber formation process.

Absorber formation process section		Relative Adhesion
Selenium introduction	**Sulfur introduction**	
Large area	Large area	1
Large area	Baseline	3
Baseline	Large area	4
Baseline	Baseline	10

Both the selenium and sulfur introduction sections of the large area reactor process have a similar detrimental impact on adhesion with the selenium introduction sections of the process having a somewhat greater impact. The results of these studies were combined with reactant concentration modeling to define processes for improved absorber adhesion in the new Phase 2 reactor.

Adhesion and electrical performance were dependent on location in the reactor for all of the above variations in selenium and sulfur introduction. Statistical analysis of the SSI baseline process indicated lower performance for absorbers formed at one position in the baseline absorber formation reactor. The first occurrence of lower performance for this position correlated with implementation of a change in substrate preparation. These devices exhibited a Voc that was systematically 5 points lower than for all other devices from the same absorber formation lot. This interaction between part location and orientation has also been the subject of investigation using both the large area and baseline reactors. ICP analysis indicated that the ratio of sulfur to selenium in the absorber is dependent on location in the reactor. These results further the understanding of the importance of materials of construction and physical layout in reactor design. In turn, the understanding gained has been applied to define a change in reactor layout with the result of decreasing the electrical performance dependence on location.

Additional insights achieved by comparing changes in the baseline reactor process with the large area process are discussed in the following sections titled "Baseline Process" and "Process Scale-up."

Baseline Process Development

During Phase 1 of this subcontract the baseline process was repeatedly executed to demonstrate the potential of the technology and in support of scale up efforts. As seen in Figure 4, a reproducible low variation baseline was demonstrated for over two thousand mini-modules. Isolation of performance differences between the baseline and the large area process were greatly aided by comparison with a stable and therefore predictable baseline process. For example, the impact of larger substrates was tested for each step in the baseline process by cutting the larger substrates and processing them through the baseline process as 10x10 cm circuit plates. Such experiments indicate that the larger-area parts should achieve the same level of performance as the smaller parts after addressing the differences between reactors.

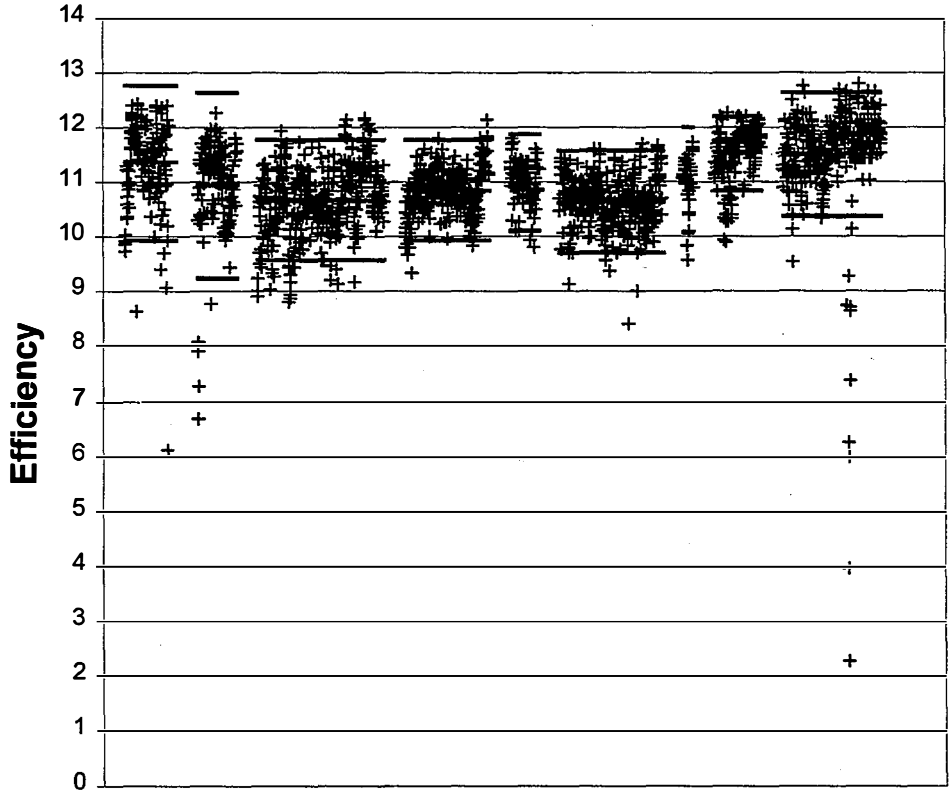


Figure 4. Control chart showing efficiency of more than two thousand mini-modules.

As discussed in the following section titled "Process scale-up," a large area reactor was not available while SSI designed and built a new large area reactor. Therefore, during this phase of the subcontract the baseline reactor was used to produce subcontract deliverables and introductory CIS-based products in addition to continued demonstration of a reproducible low variation baseline process and other subcontract tasks. Fixtures were procured for 10 cm X 30 cm circuit plates. As discussed further in the following section titled "Module Reliability and Packaging," these 10cm X 30 cm circuit plates were combined to form nominally 1x4 ft modules for the M3 and M4 subcontract deliverables and 5 and 10 W products.

Electrical performance identical to baseline 10cm X 10 cm circuit plates was achieved for 10 cm X 30 cm circuit plates after addressing adhesion issues. A correlation between the number of parts in the absorber formation process and adhesion between the CIS and Mo was observed. Poorer adhesion was also observed for the area between the pattern in the Mo and the pattern in the CIS and correlated with changes in the substrate preparation and Mo deposition process implemented in conjunction with fabrication of deliverables. Modification of the substrate preparation and Mo deposition process allowed high throughput, good Mo patterning quality over large areas and improved near-P1 adhesion. Although significant improvements have been demonstrated, sporadically poor adhesion near the Mo pattern, and substrate to substrate variations in laser scribe quality are observed and lead to lower mechanical and electrical yield.

Using the baseline reactor, SSI delivered a 1 kW set of modules (Figure 5) and an additional 10 modules for testing to NREL, fulfilling the M3 and M4 subcontract deliverables. The 1 kW set of modules replaced an existing 1 kW array based on an older absorber formation technology. Performance data for these arrays is discussed in the follow section titled "Module Reliability and Packaging -- $Cu(In,Ga)Se_2$ and $Cu(In,Ga)(Se,S)_2$ 1kW Arrays."

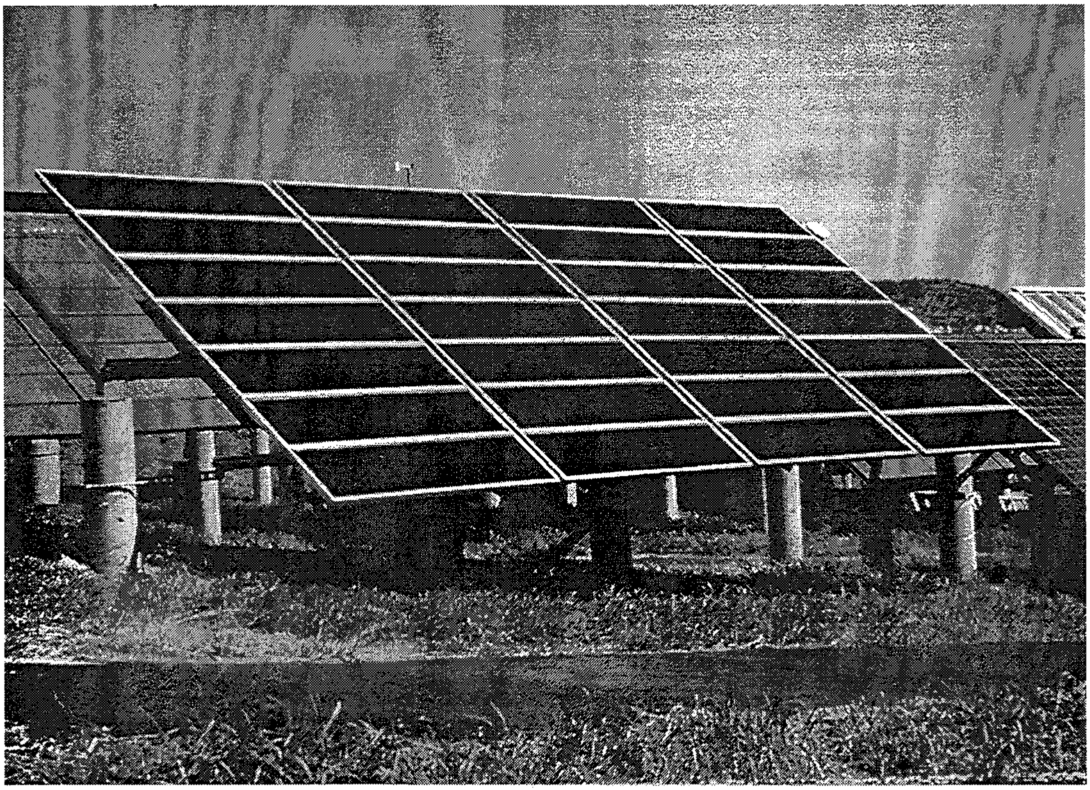
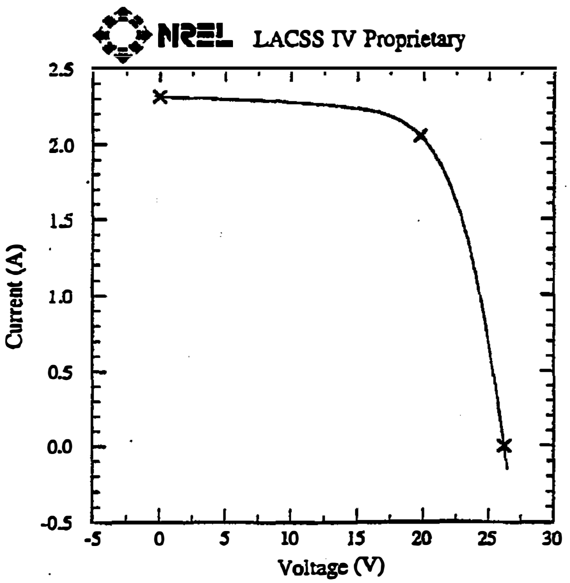


Figure 5. One kilowatt array - graded sulfur absorbers.

A module identical to the modules of this array but with an aperture physically masked to exclude both bus ribbons was confirmed by NREL to produce 40.6 watts for a new confirmed world-record efficiency of 11.1 percent on 3665 cm2 (Figure 6). This demonstrated efficiency exceeds the 1995 DOE efficiency goal for CIS prototype modules and exceeds the year 2000 DOE efficiency goals for amorphous silicon and cadmium telluride technologies (5).



	Module	per Cell	
Eff	11.1		%
Voc	26.2	0.524	V
Isc	2.3		A
Jsc		31.6	mA/cm^2
FF	66.9		%
Area	3665	73.3	cm^2

Figure 6. New world record efficiency of 11.1 percent on an aperture area of 3665 cm^2.

SSI also introduced two new CIS-based products. The product designations are ST5 and ST10 which are 21x33 cm, 5 watt and 39x33 cm, 10 watt modules designed for use in 12 V systems (Figure 7). The aluminum framed modules are fabricated from two or more circuit plates processed in the baseline reactor. SSI delivered product samples to NREL as M5 and M6 contract deliverables and NREL reported 9.6% aperture area efficiency (11.2 % circuit plate aperture area) which is the highest efficiency of any commercial non-crystalline module.

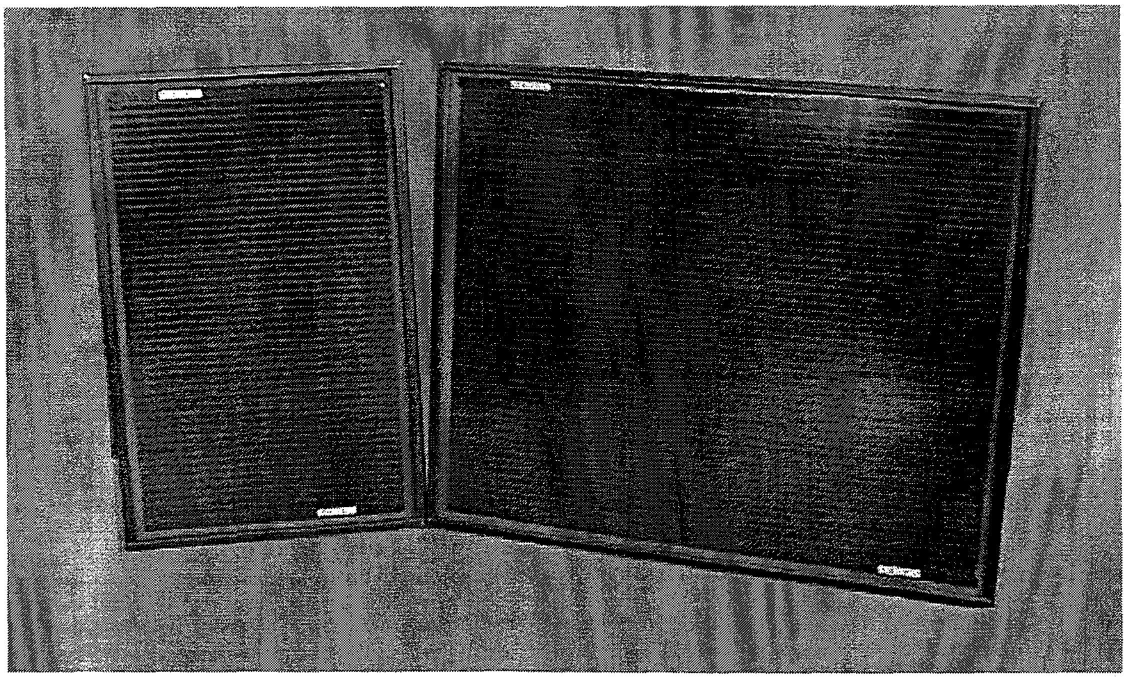


Figure 7. Introductory CIS-based 5 and 10 W products.

Process Scale-up

Large-area circuits did not achieve the performance level of the 10 cm X 10 cm baseline during Phase 1 of this subcontract. Analysis of absorber structures and device performance identified differences between devices from the baseline and large reactor including:

- Bandgap of the absorber
- Elemental concentrations in the absorber
- Elemental concentrations profile in the absorber
- Contact resistance
- Relative adhesion above the interconnect scribe in the molybdenum
- Visual appearance of the molybdenum after scraping off the absorber
- The relative amount of sulfur and selenium in the molybdenum

Studies of the differences between reactors have continued during this second subcontract phase including systematically varying process condition in the Phase 1 large area reactor and mimicking the large area reactor using the baseline reactor. For example, ICP (and other) analysis of samples from the two reactors indicated that process conditions for the large area reactor were more similar to the baseline reactor after cleaning. Subsequent operation of the large area reactor led to further divergence from the process conditions for the baseline reactor. In support of these findings, quantum efficiency based bandgap measurements (figure below) indicated increasing bandgap for successive reaction runs after cleaning the large area reactor.

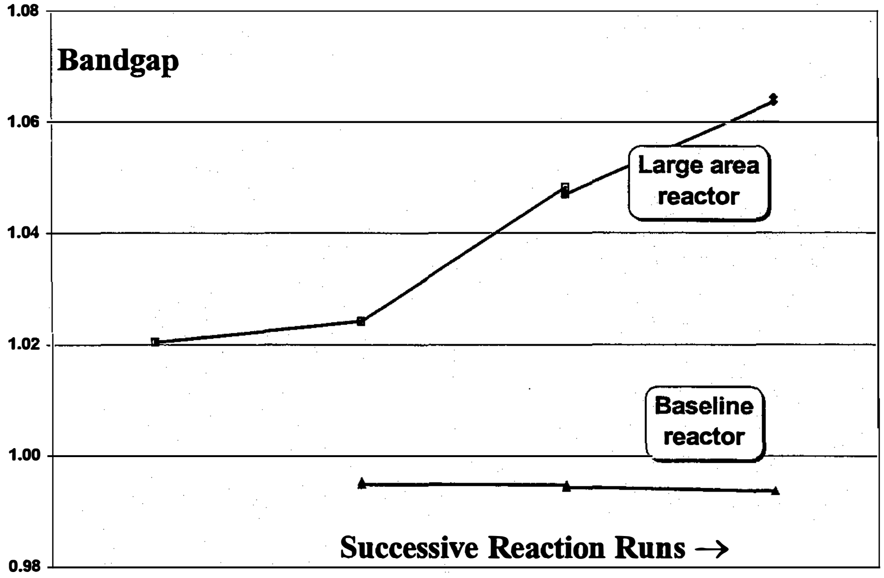


Figure 8. Bandgap for successive runs in the baseline and large area reactors.

Whereas this bandgap versus reaction run trend for the large reactor is distinct, device parameter versus bandgap trends were relatively week. Also, cleaning the large area reactor decreased interconnect contact resistance to values similar to values for the baseline process. In summary, these studies allowed adjustment of most but not all of the process conditions in the large area reactor to more closely mimic process conditions in the baseline reactor and thereby mitigate most but not all of the observed differences between the process achieved in the two reactors. Similarly, these studies allowed isolation of the remaining differences between reactors to differences in the materials of construction and the physical design of the large reactor.

During this subcontract phase, SSI designed and built a new large area reactor (Phase 2 reactor). Safe use of potentially hazardous reactants was the first consideration. SSI, with help from the TFPPP ES&H group headed by Paul Moskowitz and supported by his associates at Brookhaven National Laboratories, defined a reactor to avoid potential fire or explosion hazards resulting from system failure. These efforts progressed through the following subtasks:

- Determining the potential hazard based on the energy released and the timeframe for release
- Reviewing hazard avoidance methods
- Implementing the best hazard avoidance method

Four main uncertainties hampered determining the energy released and the timeframe for release:

- Adequate thermodynamic data was not available for H_2Se.
- The appropriate final states for the products of potential reactions was uncertain.
- The reactions that would occur for actual conditions were unknown. For the example of H_2Se, an oxygen deficient reaction is a reasonable scenario which could lead to oxidation of just hydrogen rather than oxidation of both the hydrogen and selenium.
- The dynamics of the reactions, mixing of air and fuel, etc. were unknown and expected to be dependent on system geometry and the specifics of a failure.

Brookhaven National Laboratories performed worst case calculations indicating potential damage to SSI infrastructure based on SSI supplied data on gas concentrations, thermodynamics, system geometry, and infrastructure. SSI considered fuel limiting and oxygen limiting control measures. Energy absorbing control measures were considered inappropriate. SSI implemented a nitrogen blanket and reservoir with oxygen sensors to insure safety based on limiting oxygen availability in the event of system failure.

Based on advances in understanding regarding the influence of reactor design on performance, SSI designed and built a new large area reactor which is a more direct scale-up of the baseline reactor. This reactor became operational late in this subcontract phase. Success with this reactor has been demonstrated by initial circuit performance for 28x30-cm circuits averaging 10.6% which compares very favorably to the 10x10-cm baseline.

Module Reliability and Packaging

Package development

A package design for fabricating 1x4 ft modules (M3 and M4 subcontract deliverables) and 5 and 10 W products from 10 cm X 30 cm circuit plates processed using the baseline reactor was developed during this phase of the subcontract. The more standard module configuration is illustrated in Figure 9; EVA is used to laminate a circuit plate to a tempered cover glass and the module is framed with an Al extrusion. The package design for fabricating modules from 10 cm X 30 cm circuit plates is illustrated in Figure 10; the addition of a Tedlar/Al/polyester/Tedlar backsheet unifies the 10 cm X 30 cm circuit plates for framing.

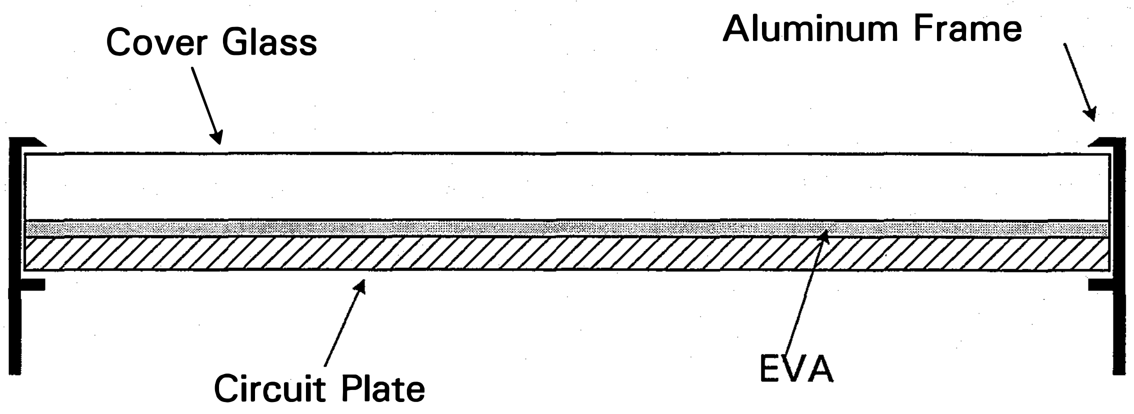


Figure 9. Single circuit plate module configuration.

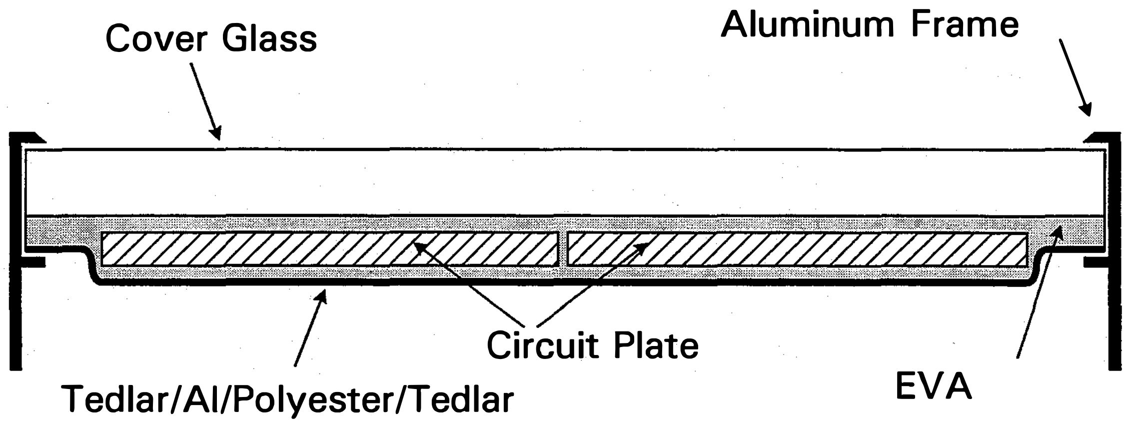


Figure 10. Multiple circuit plate module configuration.

Long-term Outdoor Stability

Long-term outdoor stability has been demonstrated at NREL where 1x1-foot and 1x4-foot modules have undergone testing for over eight years. These measurements, shown in Figure 11, were made by bringing the modules indoors, performing the measurements under standard test conditions, then returning the modules to their outdoor test location.

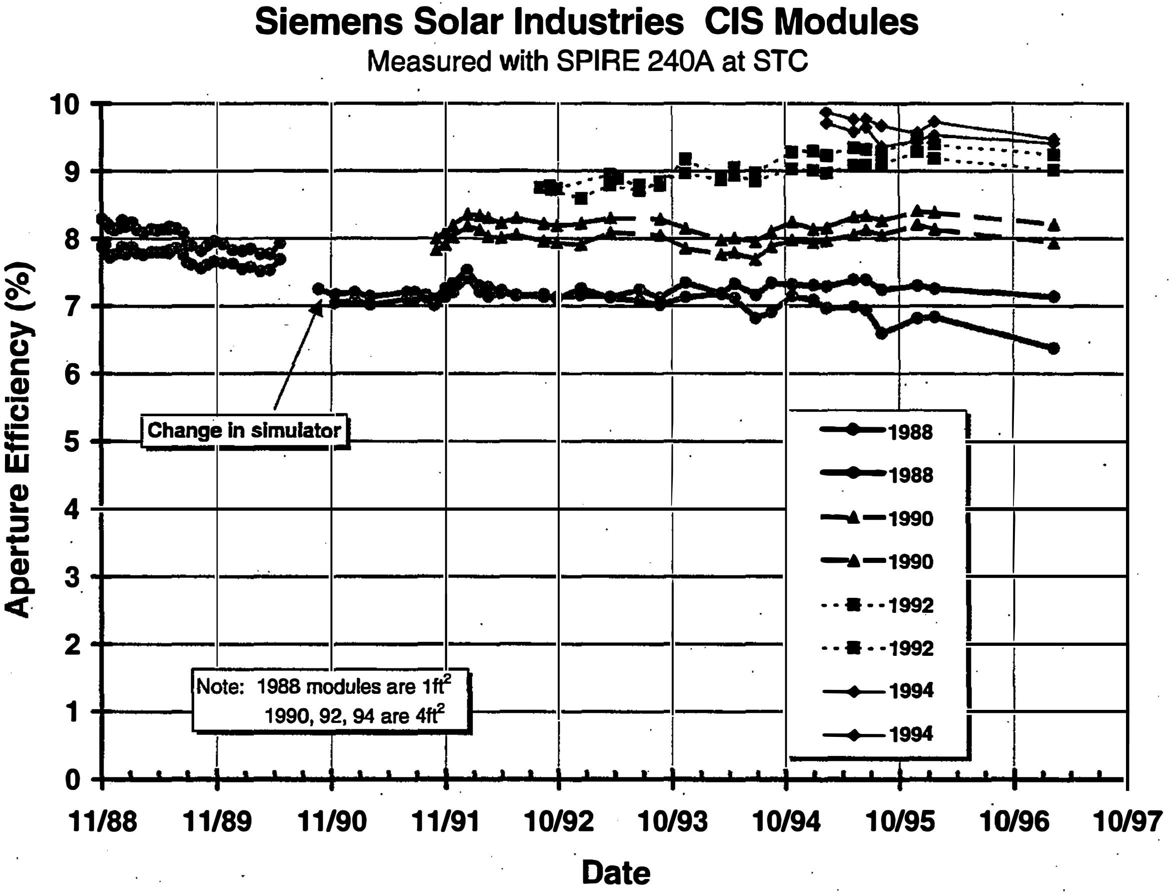


Figure 11. Long term outdoor stability has been demonstrated at NREL where 1x1 foot and 1x4 foot modules have undergone testing for as long as seven years.

$Cu(In,Ga)Se_2$ and $Cu(In,Ga)(Se,S)_2$ 1kW Arrays

During February and March SSI delivered a set of modules to NREL for a 1 kW array (Figure 5) replacing an existing 1 kW array based on an older absorber formation technology. The system was installed May 29, 1997 and data acquisition started on June 5, 1997. The array is fixed at a 40° tilt and is aligned to true south. DC power is connected to a resistive load through three maximum power trackers. The NREL Engineering and Technology Validation Team collects data including: plane-of array irradiance, dc voltage, dc current module temperature and air temperature.

Absorbers for the previous array were $Cu(In,Ga)Se_2$ whereas absorbers for this array are a graded absorber including sulfur; $Cu(In,Ga)(Se,S)_2$. Data for these arrays are summarized in Table 3. The new 28-module array has an average module power of 36 watts. NREL reports stable performance and an average efficiency without correction to standard conditions of 7.7% which is a significant improvement over the ~5.7% average efficiency for the previous CIS array. Correcting the measurements made under prevailing conditions to standard conditions yields array power of 1014 W for an unprecedented average efficiency of greater than nine percent (Figures 12). The computed temperature coefficient for power is

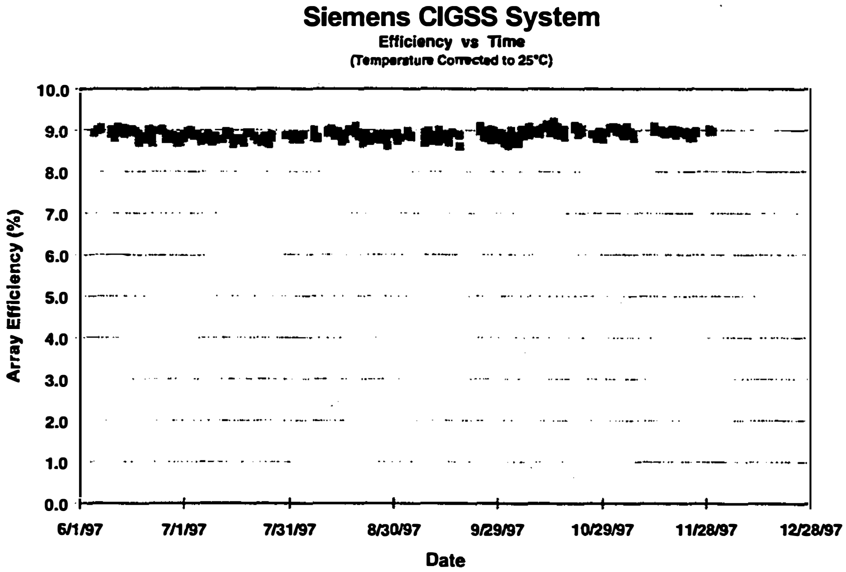
-0.44%/°C which is also a significant improvement over the -0.8%/°C temperature coefficient measured for the previous array. These demonstrated improvements in efficiency and temperature coefficient for the newer technology are significant advancements in CIS-based technology.

Table 3. $Cu(In,Ga)Se_2$ and $Cu(In,Ga)(Se,S)_2$ Array Data.

		$Cu(In,Ga)Se_2$	$Cu(In,Ga)(Se,S)_2$
Power (Corrected to STC)	(W)	865	1014
Efficiency (Corrected to STC)	(%)	6.4*	9.0
Temperature Coefficient	(% / °C)	-0.8	-0.44
Average Module Temperature	(°C)	41	54**
Average Air Temperature	(°C)	17	22**
Number of modules		34	28
Cells per module		53	50

* Calculated based on average Eff and temperature (5.7%, 40.6 °C)

** Data from summer months



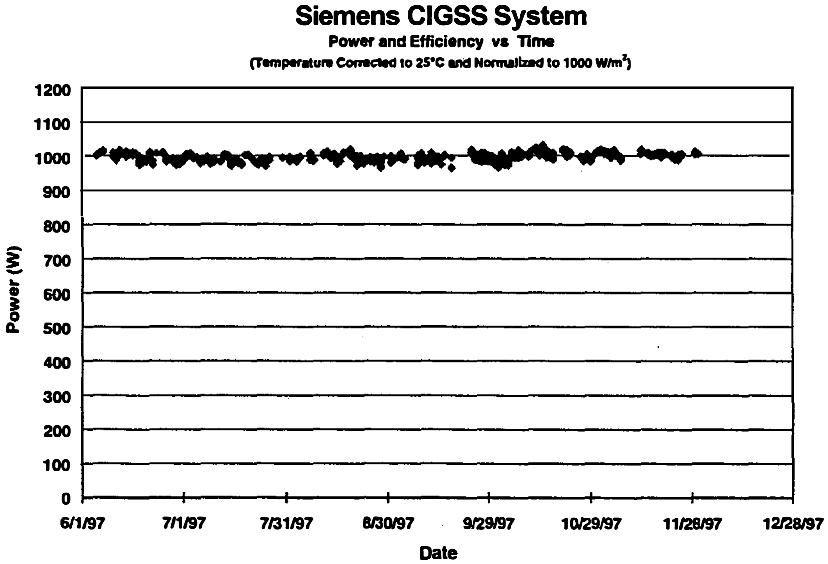


Figure 12. Field measurements, power and efficiency, of the 1 kW $Cu(In,Ga)(Se,S)_2$ array at NREL. No photo or thermally induced instability is observed.

For measurement of the 1-kW array, the modules are not brought indoors for IV measurements but rather measurements are made in the field; they are kept under load, and measured every half hour. Good stability with no seasonal variation in performance is demonstrated for temperature corrected data. These studies demonstrate that thermally induced transients, which are observed after exposure to accelerated environmental testing conditions, are not observed in the field despite daily and seasonal changes in module temperature.

Accelerated Testing -- Process Dependence And Measurements

Although long-term outdoor stability has been demonstrated at NREL, SSI fabricated CIS-based modules have failed standard accelerated environmental stress tests. As discussed in the Phase 1 subcontract report, laminates subjected to thermal cycling (TC) and humidity-freeze cycling (HF) at NREL exhibit thermally induced losses which recover with outdoor exposure. Although performance recovers with outdoor exposure to nominally the initial performance, the modules may fail these accelerated tests if the known transient effects and their impact on appropriate measurement protocols are not considered. Water vapor ingress resulting from extended damp heat testing permanently degrades performance. As discussed in the Phase 1 subcontract report, this degradation was related to degradation of ZnO sheet resistance and ZnO to Mo contact resistance and due to water vapor ingress. SSI has demonstrated packaging designs that protect laminates from water vapor ingress during damp heat testing and allow modules to pass the damp heat test; however, the yield for passing the damp heat test with this package was low and the package design is not desirable for commercialization.

During this subcontract phase, SSI continued to pursue understanding of transient and degradation mechanisms with the goal of ameliorating potential long-term degradation mechanisms. These studies include the dependence of outdoor and accelerated testing on both circuit fabrication process parameters and the lamination process. The remainder of this section discusses progress on these studies.

Transient effects are important for many topics in addition to accelerated testing: process definition, measurement protocols, process predictability and understanding of device structures. For example, transient effects confound measurements made during module fabrication and final measurements to define product rating. Therefore, SSI presently includes a light exposure *process step* for both circuit plates prior to lamination and modules after lamination. Transient effects are addressed in this section since confounding of accelerated test results by transient effects delimits Phase 2 results for environmental studies.

During this subcontract phase, baseline circuit plates were dedicated to tracking and correlating thermal stability with process conditions. A standard thermal stress and test sequence was defined to *maximize* thermally induced losses and thereby increase the probability of identifying correlation with process conditions. The standard stress was defined as at least 10 hours of uninterrupted exposure to 85°C in the dark. Four measurements were defined: plates prior to lamination, post lamination, post stress and after several days of outdoor exposure. Part handling procedures were defined to minimize exposure to incidental light sources during processing and testing, again to maximize losses. Continuous source IV tests were chosen for the initial and final tests. A pulsed light source IV test was chosen for intermediate tests to minimize the light exposure between lamination and the thermal stress. Regression analysis indicated that:

- Lamination loss is not predicted by initial efficiency
- Loss due to the thermal stress is not correlated with lamination loss
- Correlation with process conditions is impaired by the large variation in the data for pulsed source testing

The confounding of process data by large variations for pulsed source testing was addressed by redefining the standard procedure; replacing the pulsed light source test with a continuous light source test. Reduction of measurement variation was demonstrated. Also, part handling conditions were redefined to allow accumulation of light inducted rate of change data for device parameters. Measurements were taken as quickly as possible and for intermediate exposure times up to a final measurement after 5 minutes of exposure at one sun.

Variations in device parameter rates of change with light exposure time have been correlated with process parameters, however the significance of these observations have not been ascertained. The main conclusion to date is that, even with the more stringent procedures, this data may be confounded by sensitivity to thermal and light exposure histories; results may depend on relatively minor differences in thermal and light exposures during processing. The following data illustrates the dependence on light exposure history and also illustrates the differences for testing with pulsed and continuous light source solar simulators. In Figure 13, increases in efficiency for a representative mini-module is plotted versus light exposure time before and after storing the mini-module in the dark (outdoor exposure for about six months, in the dark for about two months). The data at 0.001 seconds was obtained from a pulsed solar simulator. As illustrated in Figure 13, both the absolute value of efficiency and rate of change with light exposure is dependent on the prior light exposure history. The pulsed light source simulator measurement is significantly lower than the continuous light source measurement and, based on a more extensive data set, this difference is not predictable.

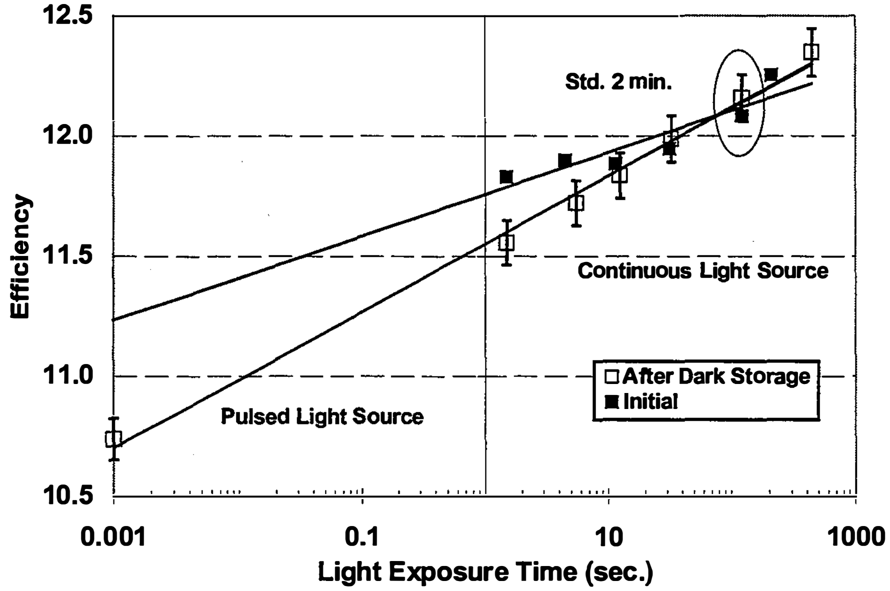


Figure 13. Efficiency for a representative mini-module versus light exposure time.

Improved prediction of continuous light source results using pulsed light simulation was studied since the largest devices that SSI can measure with the "continuous tester" is about 10x10 cm. Study of voltage biasing prior to pulsed light source measurement demonstrated correlation between device performance improvements with voltage biasing and light exposure. However, this approach did not yield adequate accuracy to predict continuous light source results using voltage biasing prior to testing with a pulsed light source.

Lamination and pseudo lamination experiments were conducted on mini-modules to determine the effect of EVA on device performance changes during lamination (Figure 14). Mini-modules were chosen to allow measurement with both continuous and pulsed light source solar simulators. Circuit plates were laminated with standard lamination procedures and pseudo lamination procedures where the circuit plates were exposed to the conditions during standard lamination but with a Mylar sheet replacing the EVA. After 939 hours of exposure to 85°C in the dark the average fraction of the efficiency measured after standard lamination is 84%. Similar measurements for the pseudo lamination (Plates) were made. After the same exposure, the average fraction of the efficiency measured after pseudo lamination is 94%. Multiple interpretations are implied by these results: an interaction with EVA, sensitivity to thermal history and inadequate simulation of the actual lamination by the pseudo lamination, or differences in results related to different absorber environments during the exposure at 85°C. The efficiency for mini-modules with the standard lamination and extended thermal stress is typically within 10% of initial efficiency after extended outdoor exposure. Therefore, independent of the several possible interpretations of the results, lamination induced losses even with a potential interaction with EVA recover with outdoor exposure.

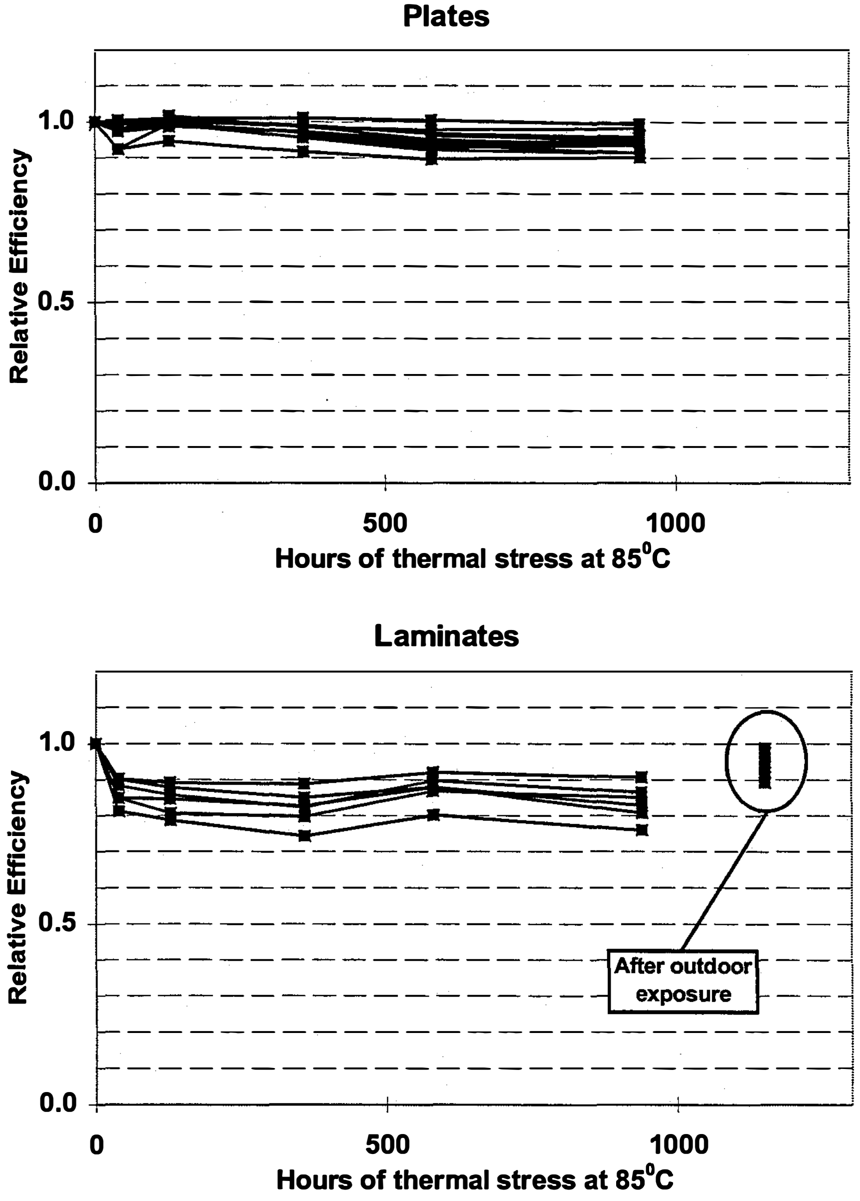


Figure 14. Thermal exposure degradation and outdoor recovery for laminates and pseudo lamination (Plates).

Studies to date have demonstrated no transient effect dependence on the circuit fabrication process with the exception of storage in an inert environment. For example, no statistically significant difference due to the

Mo deposition process is observed for thermal stress or recovery with light exposure. As illustrated in the Figure 15, devices made using two Mo deposition processes were measured after initial fabrication, lamination, 20 hours of exposure to 85°C in the dark ("Dark Heat"), and after outdoor exposure for about one week. No statistically significant difference between the two Mo deposition processes was observed for thermal stress or recovery with light exposure. Similarly, no statistically significant difference has been observed for varied glass preparation conditions.

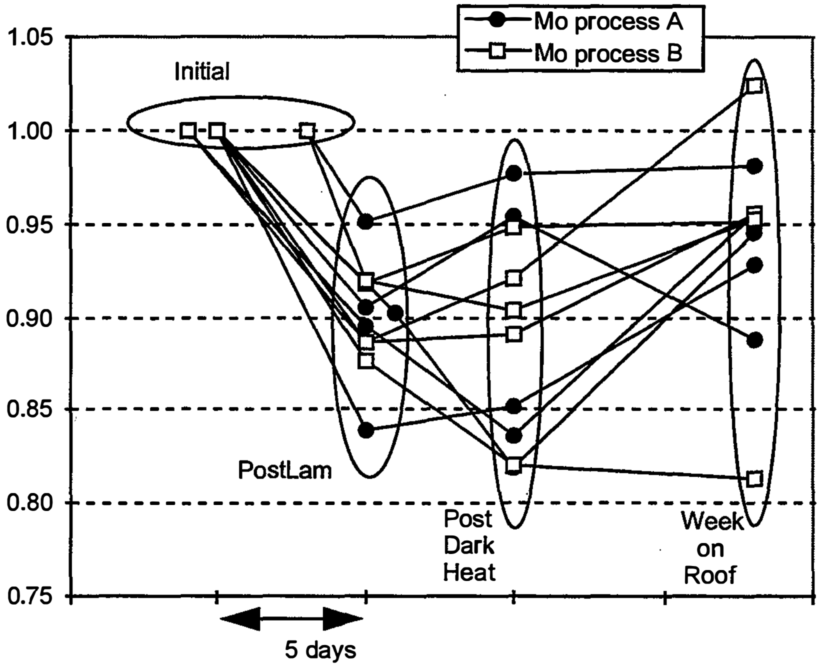


Figure 15. Normalized efficiency versus time and process or environment.

Lower lamination losses as measured using a pulsed simulator have been demonstrated for less exposure of circuit plates to air during the final stages of fabrication. As illustrated in Figure16 for 9x30 cm circuit plates, lower lamination losses are demonstrated for transporting circuit plates in a bag and in a bag with desiccant as *added process steps*. These added process step are in addition to the two light exposure process steps for testing before and after lamination. It is not known if this lower lamination loss for less exposure of circuit plates to air would be observed after extended outdoor exposure.

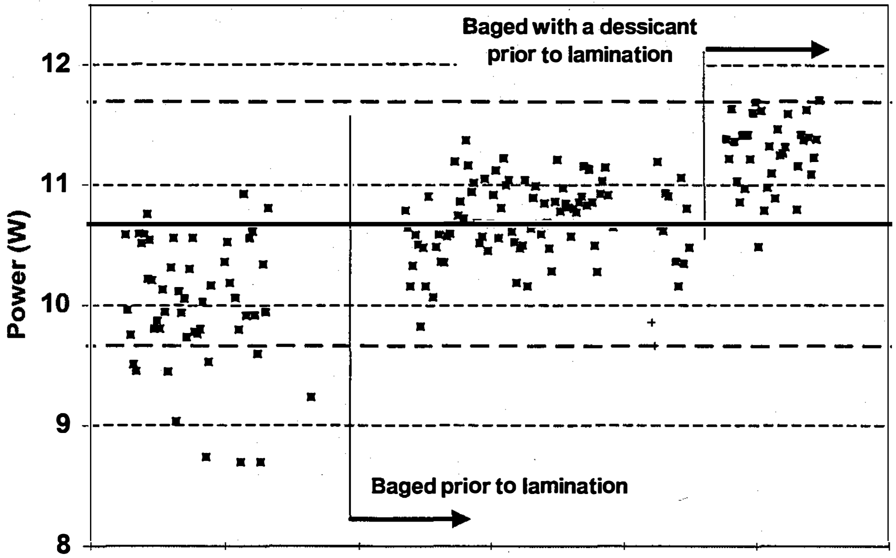


Figure 16. Module power versus atmosphere during transportation and storage for module fabrication.

Characterization and amelioration of transient and degradation mechanisms during damp heat exposure (1000 hours at 85°C, 85% relative humidity) on large area laminates was pursued during this subcontract phase. During Phase 1 of this subcontract, studies utilizing interconnect test structures and laminated ZnO coated glass plates demonstrated that:

- Both ZnO to Mo contact resistance and ZnO sheet resistance increase with water penetration into the laminate as indicated by fogging of the EVA
- Edge seal options significantly decrease water vapor ingress
- The effect of water vapor on ZnO sheet resistance is reversible.

Further edge seal options and inclusion of desiccants in test laminates have been explored during this phase of the subcontract. Since water vapor ingress is related to perimeter length while degradation is related to circuit area, these studies were based on larger circuit plates than can be measured using SSI's continuous light source simulator. Uncertainty in both initial and final measurements using SSI's large area pulsed solar simulator have confounded the results of these studies.

The confounding of experimental data and the need for two light exposure process steps and a bagging process step underscores the importance of understanding transient effects. Progress was made toward determining the role of device structures in the expression of transient effects in alliance with NREL TFPPP Teams. The NREL TFPPP Transient Effects Group with representatives from industry, NREL and universities (Keith Emery; NREL, James Phillips; University of Delaware; James Sites; Colorado State University, Dale Tarrant; Siemens Solar Industries; Hong Zhu; Penn State University) is focused on understanding the fundamental mechanisms responsible for transient effects in CIGS-based devices and thereby eliminating or minimizing their impact. The following results, observations and areas of research related to heat and light exposure studies of laminated mini-modules illustrate the work of this group:

- Changes in FF dominate changes in IV characteristics for thermal stress and light exposure.
- Changes in "series resistance" account for these changes in FF.
- Capacitance versus voltage measurements demonstrate a decrease in hole density with thermal exposure.
- Subsequent light exposure increases the hole density to approximately the concentration prior to thermal exposure.
- Although the changes in series resistance and hole density with thermal and light exposure are about the same magnitude, causality has not been demonstrated.
- Differences in the rate of recovery for the four illumination spectra suggests that the recovery process may be dependent on the spectrum of the illumination.
- Since the rate of recovery is similar for no illumination and for illumination with red light, the recovery process may depend on absorption in the window layer or in the near surface region of the absorber.
- The transient effects are not solely a lamination effect -- these observations made on devices are consistent with measurements made on mini-modules.
- SSI and Larry Olsen's group at Washington State University demonstrated light induced transient effects for SSI absorbers with and without buffer layers.
- AMPS device modeling software was applied to the study of transient effect and the insights gained from these studies are being applied to further understanding of the role of device structures in the expression of transient effects.

The present state of understanding regarding the role of device structures in transient effects is illustrated by the results of collaborations between SSI and Washington State University. SSI and Larry Olsen's group at WSU conducted studies to explore the role of the CdS buffer layer and the connection between buffer layers and light induced transient effects. SSI graded absorbers were processed by SSI and WSU with and without buffer layers and with and without degreasing and a combination of degreasing and a KCN surface treatment. Efficiencies were improved by the degreasing and KCN etch. Light exposures of 3 and 13 hours improve performance (Figure 17): 20 to 50% with CdS, saturating after 3 hr, 200 to 250% without CdS, continuing after 3 hr. With CdS, efficiency improvements were due to increases in FF. Without CdS, efficiency improvements also included improvements in Voc, Jsc and FF. A rollover of forward bias current (i.e. decreasing rather than increasing slope of the current versus voltage curve for increasing voltage) is observed for all but the case of degreasing combined with a KCN etch. This data implies that rollover is associated with CIS surface conditions and interactions of the ZnO and CdS with the CIS surface. Combining these observations regarding light induced transients with or without a buffer layer and the results from the Transient Effects Group regarding changes in hole density with light exposure implies that mechanisms responsible for transients and the role of buffer layers are related and that both induce changes in the absorber.

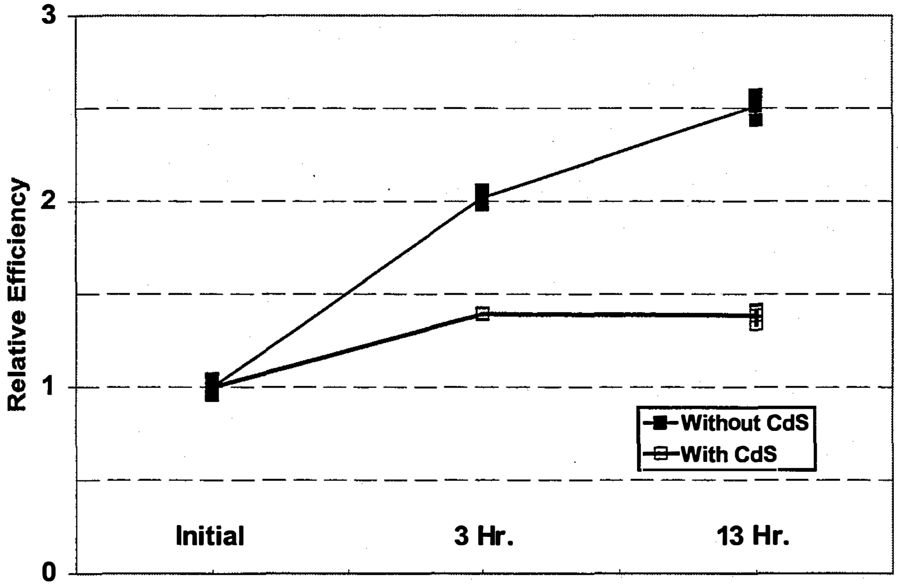


Figure 17. Relative efficiency versus light exposure time for mini-modules with and without a CdS buffer layer.

Conclusions

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 are to demonstrate performance as well as commercial viability via the milestones of a champion prototype 13% efficient large area module and sets of modules in 1-kW arrays of steadily increasing efficiency, culminating in delivery of a 1 kW array of 12% efficient large-area modules by the end of the subcontract. Progress toward achieving these goals has been demonstrated during this subcontract phase including:

- Studies furthered understanding of the importance of materials of construction and physical layout in reactor design.
- SSI designed and built a new large area reactor which is a more direct scale-up of the baseline reactor.
- SSI introduced two new CIS-based products
- SSI delivered of a set of upgraded modules to NREL for a 1 kW array
- SSI demonstration a new confirmed world-record efficiency of 11.1% on 3665 cm^2.
- Long-term outdoor stability has been demonstrated at NREL, however SSI fabricated CIS-based devices have failed standard environmental stress tests.

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13. ABSTRACT *(Maximum 200 words)*

This report describes work performed during Phase 2 of Siemens Solar Industries' (SSI) subcontract. Studies of the differences between reactors continued, resulting in adjustment of most of the process conditions to more closely mimic process conditions in the baseline reactor, thereby mitigating most of the process differences. SSI designed and built a new large-area reactor that is a more-direct scale-up of the baseline reactor. This reactor became operational during Phase 2 and was successfully demonstrated by initial circuit performance for 28-cm x 30-cm circuits averaging 10.6%, which compares favorably to the 10-cm x 10-cm baseline. SSI also defined a package for introductory products in support of the DOE long-term goal of systems that last at least 30 years. SSI also introduced two new CIS-based products: the product designations are ST5 and ST10, which are 21-cm x 33-cm/5-watt and 39-cm x 33-cm/10-watt modules designed for 12-V systems. NREL reports 9.6% aperture-area efficiency on the samples (11.2% circuit-plate aperture area), which is the highest efficiency of any commercial noncrystalline module. SSI also delivered a set of modules to NREL for a 1-kW array replacing an existing 1-kW array based on an older absorber formation technology. NREL reports stable performance and an unprecedented average efficiency of over 9%. A champion module was confirmed by NREL to produce 40.6 watts for a new world-record efficiency of 11.1% on 3665 cm^2. This demonstrated efficiency exceeds the 1995 DOE efficiency goal for CIS prototype modules and exceeds the year 2000 efficiency goals for amorphous silicon and cadmium telluride technologies.

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