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Subcontractor Report

PV Manufacturing R&D — Integrated CIS Thin-Film Manufacturing Infrastructure

Final Technical Report
2 August 2002–30 April 2004

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Shell Solar Industries, Inc.
Camarillo, California

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Operated for the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
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Preface

Shell Solar Industries (SSI), formerly Siemens Solar Industries, has pursued the research and development of $CuInSe_2$-based (CIS) thin film PV technology since 1980. In the 1980s SSI 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). Since these early achievements, SSI has made outstanding progress in the initial commercialization of high performance thin film CIS technology. Line yield has been increased from about 60% in 2000 to about 85% in 2002. This major accomplishment supports attractive cost projections for CIS. Recently, NREL confirmed a champion 12.8 percent aperture area conversion efficiency for a large area (3626 cm^2) CIS module. Other than definition of the aperture area, this module is simply one module from the upper end of the production distribution for standard modules. Prerequisites for commitment to large-scale commercialization have been demonstrated at successive levels of CIS production. Remaining R&D challenges are to scale the processes to even larger areas, to reach higher production capacity, to demonstrate in-service durability over longer times, and to advance the fundamental understanding of CIS-based materials and devices with the goal of improvements for future products. SSI's thin-film CIS technology is poised to make very significant contributions to DOE/NREL/NCPV long-term goals - higher volume, lower cost commercial products.

SSI responded to the August 7, 2000 solicitation titled “PV MANUFACTURING R&D—IN-LINE DIAGNOSTICS AND INTELLIGENT PROCESSING IN MANUFACTURING SCALE-UP" for DOE funding for Fiscal Years 2001, 2002, and 2003. SSI received a letter from NREL on May 8, 2002 conditionally authorizing limited costs incurred on or after December 1, 2001 in anticipation of award of this subcontract. This incrementally funded three phase subcontract was executed August 2nd, 2002 with the period of performance for the first phase ending April 30, 2003. SSI requested a six months no cost extension for Phase 1 because of circumstances that were not favorable for completion of Phase 1 subcontract effort. SSI received a no cost extension to the period of performance through October 31, 2003. In August 2003, SSI and NREL began discussions of an updated statement of work for the three phases of this subcontract. Due to significant delays in obtaining corporate approvals for certain CIS thin-film capital equipment expenditures, SSI and NREL began discussions early in 2004 on termination of this subcontract at the end of April 2004. A revised statement of work was executed with all subcontract work, with the exception of purely reporting tasks, ending at the end of April 2004. A no cost increase extension through October 31, 2004 was granted to present a paper, serving as a Final Review, titled "Enhanced CIS Production Using XRF for PVD Process Control" at the Solar Energy Technologies Program Review Meeting, October 25-28, 2004, Denver Colorado. This document reports on subcontract activities through October 31, 2004.

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The Shell Solar Industries CIS Team:

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Summary

Compared to traditional wafer-based crystalline silicon technologies, monolithic integration of thin film solar cells can lead to products of comparable performance but with significant manufacturing advantages: lower consumption of direct and indirect materials, fewer processing steps and easier automation. Monolithic integration is required to achieve these advantages since this eliminates multiple process steps and handling operations during module assembly. The basic module elements for all thin-film technologies (alloys of amorphous silicon, cadmium telluride and $CuInSe_2$) are the same; the module elements are a circuit-glass/cover-glass laminate, a frame, and a junction box. The basic circuit elements are also very similar; they each have a base electrode, an absorber, a junction, a top electrode and three patterning steps for monolithic integration. While the details of these module elements or equivalent module elements differ, the basic cost structures are very similar on an area-related basis. Since the cost per unit area is similar, the cost per watt is inversely proportional to the module efficiency. $CuInSe_2$-based (CIS) cells and monolithically integrated modules have demonstrated the highest efficiencies of any candidate thin-film technologies; therefore, CIS is expected to have the lowest manufacturing cost/watt.

The objective of this subcontract was to continue the advancement of CIS production at Shell Solar Industries through the development of high-throughput CIS absorber formation reactors, implementation of associated safety infrastructure, an XRF measurement system, a bar code scribing system, and Intelligent Processing functions for the CIS production line. The intent was to open up production bottlenecks thereby allowing SSI to exercise the overall process at higher production rates and lay the groundwork for evaluation of near-term and long-term manufacturing scale-up.

The goal of the absorber formation reactor subcontract work was to investigate conceptual designs for high-throughput, large area (2x5 ft.) CIS reactors and provide design specifications for the first generation of these reactors. The importance of reactor design to the CIS formation process was demonstrated when first scaling from a baseline process in reactors for substrates to a large area reactor. SSI demonstrated that lower performance for large substrates was due to differences in absorber layer properties that were due to differences in the materials of construction and the physical design of the large reactor. As a result of these studies, a new large area reactor was designed and built that demonstrated circuit plate performance comparable to the performance using small area reactors. For this subcontract work, three tasks were identified to accomplish the absorber formation reactor work: Modeling, Mockup and Vendor Search.

Modeling work was pursued with the University of Florida to support reactor design and vendor search activities. Results indicated that alternative insulator approaches can be implemented for some subsections of existing reactors and can be effective for insulating both heater and substrate areas for future reactors.

The goal of the mockup task was to demonstrate that large area substrates, nominally 2 by 5 ft., could be heated without warping and to begin exploring the achievable thermal uniformity for various reactor and substrate configurations and varied ramp rates. The mockup consisted of a metal simulation of the reactor that was placed in a large industrial furnace. Substrate

temperature variations ranged from minimal to significant with increasing substrate load. Warping ranged from minimal to significant with increasing substrate load for higher cooldown rates. Repeated mockup runs indicated that a slower cooldown does not necessarily avoid warping without improvements in thermal uniformity that could not be implemented in the mockup.

Specifications for an absorber formation reactor were defined and a vendor selected in April 2003. This task required more time than expected due to the need for multiple specification and vendor response iterations. These iterations were required because no vendor had previous experience directly applicable to SSI's large substrate requirements nor would commit to any thermal uniformity specification for their proposed designs. Therefore, the responsibility for thermal uniformity became solely SSI's responsibility. A vendor design could have been accepted with no guarantee of success or the specific design approach for implementation by a vendor could have specified, again with no guarantee of success from the vendor. Based on discussions with equipment vendors, alternative geometries for higher capacity and improved thermal uniformity are possible by emphasizing forced convection or radiative heating. Some possible implementations may be long-term options for processing as many as 100 substrates per run. However, no potential vendors would commit to achieving any level of thermal uniformity for these options. This does not preclude future reactor advances, even dramatic advances, since capital cost does not necessarily scale with design complexity or reactor capacity.

Without a commitment to any thermal uniformity specification, SSI began meetings with a selected vendor to finalize a jointly developed design that would meet immediate requirements, about 25 substrates per run. Internal documentation required to procure the system was submitted; however, approval from the financial department was not obtained. In October, the equipment vendor was authorized to begin the first phase of work with a hold on further work.

SSI implemented and reported on the implementation of infrastructure for the safe delivery of reactants and safe processing of reactor effluent. Prior to this subcontract work, multiple absorber formation reactors were supported by one set of safety systems for supplying process gas and scrubbing reactor effluent. All absorber formation production capacity was limited by the time required for scrubber maintenance or service and this down time was amplified by the preparatory time required to end processing in each reactor. Similar production capacity limitations were due to gas cylinder infrastructure that was sized for initial process development and early production rather than production in multiple large reactors. Duplication of the exhaust scrubber along with valves for selecting one scrubber at a time now allows maintenance or service work while continuing operation of the reactors. Similarly, redundancy implemented for the raceway scrubbers allows maintenance or service without interfering with production. Also, maintenance has been simplified by replacing maintenance intensive raceway scrubbers based on recirculating KOH with carbon filter units. Subcontract work has allowed the use of larger cylinders at a lower cost per pound of reactant. Cylinder changes are made in parallel with production rather than limiting production and, in addition, a limitation on the time between starting multiple reactors has been eliminated.

The majority of the bar code scribing subcontract work occurred during the preaward timeframe. Subcontract activities addressed implementation of laser-scribed barcodes on glass substrates and man and machine requirements for reading these barcodes. An additional goal was to provide high quality data for the integrated manufacturing infrastructure task. Using barcode scribing has improved production productivity; bar code reading has proven to be easier, faster and more accurate than manual reading of hand scribed serial numbers. Process data ambiguity due to duplicate and missing serial numbers has been practically eliminated. Engineering productivity has also been improved since the frustrating and time consuming task of reconciling data with erroneously logged serial numbers has been practically eliminated. The objectives of this subcontract did not directly address yield improvements; however, very significant yield improvements were obtained by implementing laser bar code scribing and thereby minimizing breakage associated with hand scribed serial numbers. Breakage associated with the serial number was reduced by about 88%.

X-ray Florescence (XRF) as a deposition feedback technique was implemented to increase capacity by increasing the throughput of existing equipment. An additional goal was to provide high quality data for the integrated manufacturing infrastructure task. Precursor sputtering diagnostics characterize and allow control of absorber thickness and the Cu/(In+Ga) ratio (CIG ratio), which are critical parameters in CIS production. Production process control using XRF measurement of sputtered copper gallium and indium precursors has been demonstrated, implemented and qualified. XRF process control has also been qualified for deposition of the Mo base electrode. The previously used control approach for CIG, based on quartz crystal measurements, required up to 40% of the potentially available production time for process feedback measurements. With XRF based production process control, system time for diagnostics rather than part production has been practically eliminated. Experience has demonstrated that more frequent measurements, without interrupting production, also allows more immediate detection of special cause events, such as sputtering target or power supply problems, that might otherwise erode yield.

Integrated CIS manufacturing infrastructure work included expanding production documentation and procedures for more effective work, expanding process diagnostics capabilities and associated data collection, and expanding data collection, maintenance, retrieval and analysis capabilities. Preaward activities addressed structured qualification of new equipment emphasizing passing equipment from engineering and procurement groups to the production and maintenance groups. Discussions with management, engineers and technicians clearly identified the need to decrease the time that engineers and technicians spent on production support and maintenance thereby making their time available for scaleup activities - experimentation and support of procurement and qualification of new equipment. To this end, procedures were developed to guide and expedite release of equipment to production.

Integrated manufacturing tasks similar to manufacturing execution system (MES) activities were based on working closely with SSI's Information Services group and using consultants with MES experience to implement the majority of the work. In addition to experience, the plan to use consultants was driven by the need to minimize workload on CIS personnel during all phases of this work. Discussions between the CIS group, the Information Services group and the consultant led to a mission statement and goals and objectives for implementation of MES. Work to implement these tasks was expected to begin early in 2003. However, this work was repeatedly delayed while the consultant worked on other tasks including selection of previously unplanned upgrades in software for company wide Enterprise Resource Planning (ERP) requirements. A second consultant was chosen to implement these plans with the primary focus on integrating existing data sources and existing reports for statistical process control and production management. System specific packages of information for reviews with the engineers responsible for production systems were generated to expand on the general specification. With the goal of maximizing the effectiveness of working with the responsible engineers while minimizing their workload, each package combined detailed tables of proposed data IO for each process (procedure) and reference materials.

SSI's thin-film CIS technology is poised to make significant contributions to DOE/NREL/NCPV long-term goals - higher volume, lower cost commercial products. Subcontract work has allowed SSI to address multiple production bottlenecks thereby allowing SSI to exercise the overall process at higher production rates and to lay the groundwork for evaluation of near-term and long-term manufacturing scale-up options.

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Introduction

Overview

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 cells have exceeded 19% efficiency for devices fabricated at NREL [1]. Small area, fully integrated modules exceeding 13% in efficiency have been demonstrated by several groups [2]. Record breaking efficiencies of over 12% for a commercial large area module have been verified by NREL [3]. Long-term outdoor stability has been demonstrated at NREL by ~30x30 cm and ~30x120 cm SSI modules which have been in field-testing for over fourteen years. Projections based on current processing indicate production costs well below the cost of crystalline silicon [2].

Compared to traditional wafer-based crystalline silicon technologies, new thin film technologies yield products of comparable performance but with significant advantages in manufacturing [2, 4]:

- Lower consumption of direct and indirect materials
- Fewer processing steps
- Easier automation

Lower consumption of direct and indirect materials results in part from the thin-film structure for the semiconductor used to collect solar energy. All three of these manufacturing advantages are in part due to an integrated, monolithic circuit design illustrated in Figure 1. Monolithic integration eliminates multiple process steps that are otherwise required to handle individual wafers and assemble individual solar cells into the final product.

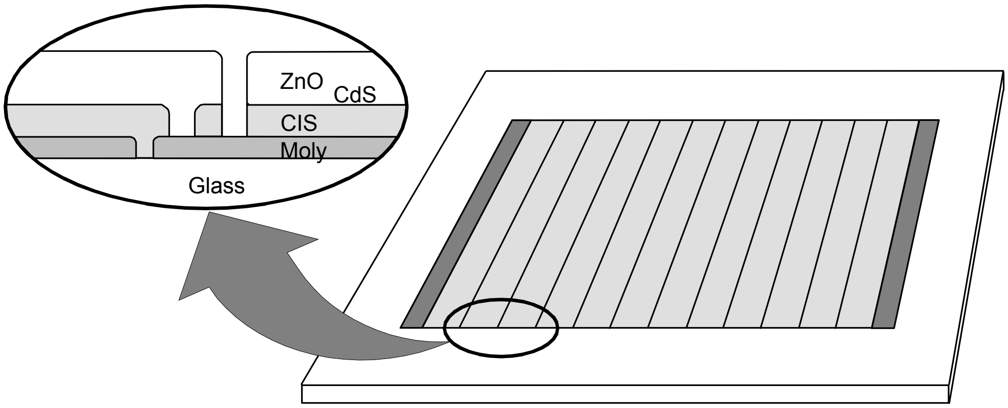


Figure 1. Structure of SSI's monolithically integrated thin-film circuits.

A number of thin film photovoltaic technologies have been developed as alternatives to the traditional solar cells based on crystalline silicon wafers [2]. The technologies with the greatest potential to significantly reduce manufacturing costs are based on alloys of amorphous silicon (a-Si), cadmium telluride (CdTe), CIS and film silicon (Si-film). These photovoltaic thin film technologies have similar manufacturing costs per unit area since all share common elements of design and construction:

- Deposition of typically three layers on a suitable substrate – window/electrode, absorber, and back electrode
- Patterning to create monolithically integrated circuit plates
- Encapsulation to construct modules

Cost per watt is a more appropriate figure of merit than cost per unit area [2]. All thin film technologies have similar manufacturing costs per unit area since they all use similar or equivalent deposition, patterning, and encapsulation processes. About half of the total module cost – material, labor, and overhead – originates in the encapsulation scheme which is for the most part independent of the thin film technology. Costs for alternative encapsulation schemes are typically similar or even higher. The average efficiency of large, ~30x120 cm modules in pilot production at Shell Solar is approximately 11%. This performance is comparable to many modules based on crystalline silicon, and is substantially better than the performance reported for competing thin-film technologies. The lowest cost per peak watt will result from the technology with the highest efficiency, CIS technology, since most thin film technologies have similar cost per unit area.

SSI CIS Process

Most terrestrial photovoltaic products today are designed to charge a 12-volt battery, however the output voltage of an individual solar cell is typically about 0.5 volts. Wafer-based technologies build up the voltage by connecting individual solar cells in series. In contrast, CIS circuits are fabricated monolithically (Figure 1); the interconnection is accomplished as part of the processing sequence to form the solar cell by alternately depositing a layer in the cell structure and patterning the layer using laser or mechanical scribing.

The structure of a SSI CIS solar cell is shown in Figure 2. The full process to form CIS circuit plates, including monolithic integration, is outlined in Figure 3. This process starts with ordinary sodalime window glass, which is cleaned and an SiO_2 barrier layer is deposited to control sodium diffusion and improve adhesion between the CIS and the molybdenum (Mo) base electrode. The Mo base electrode is sputtered onto the substrate. This is followed by the first patterning step (referred to as "P1") required to create monolithically integrated circuit plates – laser scribing to cut an isolation scribe in the Mo electrode. Copper, gallium and indium precursors to CIS formation are then deposited by sputtering. Deposition of the precursors occurs sequentially from two targets in an in-line sputtering system, first from a copper-gallium alloy target (17 at% Ga) and then from a pure indium target. CIS formation is accomplished by heating the precursors in H_2Se and H_2S to form the CIS absorber. Beginning at room temperature, furnace temperature is ramped to around 400ºC for selenization via H_2Se, and ramped again to around 500ºC for subsequent sulfidation via H_2S, followed by cool-down to room temperature. This deposition of copper and indium precursors followed by reaction to form CIS is often referred to as the two-stage process. A very thin coating of cadmium sulfide (CdS) is deposited by chemical bath deposition (CBD). This layer is often referred to as a "buffer" layer. A second patterning step (P2) is performed by mechanical scribing through the CIS absorber to the Mo substrate thereby forming an interconnect via. A transparent contact is made by chemical vapor deposition (CVD) of zinc oxide (ZnO). This layer is often referred to as a "window layer" or a transparent conducting oxide (TCO). Simultaneously, ZnO is deposited on the exposed part of the Mo substrate in the interconnect via and thereby connects the Mo and ZnO electrodes of adjacent cells. A third and final patterning step (P3) is performed by mechanical scribing through the ZnO and CIS absorber to isolate adjacent cells.

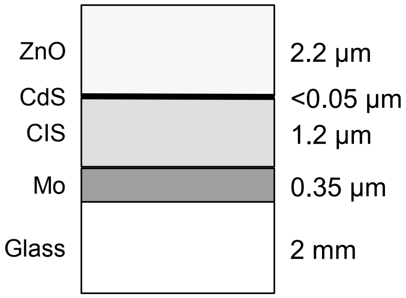


Figure 2. SSI's CIS cell structure (not to scale).

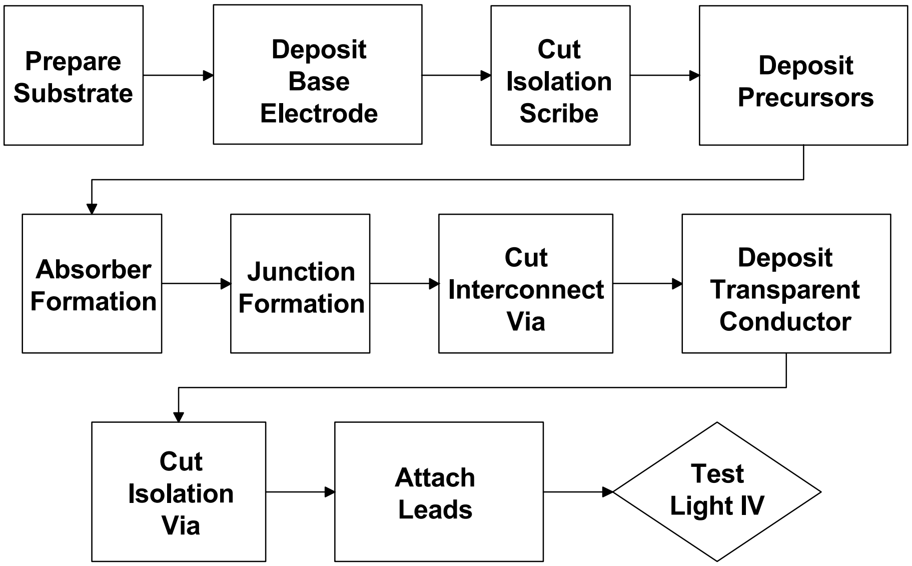


Figure 3. SSI CIS Circuit Processing Sequence.

The CIS-based absorber referred to in this report is composed of the ternary compound $CuInSe_2$ combined with sulfur and gallium to form the multinary compound $Cu(In,Ga)(S,Se)_2$. Gallium and sulfur are not uniformly distributed throughout the absorber but the concentrations are graded; hence, this structure is referred to as a "graded absorber." The graded absorber structure is a graded $Cu(In,Ga)(Se,S)_2$ multinary with higher sulfur concentration at the front and back and higher Ga concentration at the back. Elemental profiles typical of the SSI graded absorber structures are presented in Figure 4. Efficiency, voltage, and adhesion improvements have been reported for the SSI graded absorber structure [4, 5, 6].

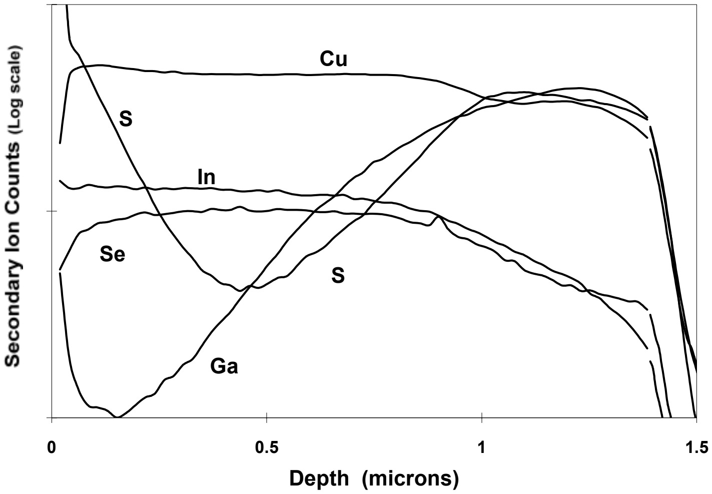


Figure 4. Typical elemental profile for the SSI graded absorber (SIMS from NREL).

Figure 5 illustrates the module configuration used for prototypes and products during this subcontract period. EVA is used to laminate circuit plates to a tempered cover glass and a Tedlar/polyester/Al/Tedlar (TPAT) backsheet provides a hermetic seal. Aluminum extrusions are used to build frames for the modules. In addition to providing a hermetic seal, the combination of the TPAT backsheet and the offset between the circuit plate and the frame provides electrical isolation from the frame.

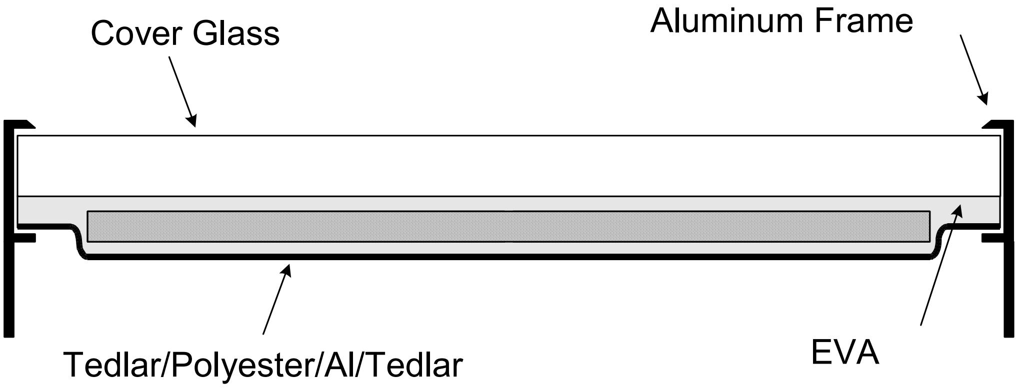


Figure 5. Single circuit plate module configuration with a TPAT backsheet.

Subcontract Activities

Background

The U.S. Department of Energy (DOE), in cooperation with the U.S. Photovoltaics (PV) Industry, has the objective of retaining and enhancing U.S. leadership in the world market. To further this objective, the Photovoltaic Manufacturing Technology (PVMaT) project was initiated in FY 1990 to form a partnership between DOE and the U.S. PV industry, assisting in the improvement of module manufacturing processes and in the substantial reduction of module manufacturing cost. The goals of the project were to improve PV manufacturing processes and products for terrestrial applications, accelerate PV manufacturing cost reduction, lay the foundation for significantly increased production capacity, and assist the U.S. industry in retaining and enhancing its world leadership role in the commercial development and manufacture of terrestrial PV systems. The focus of the program emphasized research and development (R&D) manufacturing process issues.

Four solicitations have been completed since inception of the PVMaT Project and a fifth solicitation is near completion. These solicitations addressed, respectively: (1) process-specific R&D on PV module manufacturing (open only to companies that completed successfully a preliminary problem-definition phase; (2) generic research on problems of interest to all, or to a large portion of the PV industry; (3) process-specific R&D on PV module manufacturing; (4) product-driven PV manufacturing R&D addressing process-specific problems, as well as manufacturing improvements for balance-of-systems (BOS) components and system design improvements; and (5) PV module manufacturing technology and PV system and component technology.

The FY2000 solicitation, “PV Manufacturing R&D—In-Line Diagnostics and Intelligent Processing in Manufacturing Scale-Up,” was a continuation of the PV Manufacturing R&D Project which focused on further accelerating the PVMaT achievements and was designed to be impartial to various PV technologies and manufacturing approaches. The goals are to improve PV manufacturing processes and products while reducing costs and providing a technological foundation that supports significant manufacturing scale-up (100-MW level). Letters of Interest under this solicitation were to address areas of work that could include, but were not be limited to, issues such as improvement of module manufacturing processes; system and system component packaging, system integration, manufacturing and assembly; product manufacturing flexibility; and balance-of-system development including storage and quality control. The primary emphasis was on new and improved in-line diagnostics and monitoring with real-time feedback for optimal process control and increased yield in the fabrication of PV modules, systems, and other system components.

Objective

The objective of this subcontract was to continue the advancement of CIS production at Shell Solar Industries through the development of high-throughput CIS absorber formation reactors, implementation of associated safety infrastructure, an XRF measurement system, a bar code scribing system, and Intelligent Processing functions for the CIS production line. The intent is to open up production bottlenecks thereby allowing Shell Solar to exercise the overall process at higher production rates and lay the groundwork for evaluation of near-term and long-term manufacturing scale-up.

Scope Of Work

The subcontract consisted of the following tasks:

Phase I.

- Task 1. - Investigate conceptual designs for high-throughput CIS absorber formation reactors and implement bar code scribing and circuit plate tracking
- Task 2 - Design, fabricate, and debug XRF measurements for in-line diagnostics and real-time monitoring of precursor sputtering as deposition feedback techniques for improved quality and higher throughput
- Task 3. - Evaluate and specify the requirements for an integrated CIS manufacturing infrastructure such as comprehensive diagnostics capabilities.

Phase II.

- Task 4. - Report on design and specification of a high-throughput CIS absorber formation reactor and the implementation of associated infrastructure for the safe delivery of reactants and safe processing of reactor effluent.
- Task 5. - Fabricate, debug and qualify an in-line XRF diagnostic monitor for improved process diagnostics that is compatible with large-scale production.

Technical Review

Equipment Development

Absorber Formation Reactor

The reactor procurement tasks addressed implementation of the SSI absorber formation process in improved high capacity reactors. The goal was to open up a production bottleneck and allow larger part sizes thereby allowing exercise of the overall process at higher production rates.

Background

SSI's CIS processing facility produces nominally 1x4 ft. circuit plates for production and process R&D. Full size 1x4 ft. circuit plates are used for SSI's 40 W product (product designation ST40). Multiple smaller modules are also produced from 1x4 ft. circuit plates. Most infrastructure, with the exception of absorber formation reactors, is compatible with larger circuit plates - up to nominally 2x5 ft. Overall capacity increases can be achieved by increasing the substrate size processed in the absorber formation reactors.

Reviewing this approach in light of recent process development has led to the conclusion that substrate size scale up may not be the only or best route to increasing capacity. Production capacity increases have been achieved through process development to increase the number of substrates processed in a reactor batch. This process development addressed tendencies toward increased warping and poorer adhesion for larger substrate loads. Increased capacity by stacking reactors one over another, using the floor space that would normally be required for one reactor, has also been demonstrated. Higher power products can be fabricated using multiple circuit plates rather than larger circuit plates; prototype modules using two 1x4 ft. circuit plates have been demonstrated. In total, the advantage of larger circuit plates may not be as great as expected prior to these developments. Even so, increasing the substrate size is an option that has potential value and was defined as a figure of merit to pursue with vendors for new reactors. Vendors were asked to respond to a request for reactor designs combining:

- Nominally 2x5 ft. substrates
- Enough substrates in a reactor load to increase capacity
- Demonstration or otherwise guaranteeing temperature uniformity adequate to implement the SSI process without warping the substrates by more than about 2 mm.

The importance of reactor design to the CIS formation process was demonstrated when first scaling from a baseline process in small reactors to a reactor capable of processing large (1x4 ft.) areas. Differences between a baseline process for relatively small substrates and the process executed in the first large area absorber formation reactor were responsible for differences in absorber layer properties and cell performance. These differences were then related to differences in the materials of construction and the physical design of the large reactor. As a result of these advances in understanding the influence of reactor design on performance, SSI designed and built three generations of 1x4 ft. reactors based on a more direct scale-up of the baseline reactor. Success with this development effort was demonstrated by comparable performance for baseline and large area circuit plates.

Reactor Design And Specification

The majority of subcontract work began after execution of the subcontract rather than during the preaward timeframe. During the preaward timeframe, the schedule for reactor procurement work was reviewed with the goal of accelerating procurement after subcontract award and minimizing risk. In particular, completion of the "Reactor design selection" task was scheduled for the end of 2002. Three tasks were identified to accomplish this work:

- Modeling
- Mockup
- Vendor Search

Modeling work was pursued with University of Florida to support vendor search activities. The goal of the mockup task was to demonstrate that large area substrates could be heated without warping. The vendor search task included generating a list of potential vendors from known vendors and new vendors found through the Thomas Register and the Internet.

Modeling

Preaward activities included beginning thermal modeling collaborations with Prof. Tim Anderson, University of Florida (UF), Chemical Engineering Department. Themes for these collaborations were related to the UF interests in modeling CIS reactions. The main effort was modeling reactors or reactor components to achieve thermal uniformity and to avoid warping while increasing capacity. Data including sketches of design options, previous modeling results, and previous reactor mockup results were sent to UF as an introduction to SSI tasks for this subcontract. Suku Kim was a graduate student with a thesis topic related to the reaction of precursors to form CIS. During the preaward timeframe, Suku Kim modeled the basic performance of insulator designs with unique potential for use in new reactors. Gaining a general understanding of the performance of these insulators would allow consideration of new reactor design options. Preaward activities for this task also included sketching potential reactor designs and outlining requirements for new reactor systems.

Quartz is one material that can be in contact with the reactants for CIS formation at high temperatures without corroding. UF modeled insulator designs based on surrounding insulation or IR reflectors with quartz to achieve good insulation while simultaneously isolating the metallic portions of structures from the reactants. Similar structures are used in many technologies from artificial hearts to annealing furnaces. The following sketch, Figure 6, shows the basic construction. Modeling focused on a design based on multiple thin stainless steel reflectors separated by quartz plates, quartz felt insulation, or vacuum.

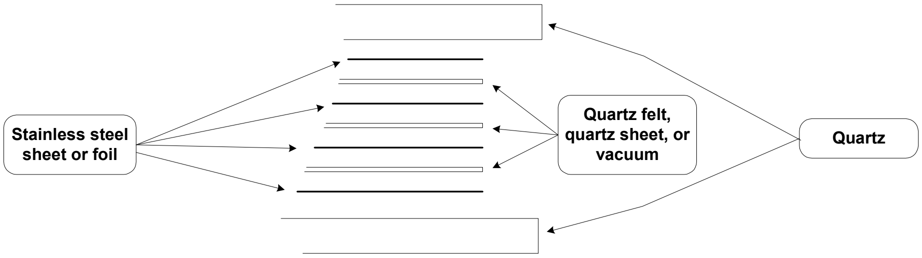


Figure 6. Sketch of a generic insulating structure.

A report was received with initial results indicating that this insulator design is effective over a broad temperature range. The insulator design is effective for heaters operating at about 1000°C and effective at the temperature of substrates, ~500°C. Additional modeling results for minimal insulation were requested to have a more direct comparison with the insulating approach for some subsections of existing reactors. Combined results of UF modeling indicated that dramatic improvements in insulating properties are possible. The approach modeled can be applied to some subsections of existing reactors and can be effective for insulating both heater and substrate areas in future reactors.

The possibility of interacting with a group at Sandia to model reactors was pursued. "The DAKOTA Project: Large-scale Engineering Optimization and Uncertainty Analysis" modeled relatively small multi-wafer low-pressure chemical-vapor-deposition (LPCVD) reactors that are widely used in the microelectronics industry [7]. This experience and the computer modeling tools used for this analysis were potentially applicable to SSI's large area reactor needs. A relatively detailed discussion of SSI's needs and the potential value of similar modeling were sent to Sandia representatives. Review of this material indicated promise for modeling work. However, SSI's contract with NREL precluded working with Sandia since Sandia and NREL are at least partly funded from a common source. Modeling options were also discussed with each potential vendor for reactor procurement.

Mockup

The goal of the mockup task was to demonstrate that large area substrates, nominally 2 by 5 ft., can be heated without warping and to begin exploring the achievable thermal uniformity for various reactor and substrate configurations. Dimensional changes during thermal processing are observed; therefore, mockup efforts included characterizing dimensional changes for large substrates.

An adequately large industrial furnace within driving distance was found for the mockup work. The interior dimensions of the furnace were 5 ft. by 5 ft. by 15 ft. (Figure 7). Heat is provided by two gas jets in the front bottom left of the furnace and the rear bottom right of the furnace. Thus, air tended to swirl around in the furnace. The temperature uniformity achieved in this furnace combined with the simulated reactor walls was expected to allow for adequate testing; however, some features for achieving thermal uniformity that might be incorporated in reactor designs could not be accommodated.

Figure 7. Furnace for reactor mockup work.

Reactor walls and internal structures for holding substrates were simulated in metal. This mockup was then placed in the large industrial furnace for heating. The mockup did not have the advantage of multiple heater zones as in production reactors. On the other hand, the mockup did not have some of the problem areas of a real reactor. Figure 8 shows glass substrates loaded in the bottom half of the simulated reactor. Figure 9 shows the full simulated reactor ready for loading into the furnace.

Figure 8. Glass substrates loaded in the bottom half of the simulated reactor.

Figure 9. Simulated reactor ready for loading into the furnace

Multiple mockup runs were made varying the number of substrates: 5, 21 and 41 substrates. Additional mockup runs were made varying the cooldown rate. For the 21-substrate load, temperature variation within the simulated load was similar to the temperature variation observed for 1x4 ft. substrates in present reactors. Temperature variations ranged from minimal (< 10 ºC) to significant (> 100 ºC) with increasing substrate load. Substrate warping ranged from minimal to significant with increasing substrate load for higher cooldown rates. Repeated mockup runs with slower cooldown rates indicated that a slower cooldown does not necessarily avoid warping.

Dimensional changes of substrates are produced by thermal exposure during normal CIS processing. These small dimensional changes are not an issue if the separation of interconnect patterns in the Mo is consistent over a substrate and predictable, i.e. if the dimensional changes are uniform. Test substrates were made using standard Mo electrodes with laser-scribed patterns as references. Offsets from the original pattern positions were measured after heating for various mockup loading conditions. For each loading condition, offsets were measured for multiple substrates and multiple positions on substrates. Results of these dimensional change measurements paralleled the substrate warping results – variation from minimal to significant with increasing substrate load. Alignment or separation errors over the whole 2x5 substrate, with the exception of an approximately 1 inch boarder, were measured as 0.002 inches and 0.004 inches for the 21 and 41 substrate runs respectively. Dimensional changes followed the same trends as substrate warping and therefore should not be a problem if substrate warping is minimal.

Vendor Search and Reactor Specification

New equipment requirements were defined during joint meetings with engineering and procurement personnel:

- Thermal requirements for the reactors and parts
- Location and orientation of substrates
- Limitations on the materials of construction for use in contact with the reactant gasses at high temperatures
- Limitations on the physical layout of the reactor

Containment of toxic and flammable gasses, even in the event of system failure, was a design prerequisite for new reactors. This primary consideration was addressed for two types of containment in three different large area reactor designs. One approach achieved containment by surrounding the reaction vessel with a second nitrogen filled vessel. The second approach achieved containment by dilution of the hazardous gasses with nitrogen from a ballast tank. A consensus was reached that modified versions of either of the two types of containment may be viable for future systems.

An additional figure of merit was system loading and unloading with the aid of “automation”. This could mean aids for operators when handling substrates and groups of substrates or full automation - mechanical systems that do not require operator assistance.

A list of about fifty potential equipment vendors for large area reactors was generated from known vendors and new vendors found through the Thomas Register and the Internet. A statement of work (SOW), including a specification and terms and conditions, was outlined for group discussion, drafted, and consensus was reached on a final version for distribution to potential vendors. Nondisclosure agreements were distributed to the potential vendors and the

SOW was distributed. SSI hosted visits by potential vendors, visited potential vendors and received proposals from a relatively small subset of the original list of potential vendors.

The specification requested that vendors respond with a design approach and a commitment to thermal uniformity. Guidelines supplied to the vendors for the required thermal uniformity were based on a range between the uniformity that SSI has achieved for ~1x4 ft. substrates and better uniformity that, based on preliminary discussions with vendors, should be readily achievable for a symmetric part load (a few degrees centigrade). However, no vendors had previous experience directly applicable to SSI's large substrate and asymmetric load requirements. Vendors in general had some applicable experience but typically experience with only some aspects of heating an asymmetric load of large substrates. No vendor was willing to define and commit to a thermal uniformity specification.

Most vendors proposed modeling potential design approaches using a third party. Other vendors proposed in-house modeling but had minimal experience. Outsourcing of the analytical engineering is typically required since most vendors have hardware design and assembly engineers rather than personnel with the analytical engineering capabilities needed to verify an appropriate approach. All vendors would have been glad to build a system based on a SSI hardware definition if they were not responsible for the design approach or success of the implementation. Since no vendor committed to achieving any level of temperature uniformity, the responsibility for temperature uniformity became solely SSI's responsibility. SSI could accept a vendor design with no guarantee of success or define the design approach for implementation by a vendor, again with no guarantee of success from the vendor.

Modeling results and discussions with vendors indicate that alternative geometries for very high capacity and improved thermal uniformity are possible based on emphasizing forced convection or radiative heating. Some possible implementations may be long-term options for processing as many as 100 substrates per run. Discussed and proposed design options ranged from inadequate to overly complex. A system that will achieve good thermal uniformity for very high capacity is apparently possible but only with additional analytical engineering and probably corrections to the first implementation. And again, all risk for success would be solely SSI's risk. For example, thermal uniformity might be achieved using directional IR heaters and using absorbing or reflecting rods between the substrates to increase heating at the center of the stack of substrates. Corrections to the first rod designs might be relatively easy but also inevitable. When adding consideration of the enclosure, this design concept becomes complex and therefore risky. However, discussions with potential vendors indicated that the capital cost does not necessarily scale directly with reactor size, design complexity or the extent of required basic engineering. Therefore, capital cost does not necessarily become unacceptably high for future very high capacity reactors.

SSI requested that all potential vendors provide additional information since no vendor had previous experience directly applicable to SSI's large substrate requirements or would commit to any thermal uniformity specification. The objective was to define a design that would meet SSI immediate requirements, about 25 substrates per run. Information was also requested regarding how the vendors would demonstrate capabilities during each stage of design and equipment fabrication and thereby minimize the risk for procurement of a viable production machine. The additional information requested included:

- Definition of the method to be used to obtain temperature uniformity
- Definition of the theoretical or physical modeling with temperature profiling that would be used to demonstrate viability of the proposed design
- Additional resources needed
- Schedules
- Costs

SSI reviewed this information and defined additional design specific requirements for selected vendors. These requirements were defined to:

- Minimize the risk of inadequate temperature uniformity
- Minimize the risk in realizing a viable system
- Minimize the risk of major system failures
- Maximize reliability by applying SSI experience to the definition of system details

System attributes that were considered included:

- Number and geometry of heater zones
- Reactor access hardware
- Vacuum seal methods
- Vacuum and gas flow equipment
- Materials requirements
- Substrate handling hardware
- Reactor control systems and integration with existing systems
- Specifics of safety systems
- Software and hardware design approval hold points
- Specifics of boats for two glass substrate sizes

A vendor for the absorber formation reactor was selected in April 2003 based on the response to this request. In October, SSI authorized the equipment vendor to begin the first phase of work with a hold on further work.

The selected configuration was a simple tube furnace similar in construction to conventional diffusion furnaces. As seen in the following photograph of an existing furnace for 1x4-foot substrates, Figure 10, a group of substrates is loaded in a boat or carrier, placed into the tube, and processed as a batch. Cooling in this reactor should be similar to cooling in the mockup. Design features that were not simulated by the mockup were included in the equipment specification to improve thermal uniformity during heating.

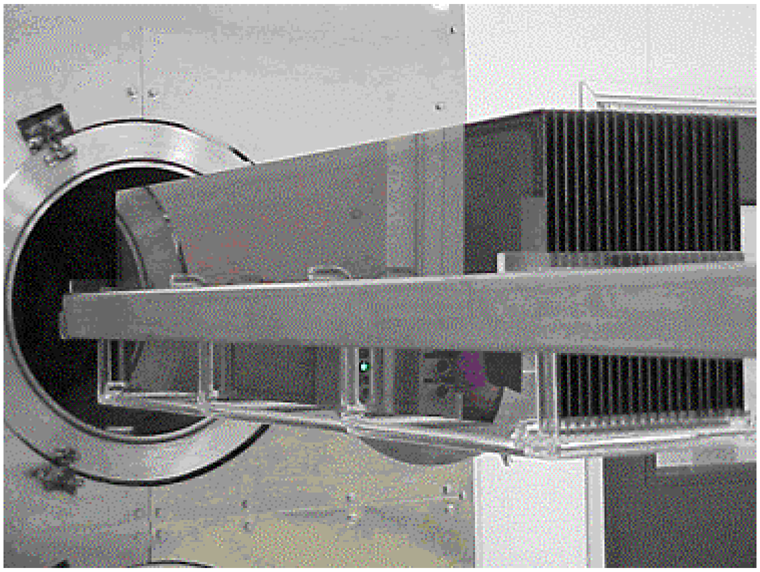


Figure 10. Tube furnace substrate loading.

The equipment vendor began design work on the absorber formation reactor with emphasis on heater options and constraints. SSI and the equipment vendor met to discuss hardware design constraints that required modification of the original specification. Tube size considerations imposed limitations on the practical length for heater zones. The position of heater dead zones was also considered.

The equipment vendor visited the heater fabricator with the goal of learning as much as possible about furnace fabrication and meeting SSI's needs. Discussions included the fabrication process, wiring, control, geometric constraints and heater geometry. Since the heater enclosure would be one part of the gas containment assembly, discussions with the furnace vendor also included design options for the most appropriate approach to containment of toxic and flammable gasses in the event of tube failure. The furnace vendor completed work on selection of hardware approaches and development of these approaches for review. A final design review was held on April 1, 2004. All previously discussed issues were resolved.

Safety Infrastructure

The following general discussion of safety systems at SSI is intended as an overview of engineering and procedural control measures used to handle H_2Se and H_2Se. The information is generic and highlights subcontract work with no attempt to elaborate on all considerations necessary to implement similar infrastructure. Do not use this report as a guide. Publications such as, "Reference Guide For Hazard Analysis In PV Facilities" by V. M. Fthenakis from Brookhaven National Laboratory are possible resources for beginning consideration of similar infrastructure [8 , 9].

Pre-subcontract Infrastructure

The objective of this subcontract work was to continue advancement of CIS technology at SSI by increasing throughput for processes that are production bottlenecks thereby allowing exercise of the overall process at higher capacity. Prior to this subcontract work, multiple absorber formation reactors were supported by one set of safety systems for supplying process gas and scrubbing reactor effluent. Scrubbing capacity was sufficient for increasing throughput by adding additional reactors. However, all absorber formation production capacity was limited by the time required for scrubber maintenance or service and this time was amplified by the preparatory time required to end processing in each reactor; in particular, waiting for the end of processing in the last reactor started. Similar production capacity limitations were due to gas cylinder infrastructure that was sized for initial process development and early production rather than production in multiple large reactors. Replenishing the process gas supply occurred often because of the use of small cylinders. Also, engineering and procedural hazard control measures dictated that absorber formation reactors were not operated while the gas supply was replenished. These limitations related to safety system infrastructure and procedures significantly inhibited production.

The following sketch, Figure 11, depicts the overall safety system infrastructure for supplying process gas and scrubbing reactor effluent. This sketch depicts this infrastructure prior to subcontract work.

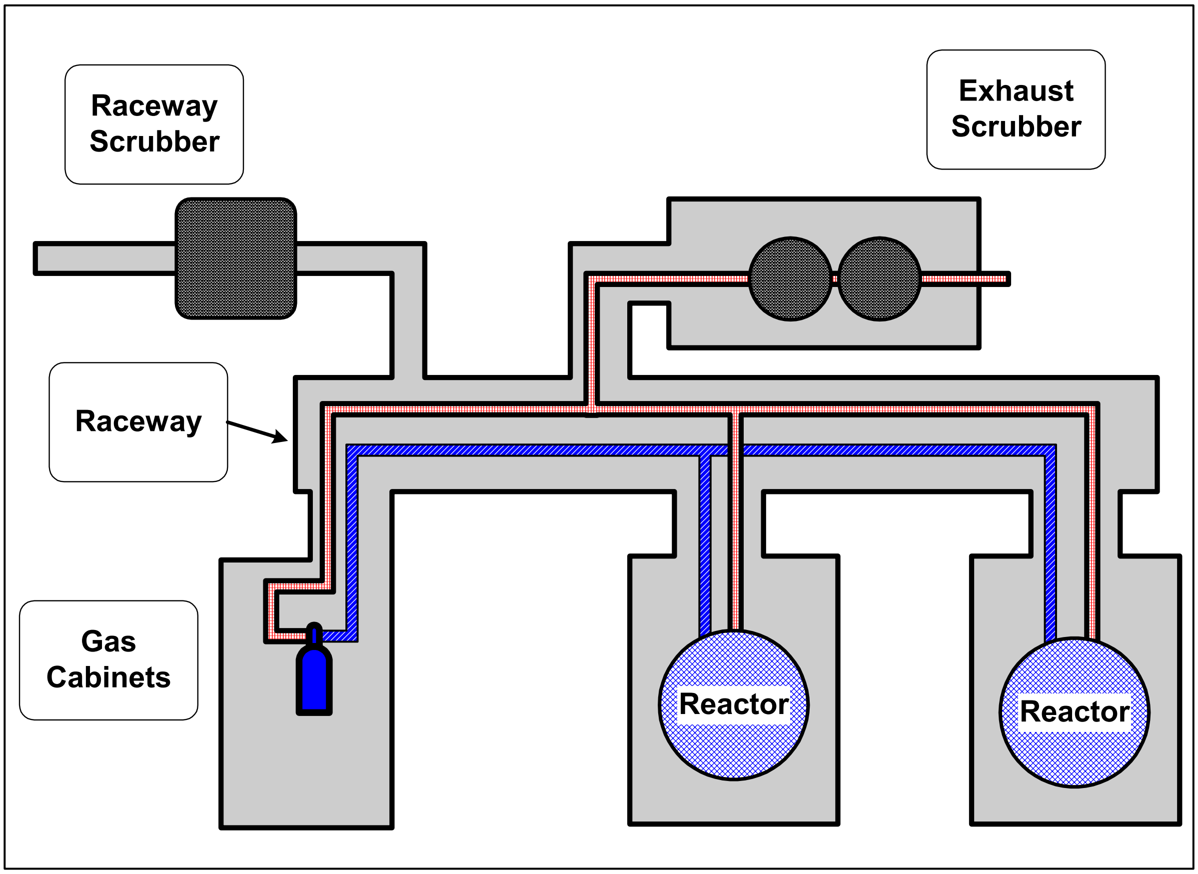


Figure 11. Presubcontract safety system infrastructure.

Figure 11 depicts a raceway or a secondary enclosure connected to the raceway (gray background) encompassing all vessels that may contain hazardous gas: reactors, gas cylinders, gas distribution lines and effluent lines. Forced airflow is maintained from vents in each enclosure through the raceway to the raceway scrubber. In an extraordinary event leading to a gas release, the gas is confined to the raceway, swept to the raceway scrubber and decomposed. The exhaust scrubber, actually two redundant scrubbers in series, decomposes process gas from the reactors and from pump purge systems for the gas cylinders. Hydride gas detectors monitor the air at multiple locations throughout this infrastructure. A "watchdog" computer receives status information from the gas detectors, reactors, gas cabinets and scrubbers. The watchdog computer logs events related to reactor and system operation and responds to fault conditions with warnings or shutdown of operations as appropriate.

Subcontract Work

Subcontract work expanded the exhaust scrubber, raceway scrubber and gas cylinder infrastructure for increased throughput. The following sketch, Figure 12, depicts the overall infrastructure with implemented subcontract improvements.

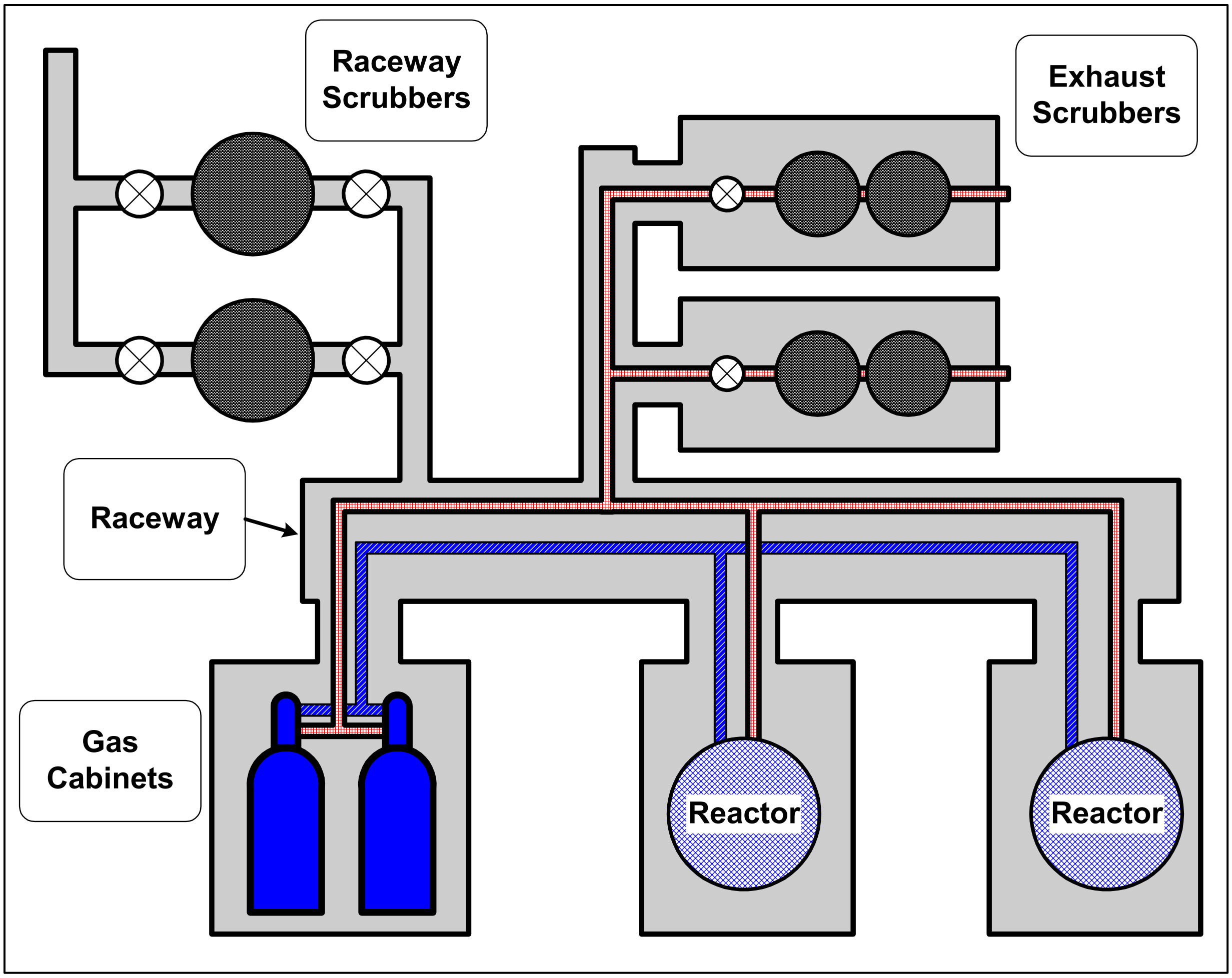


Figure 12. Upgraded safety system infrastructure.

Gas cylinder cabinets and associated infrastructure for larger gas cylinders were installed. Parallel exhaust and raceway scrubbers and associated infrastructure were installed to allow reactor operations using one set of scrubbers while simultaneously performing maintenance or service on of the other.

Duplication of the exhaust scrubber along with valves for selecting one scrubber at a time now allows maintenance or service work while continuing operation of the reactors. Figure 13 is an image of the new scrubber taken through the enclosure door. One of the two series connected scrubbers is centered in the picture and part of the second is visible in the right hand side of the picture. One unit adequately scrubs reactor effluent. The second series connected scrubber provides redundancy for safety. These scrubbers are commercially available compact, highly efficient scrubbers designed for this and similar applications. The scrubbers consist of a venturi eductor and a packed column constructed using corrosion resistant materials – primarily PVC and stainless steel. A potassium hydroxide solution (KOH) is pumped through the eductor thereby entraining gas, creating suction on the effluent lines and beginning the reaction of effluent with the KOH. The reactor effluent then flows through a packed column that is continuously sprayed with KOH thereby providing a large surface area for completion of effluent reaction with the KOH. Although this type of scrubber requires more maintenance than other types, it is cost effective for this application where effluent is continuously reacted.

Figure 13. Effluent scrubber.

The precontract raceway scrubber was a design similar to the effluent scrubbers but with a very large packed column and a blower to handle the high air volume required for the raceway. Subcontract work implemented new technology for lower cost and minimal maintenance rather than adding a parallel scrubber with a similar design. As pictured in Figure 14, two parallel radial flow carbon adsorber units were implemented. Ducting and valves are visible in the top half of the picture. The top half of the 48-inch diameter, 91-inch high absorption canisters is visible in the lower half of the picture. Valves allow selection of either unit thereby allowing maintenance or service while continuing operation of the reactors. Each unit is a radial flow carbon adsorber designed for efficient scrubbing at high flows with a low pressure drop. The adsorber units consist of a distributor tube and a retention screen for the activated carbon. Inlet vapors enter the distributor tube, then flow horizontally through the carbon bed, and then through the retention screen to free air space inside the canister wall. The purified vapors then travel to the upper section of the unit and the outlet duct. The units are equipped with forklift channels for easy maintenance. The carbon adsorber units require less maintenance than recirculating KOH scrubbers and are therefore cost effective for this backup application where the carbon absorber is not regularly depleated.

Figure 14. Raceway scrubber.

Manually purged gas cabinet modules designed for limited capacity gas cylinders were replaced with automated modules for larger cylinders. Figure 15 is a photograph of the new gas cabinet modules. A dedicated computer based control system provides functions such as switching from an empty to a full process gas cylinder and purge procedures required to connect and disconnect cylinders. The cabinets are located in a room separate from the reactors thereby allowing replacement of gas cylinders without requiring procedural control measures that would interfere with reactor operations. Fewer cylinder changes are required using the larger cylinders. Also, using smaller cylinders required a wait time between starting reactors while evaporation of the liquid reactants reestablished pressure in the reactant supply lines. This imposed procedural limitation on production operations whereas the pressure drop is insignificant for large cylinders and therefore there are no similar limitations for production. In contrast to precontract capabilities, gas cylinder changes occur in parallel with production and there are no limitations on reactant availability that previously inhibited production.

Figure 15. Automated cabinets for larger cylinders.

Figure 16 is a picture of the computer based watchdog system that monitors lab sensors, displays and logs lab status, and enables operation of production systems based on the status of all safety infrastructure. Hydride gas monitors are mounted on the wall near the computer. This subcontract work included implementing additional hydride gas monitors necessary for extended monitoring at new locations for the new scrubbers, gas cabinets, and extensions of raceways and gas manifolds.

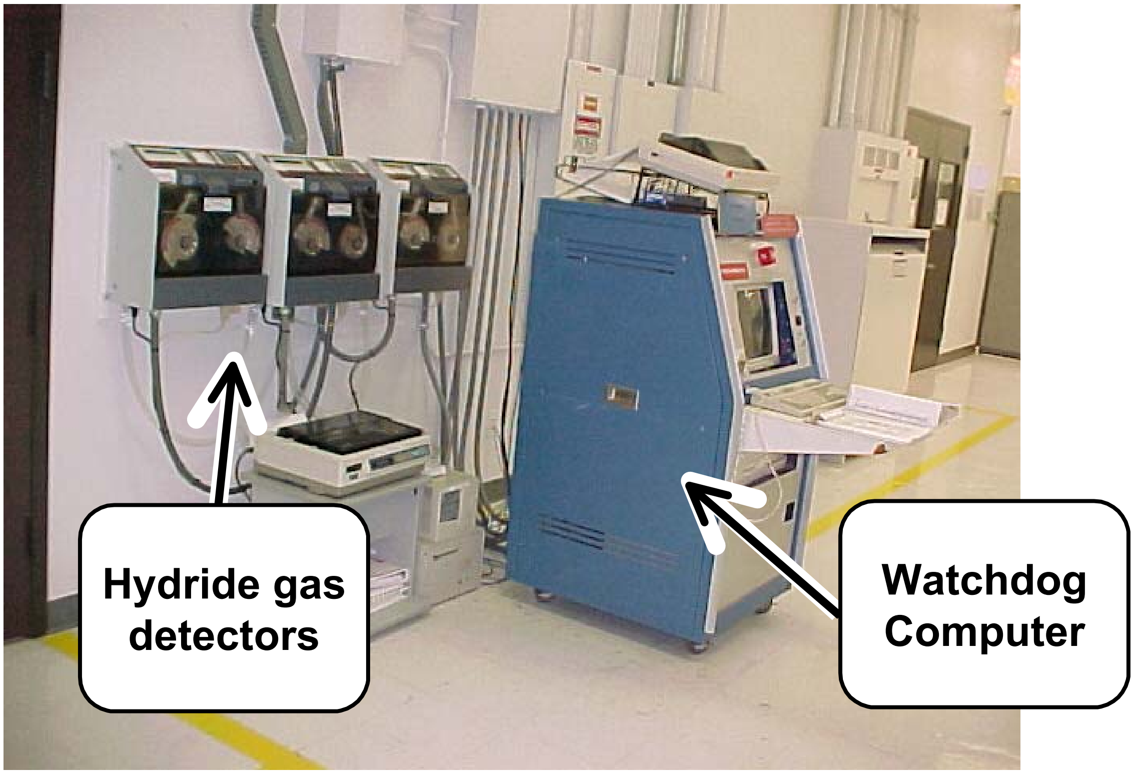


Figure 16. Watchdog computer and hydride gas detectors.

In summary, prior to this subcontract work, multiple absorber formation reactors were supported by one set of safety systems for supplying process gas and scrubbing reactor effluent. All absorber formation production capacity was limited by the time required for scrubber maintenance or service. The time required for this work was amplified by the preparatory time required to end processing in all reactors. Duplication of the exhaust scrubber along with valves for selecting one scrubber at a time now allows maintenance or service work while continuing operation of all reactors. Similarly, redundancy implemented for the raceway scrubbers allows maintenance or service without interfering with production. Also, maintenance has been simplified by replacing maintenance intensive raceway scrubbers based on recirculating KOH with carbon filter units. Similar production capacity limitations were due to gas cylinder infrastructure that was sized for initial process development and early production rather than production in multiple large reactors. Subcontract work has allowed the use of larger cylinders at a lower cost per pound of reactant. Less time is required for cylinder changes and a limitation on the time between starting multiple reactors has been eliminated.

Bar Code Scriber

Bar code scribing and substrate and circuit plate tracking improving productivity and also provided high quality data for tasks related to integrated manufacturing infrastructure. The majority of this subcontract work occurred during the preaward timeframe.

Background

Prior to implementing barcode scribing, individual substrates were tracked through each process steps based on a hand scribed serial number on the substrate. At each process step, the operator read the serial number and then filled in a form with the serial number and status of each part. This rudimentary system was indispensable for yield tracking. However, this tracking method was not scalable to high capacities and the accuracy of transactions was an issue even at low production rates. Barcode labels could have been used after circuit plate fabrication; however labels are compatible with circuit plate fabrication only after completion of all high temperature and wet processing.

Implementation

Subcontract activities addressed implementation of laser-scribed barcodes on glass substrates and the requirements for reading these barcodes. Decisions on implementation options were made during a design analysis phase. Minimization of additional operator tasks for part tracking at each process step was a major consideration. Manual data entry and scanning operations were eliminated wherever appropriate. A comprehensive solution was defined by surveying available barcode scribing and reading options for compatibility with SSI processing of coated glass circuit plates.

Barcode scribing using a CO_2 laser was selected based on discussions with potential vendors and test results using SSI substrates. In addition, selection of the best equipment set for SSI's needs included consideration of: machine and human readability, equipment durability for industrial use, cost of operation, the desired size of the area to be scribed, and the availability of a complete as possible equipment set with pre-integration hardware and software for scribing and scanning. Both a "barcode" and a large numeric serial number that is readable at arm's length were specified. Figure 17 illustrates the corner of a substrate with both a readable serial number for humans and a 2-dimensional barcode for machines.

A local system integrator accomplished fabrication and installation of the barcode scribing systems. Barcode readers were placed in conjunction with production equipment at multiple sites throughout the production facility.

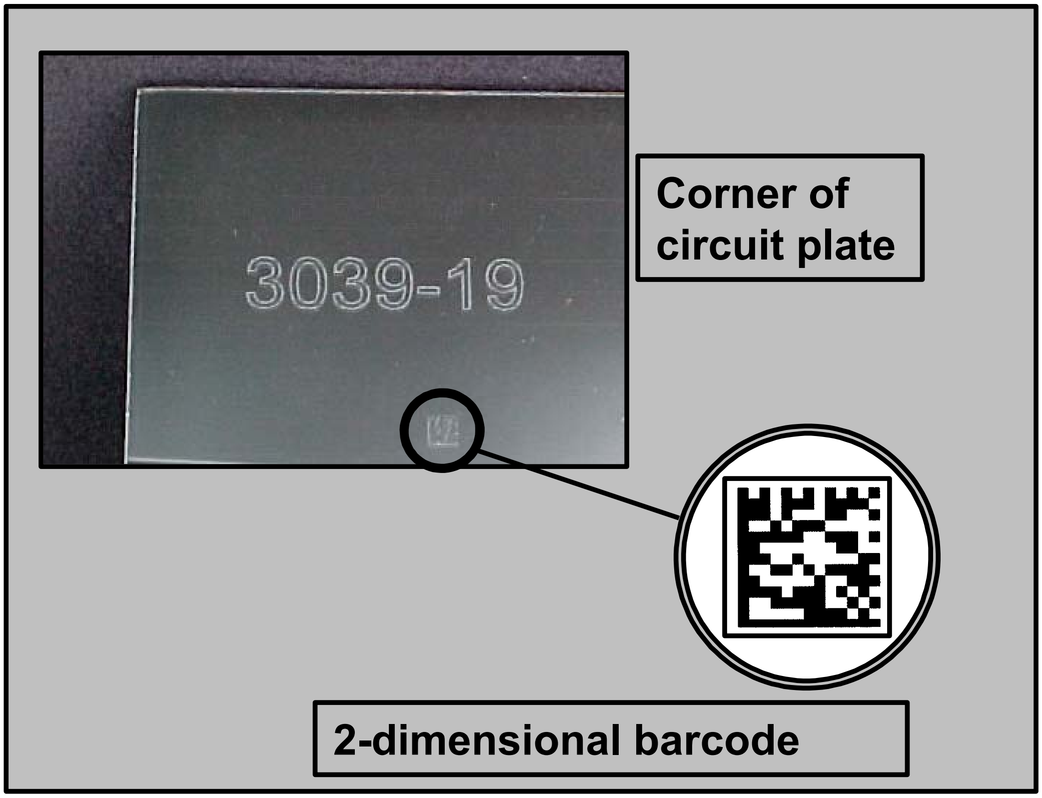


Figure 17. Laser scribed readable serial number and a 2-dimensional barcode.

Barcode scribing has improved production productivity; bar code reading has proven to be easier, faster and more accurate than manual reading of hand scribed serial numbers. Process data ambiguity due to duplicate and missing serial numbers has been practically eliminated. Engineering productivity has also improved since the frustrating and time consuming task of reconciling data with erroneously logged serial numbers has been practically eliminated.

The objectives of this subcontract did not directly address yield improvements; however, yield improvements were obtained through process development for equipment procured and implemented for this subcontract [10]. A study of yield loss due to breakage during the absorber formation process demonstrated that breakage associated with hand scribed serial numbers was one of the major causes of breakage. Hand scribing serial numbers using a diamond scribe damages the glass in a way similar to the purposeful damage used to make a controlled break. Stresses induced by the thermal cycle during the absorber formation process would preferentially trigger glass breaking at the hand-scribed serial number. The use of laser scribed bar codes reduced this kind of breakage by 88%.

XRF Process Diagnostics

X-ray Florescence (XRF) as a sputtering deposition feedback technique was pursued to provide both improved data quality and higher sputtering system throughput. Subcontract work for this and prerequisite tasks included developing conceptual designs for alternative XRF measurement approaches, selecting the best approach, developing specifications, procuring a system, demonstrating applicability and qualifying the system for use by production.

Background

SSI has demonstrated that precursor sputtering is a good choice for large scale production with appropriate:

- Equipment
- Process definition
- Process diagnostics
- Procedures
- Maintenance
- Training for operators and maintenance personnel
- Qualification of source materials

Precursor sputtering diagnostics characterize and lead to the control of the absorber thickness and the Cu/(In+Ga) ratio (CIG ratio), which are critical parameters in the production of high efficiency CIS devices. Precursor deposition occurs sequentially from two targets in an in-line sputtering system, first from a copper-gallium alloy target and then from a pure indium target. Prior to this subcontract, the deposition uniformity and rate of each target was measured based on a modified quartz crystal technique. Quartz crystals on a glass carrier were run through the sputtering system twice, the first pass for deposition of the copper-gallium film, and the second for deposition of the indium film. The thickness of each layer was determined based on crystal resonant frequency differences before and after the depositions.

A set of 10 crystals was distributed across a substrate to characterize the uniformity of deposition across the substrate width. This was especially important during initial system setup since a shift in deposition uniformity for either precursor deposition can lead to regions of unacceptable CIG ratio even if the measurement of an average composition appears acceptable. The procedure was executed at the beginning of each production run to set the deposition parameters within specifications and executed again after the run to assure that processing of all substrates was within specifications. A model using this data and including the effects of changes in sputter rate with target age was the basis for production process control - the maximum duration for a run of substrates without additional measurements and when to change sputtering targets [11].

The quartz crystal based process control approach assured high reproducibly and yields for the precursor sputtering process. However, implementation of the approach required up to 40% of the potentially available production time! Implementation of process control based on XRF measurements was proposed primarily to decrease the time required for diagnostics.

X-ray Fluorescence is a form of atomic spectroscopy based on exciting a sample with X-rays and measuring the fluorescence spectrum. The energies and amplitudes in the fluorescence spectrum characterize the atomic species and their concentration. SSI and other groups have applied XRF measurements to the fabrication of CIS solar cells [12, 13]. SSI's previous experience was with small samples cut from large substrates and then either directly measured or dissolved before measurement. XRF system sample size limitations dictated cutting up the large substrates. Dissolving samples before analysis avoided, substrate background noise issues, potential measurement ambiguities related to the nature of the layered structures and the potential for change in the structure with time due to interdiffusion of the three precursor elements. These approaches to XRF based process control were unacceptable primarily because of long measurement turnaround time.

Considerations for this subcontract work included:

- Safety
- Evaluation of wavelength versus energy dispersive signal analysis
- Evaluation of in-line versus in-situ approaches
- Measurement idiosyncrasies related to SSI layered precursor structures
- Ease of use and integration with SSI production protocols
- Process quality
- Cost
- Productivity

Implementation

Delays in this work occurred due to the voluntary resignation of the responsible engineer. Engineering consultants, William Pope and later Robert Erickson, IPC Systems Engineering Inc., were hired to continue this work while finding a permanent replacement.

The equipment vendor for this subcontract work could not meet the delivery schedule for the system as originally specified, which included an X-Y mechanical table. To minimize the impact of delays, the vendor provided a leased unit without a mechanical table in early December 2003. Automated sampling of multiple areas on a large substrate was not possible with this system; however, renting allowed process development on similar equipment and use by production before delivery of the fully capable system. Production use of the leased system required additional operator time but goals for improved sputtering system utilization were met.

Initial testing indicated the need for process and equipment development to address:

- Precision and accuracy

- Calibration algorithms for determining the individual thickness of indium and copper gallium alloy layers based on measurement of a stack of thin films
- Compensation for the background signal from the glass substrate

Accuracy and Precision

Accuracy and precision tests were based on automated measurements of the same spot on multiple CIG structures. Results for the copper gallium layer were on target (within 0.1%) with very little variation (0.5% std. dev.). However, results for the indium target were inadequate. The indium measurements were off by 8.7% with high variation (16.1% std. dev.). The source of the problem was traced to overlap of the indium peak and background noise from the glass substrate.

As shown in Figure 18, the XRF signal peak for copper gallium is located in a region where there is relatively low emission from the glass substrate. In contrast, the indium peak has lower signal strength and is located where the emission from the glass substrate is greatest. Hence, the signal to noise ratio for indium measurements was poor.

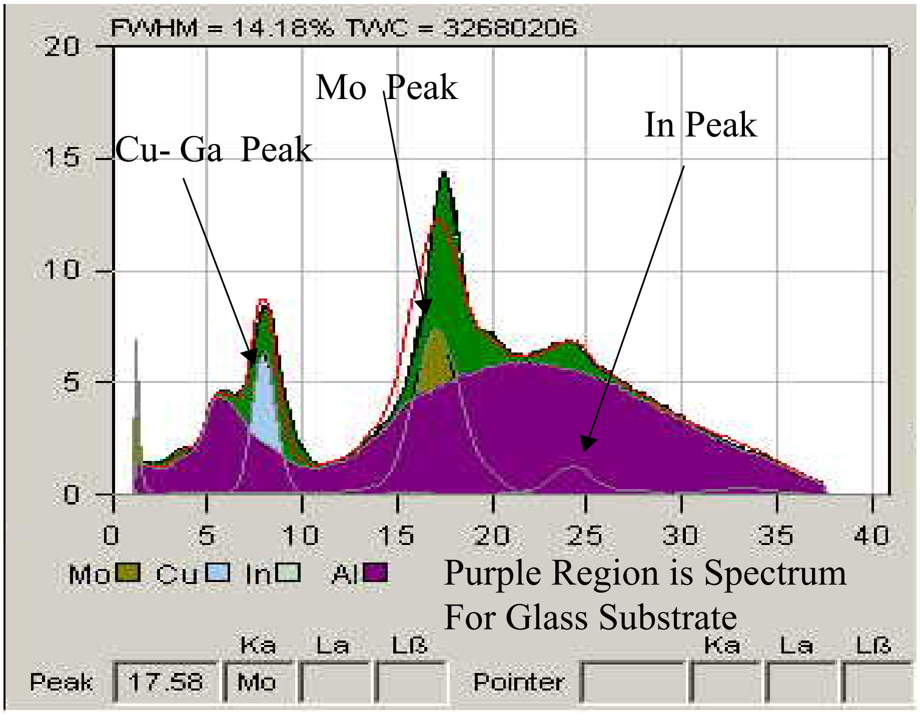


Figure 18. XRF Spectrum of CIG Structure.

Two advancements were made to minimize the effects of this low signal to noise ratio. First, the integration time for each measurement was doubled to improve counting statistics. Second, software upgrades by the system vendor allowed compensation for background noise from the substrate. Results for both the copper gallium and indium layers were on target (both within 0.1%) with very little variation (respectively 0.1% and 0.4% std. dev.).

Qualification

Qualification activities began using the leased XRF unit without a mechanical table. Feedback from the XRF measurements and knowledge of the deposition process is now the qualified basis for computer based updates to the CIG process parameter set points. XRF process control has also been qualified for the relatively straightforward deposition of the Mo base electrode.

Interruption of part production was required for crystal-based process control. For XRF based process control, production procedures have been developed that practically eliminate the time used for diagnostics instead of part production. Nondestructive measurements are made directly on production substrates without the need for the special sputtering system setup procedures required for quartz crystal based measurements; there is virtually no sample preparation time. With the exception of a first measurement made while setting up the sputtering system, all measurements are made in parallel with processing for production; there is effectively no lost production time. Experience has demonstrated that additional measurements without interruption of production also allows more immediate detection of special cause events, such as sputtering target or power supply problems, that might otherwise erode yield. Production run duration has increased to the point that only maintenance, shield cleaning and target replacement tasks limit equipment utilization for part production.

Data processing is transparent to the operator. A computer processes the XRF measurement data and then presents the data to the operator as appropriate changes in process parameters. The operator is directed to make no changes, make a small adjustment to process parameters, or terminate production in the unlikely event of system failure. In addition, a chart of historic data is generated that allows long-term tracking of system capabilities.

The system as originally specified, including an X-Y mechanical table, was delivered and installed in March 2004. Figure 19 is a photograph of the system. The large white rectangle between the production engineer and the computer screen is two CIG coated 1x4 ft. substrates loaded side by side on the X-Y mechanical table. Additional procedure development since receiving this system has included improving the handling of reference samples for calibration and developing procedures to insure that each sampled area is in focus as the substrates are scanned.

Figure 19. Production XRF system.

In summary, production process control using XRF measurement of sputtered copper gallium and indium precursors has been demonstrated, implemented and qualified. XRF process control has also been qualified for deposition of the Mo base electrode. The previously used control approach, based on quartz crystal measurements, required up to 40% of the potentially available production time for process feedback measurements. Experience has demonstrated that additional measurements without interruption of production also allow more immediate detection of special cause events, such as sputtering target or power supply problems, that might otherwise erode yield.

Integrated Manufacturing – Design and Specification

Background

SSI has applied systematic research, development, production and business methodologies to a carefully planned substrate size and capacity scale-up of CIS-based thin-film technology. To date, these systematic approaches, which are generally recognized as being appropriate for manufacturing businesses, have included SPC, Analysis of Variation, design of experiments, and the methodologies defined for sound business practices under ISO9000 guidelines. SSI's accomplishments utilizing these methodologies indicate extension to include Manufacturing

Execution Systems (MES) as part of SSI's implementation of an integrated manufacturing infrastructure.

Preaward activities

Preaward activities addressed structured qualification of new equipment with emphasis on the tasks necessary to pass equipment from engineering and procurement groups to the production and maintenance groups.

Discussions with management, engineers and technicians clearly identified the need to decrease the time that engineers and technicians spend on production support and maintenance. This would make their time available for experimentation and to support procurement and qualification of new equipment. To this end, procedures were developed to guide the release of equipment to production. These procedures defined the following implementation and qualification tasks to release equipment to production, i.e. make the equipment ready for sustainable production with a more appropriate level of support from engineers and technicians:

- Completion of Health, Safety and Environmental tasks including safety reviews and permitting
- Completion of a test plan to demonstrate process capability and compatibility with all module processing steps
- Release of safety procedures
- Release of process documents for incorporation of the system into the overall CIS module process
- Release equipment process documents
- Release equipment maintenance documents
- Training of production personnel
- Training of maintenance personnel
- Documentation and retention of OEM documents
- Documentation of calibration requirements and release of calibration procedures
- Documentation of software backup requirements and release of backup procedures
- Identification and procurement of spare parts

These activities augmented previously defined approaches, such as well-defined procedures and work instructions, to define and implement infrastructure that forms a solid foundation for systematic CIS production and substrate size and capacity scale-up.

Data Warehouse

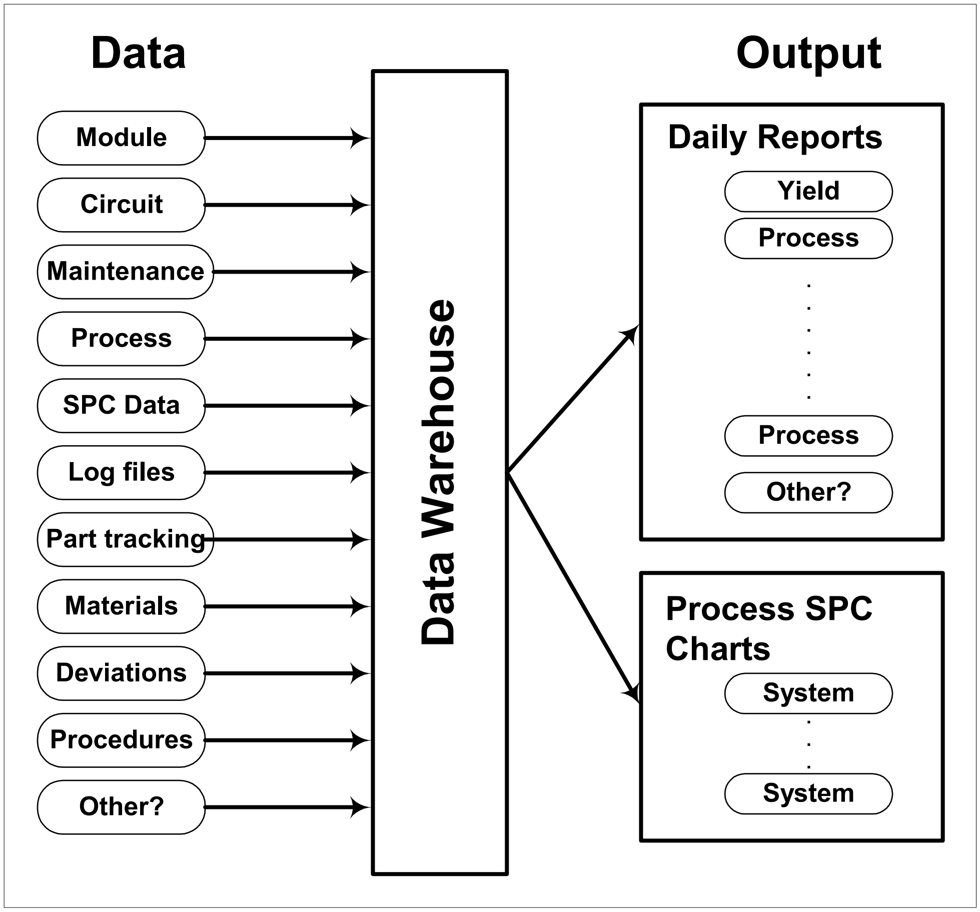
Task execution plans were based on working closely with SSI's Information Services group and using consultants with MES experience to implement the majority of the work. In addition to experience, the plan to use consultants was driven by the need to minimize workload on CIS personnel during all phases of this work. Meetings between the CIS group and Jeff Millard, Director of Information Services, were held to discuss the design and specification phase of this subcontract work. A consultant, Vijay Bharti, The Comdyn Group, Inc., was selected as the primary consultant for this subcontract work. Considerations for this selection included manufacturing experience, experience with the infrastructure in SSI's Information Services department and experience with production support at SSI. The consultant drafted a mission statement and Goals and Objectives for review.

Based on the draft mission statement, the design and specification phase of this subcontract work was discussed with the consultant and the manager of Information Services. The consultant's recommended approach was based on the following information from that timeframe:

- Our procedures and work instructions do a good job of documenting the CIS circuit and module process and all process data collection.
- A standard MES software package would duplicate some existing functions in SSI's part tracking, maintenance, and accounting systems.
- The software interfaces to other parts of the company may change with potential changes in the main software package used company wide and thereby also change links from an MES package to information on sales, marketing, purchasing, accounting, etc.
- The CIS group spends a considerable amount of time merging part tracking data, process data, and module measurements. Maintenance data from existing software that might be valuable for consideration was not easily compared to process results.
- One functional definition of a MES package is that it predicts the impact on production of changes in operations. However, a software package that doesn't fit this definition of MES would be a better fit to SSI's needs for "integrated manufacturing." - a package described by the consultant as "directed analysis." Coining the term "Software for Integrated Manufacturing Infrastructure" (SIMI) for this directed analysis software, goals for the SIMI software were defined:
- Integrate data from multiple sources for standard reports
- Include these standard reports in CIS process documentation
- Include user instruction for SIMI software in CIS documentation
- Integrate and release SIMI software
- Make process data available in a "data warehouse"
- Make data from maintenance software available in a "data warehouse"
- Make engineering comments on data available in a "data warehouse"

- Facilitate "directed analysis" of the data warehouse for process analysis and improvement

The following diagram depicts the first cut at defining a statement of work for the SIMI software tasks.



Follow on subcontract work related to this task was expected to begin early in 2003. However, this work was delayed while the consultant worked on previously unplanned tasks including selection of software for company wide Enterprise Resource Planning (ERP) requirements. This work was a prerequisite for subcontract work since implementation of integrated manufacturing must be compatible with company wide plans for ERP. Software for company wide ERP requirements was chosen based on compatible with existing databases and expectations for improved data availability intended for improved decision making. Touted features of the software included the following abilities:

- Turn large volumes of data into meaningful information
- Identify and consolidate various data sources and supporting information
- Report on the data in intuitive formats

- Applicability to many business functions
- Extensible to new business functions

Additional manpower for these tasks was added in October because of the consultant's continuing high workload for company wide rather than subcontract tasks. The consultant would continue to be involved with this subcontract work; particularly with prerequisite work for company wide ERP requirements. A second consultant, John Andleman JSA Software, Inc. was chosen to implement these plans based on his manufacturing experience, experience with the infrastructure in SSI's Information Services department and experience with production support.

The second consultant advanced previous task definitions to a specification for the implementation of SIMI and presented his work to SSI. The attached diagram, Figure 20, is an overview of this specification. The core of this specification is the SIMI Transactional Database that was derived from "data warehouse" software selected for company wide applications based on compatibility with existing databases and capabilities that improve data availability. SIMI would integrate data from multiple sources including existing production and maintenance databases and data collected and stored as hard copy. Hard copy data defined in procedures and work instructions does a good job of documenting the CIS circuit and module process and all process data collection. Integrating these existing data sources and existing reports for SPC and production management would be the primary focus. Real-time and off-line outputs from production and analytic systems would be included in planning and a near-term SIMI review by CIS engineering.

Software specifications were defined and data warehouse data fields and field relationships were defined for all processes. System specific packages of information for reviews with the responsible engineers for production systems were generated to expand on the general specification. The goal was to maximize the effectiveness of working with the responsible engineers while minimizing their workload for these efforts. Each package combined detailed tables of proposed data IO for each process (procedure) and reference materials.

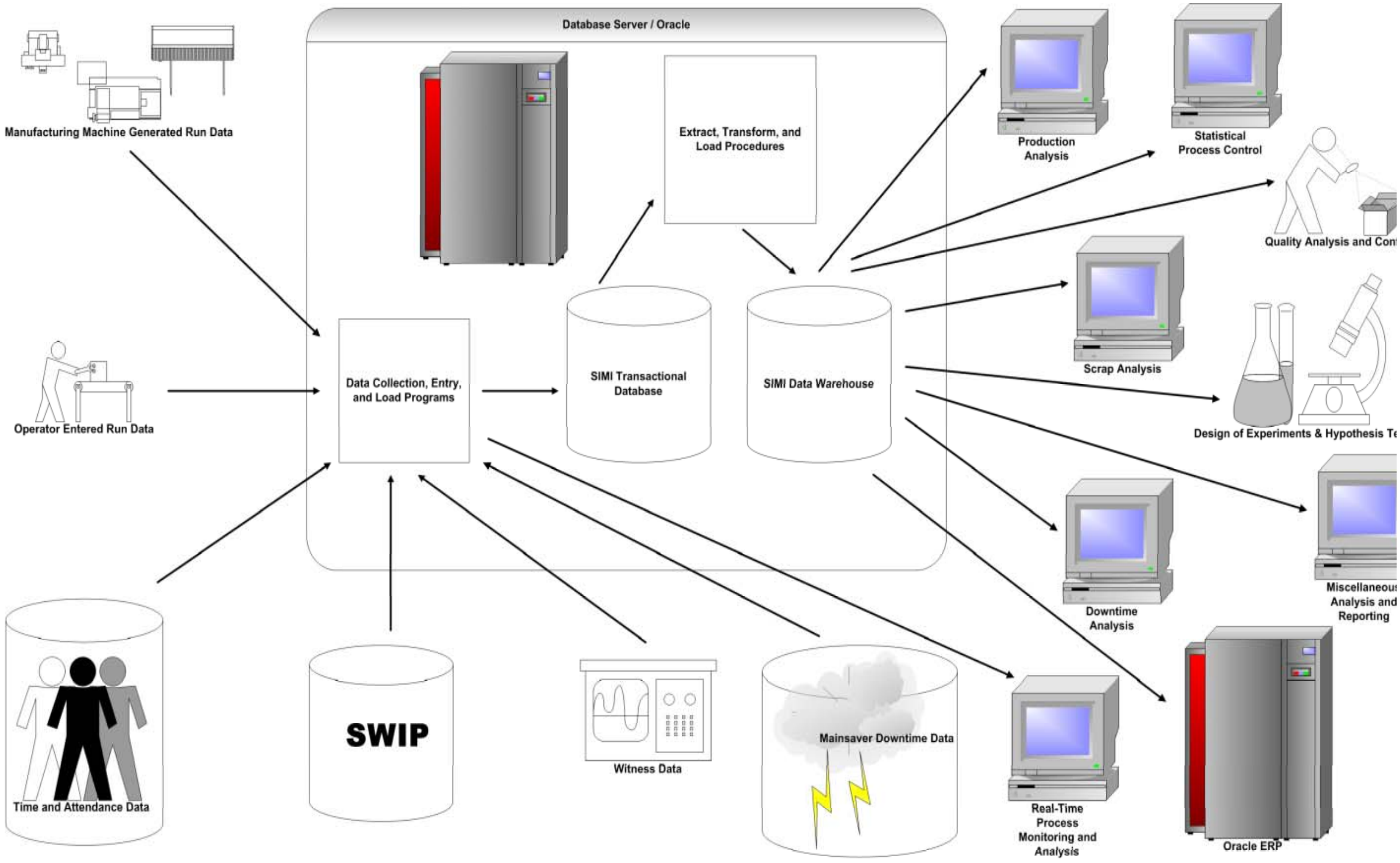


Figure 20. SIMI software overview.

Conclusions

SSI's thin-film CIS technology is poised to make significant contributions to DOE/NREL/NCPV long-term goals - higher volume, lower cost commercial products. Subcontract work has allowed SSI to address multiple production bottlenecks thereby allowing SSI to exercise the overall process at higher production rates and to lay the groundwork for evaluation of near-term and long-term manufacturing scale-up options.

High-throughput CIS absorber formation reactor

Modeling work pursued with the University of Florida demonstrated dramatically improved insulating properties for new insulator approaches that can be effective for some subsections of existing reactors and both heater and substrate areas for future reactors.

Reactor mockup work demonstrated temperature variations from minimal to significant with increasing substrate load. Substrate warping varied from minimal to significant with increasing substrate load for higher cooldown rates while slower cooldown does not completely avoid warping. Substrate dimensional changes follow the same trends as substrate warping and should not be a problem if substrate warping is minimal.

Specifications for an absorber formation reactor were defined. This task required more time than expected because no vendor had previous experience directly applicable to SSI's large substrate requirements or would commit to any thermal uniformity specification.

Alternative geometries for very high capacity, such as 100 substrates per run, and improved thermal uniformity are possible based on emphasizing forced convection or radiative heating. Since no vendor would commit at any level of performance for these approaches, all risk for success became solely SSI's risk. However, this does not preclude future reactor advances, even dramatic advances, since capital cost does not necessarily scale with the design complexity or capacity.

SSI selected a vendor that would meet immediate requirements, about 25 substrates per run, in April 2003 and submitted the internal documentation required to procure the system. In October, SSI authorized the equipment vendor to begin the first phase of work.

Safety Infrastructure

Duplication of the exhaust scrubbers along with valves for selecting one scrubber at a time now allows maintenance or service work while continuing operation of all reactors. Absorber formation production capacity is no longer limited by the time required for scrubber maintenance or service which was amplified by the preparatory time required to end processing in all reactors.

Similarly, redundancy implemented for raceway scrubbers allows maintenance or service without interfering with production. Maintenance has been simplified by replacing maintenance intensive scrubbers based on recirculating KOH with carbon filter units.

Subcontract work has allowed the use of larger cylinders at a lower cost per pound of reactant. Cylinder changes occur in parallel with production and a limitation on the time between starting multiple reactors has been eliminated.

Laser bar code scribing

Laser bar code scribing and reading equipment was procured and implemented.

Laser bar code scribing has proven to be easier, faster and more accurate than hand scribing serial numbers. Productivity has been improved for both production and engineering.

Laser bar code scribing also significantly improved yield by minimizing breakage associated with hand scribed serial numbers. Breakage associated with the serial number was reduced by about 88%.

XRF process control

SSI implemented XRF measurement methods on leased equipment while waiting for delivery of specified equipment. Leasing allowed process development and use by production before receiving the specified equipment.

Methods were developed to achieve the prerequisite measurement accuracy for each precursor layer.

XRF process control has also been qualified for both precursors and the base electrode.

XRF based process control has practically eliminated system time used for diagnostics instead of part production.

Integrated Manufacturing

Procedures for structured qualification of new equipment were developed and implemented. These activities have improved productivity and augmented previously defined approaches, such as well defined procedures and work instructions, to define and implement infrastructure that forms a solid foundation for systematic CIS production and substrate size and capacity scale-up.

Bar code scribing and XRF diagnostics now provide high quality production data for integrated manufacturing infrastructure.

The CIS group, the Information Services group and a consultant jointly defined a mission statement, goals and objectives for implementation of MES.

A consultant was chosen to implement plans with the primary focus on integrating existing data sources and existing reports for SPC and production management.

Software specifications were defined and data warehouse data fields and field relationships were defined for all processes.

System specific packages of information for reviews with the responsible engineers for production systems were generated to expand on the general specification. These activities were discontinued with termination of the subcontract.

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REPORT DOCUMENTATION PAGE

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14. **ABSTRACT** *(Maximum 200 Words)*

The objective of this subcontract was to continue the advancement of CIS production at Shell Solar Industries through the development of high-throughput CIS absorber formation reactors, implementation of associated safety infrastructure, an XRF measurement system, a bar code scribing system, and Intelligent Processing functions for the CIS production line. The intent was to open up production bottlenecks thereby allowing SSI to exercise the overall process at higher production rates and lay the groundwork for evaluation of near-term and long-term manufacturing scale-up. The goal of the absorber formation reactor subcontract work was to investigate conceptual designs for high-throughput, large area (2x5 ft.) CIS reactors and provide design specifications for the first generation of these reactors. The importance of reactor design to the CIS formation process was demonstrated when first scaling from a baseline process in reactors for substrates to a large area reactor. SSI demonstrated that lower performance for large substrates was due to differences in absorber layer properties that were due to differences in the materials of construction and the physical design of the large reactor. As a result of these studies, a new large area reactor was designed and built that demonstrated circuit plate performance comparable to the performance using small area reactors.

15. **SUBJECT TERMS**
PV ; module; manufacturer; absorber formation reactors; substrate; large area; solar cells, thin film; bar code scribing; X-ray florescence (XRF); manufacturing execution system (MES); transparent conducting oxide (TCO); chemical vapor deposition (CVD);

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