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Innovation for Our Energy Future

Development of Robust High Efficiency Thin-Film CdTe Photovoltaic Modules

Phase I Annual Report
30 September 2006 – 28 December 2007

R.T. Green
First Solar, Inc.
Perrysburg, Ohio

Subcontract Report
NREL/SR-520-43871
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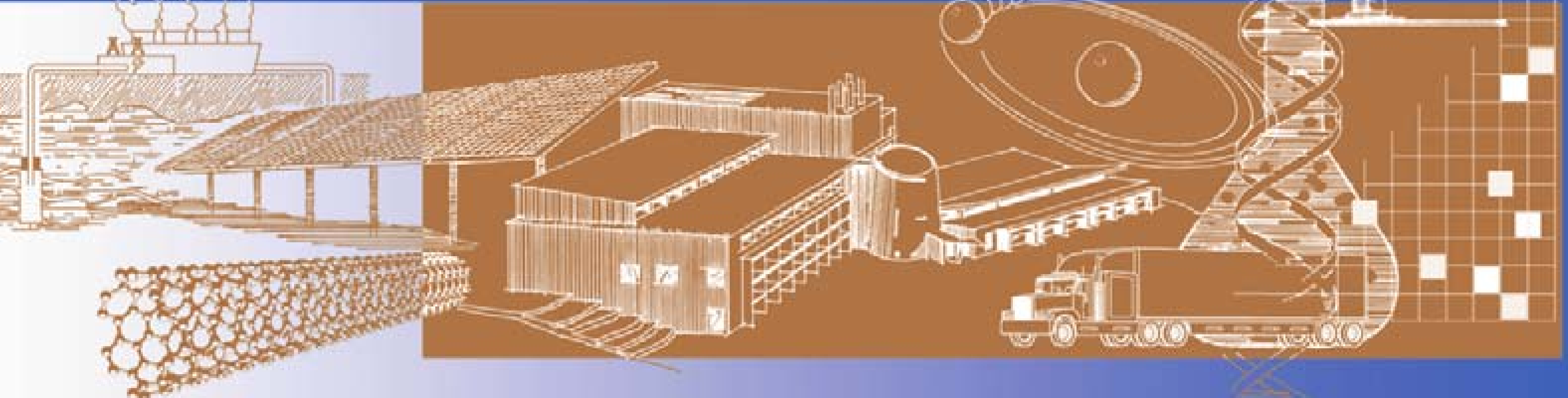

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PROGRAM OVERVIEW: THIN FILM PHOTOVOLTAIC PARTNERSHIP PROGRAM (TFPPP)

NREL supports thin-film R&D and National R&D Team activities with team members from academia, the thin-film photovoltaic (PV) industry, NREL, the National Center for Photovoltaics (NCPV), and the Center of Excellence for Thin Film Photovoltaics at the Institute of Energy Conversion, University of Delaware. The purpose of the Thin-Film Photovoltaics Partnership Program (TFPPP) is to accelerate the progress of thin film solar cell and module development as well as to address mid- and long-term research and development issues. The long-term objective of the TFPPP is to demonstrate commercial, low-cost, reproducible, high yield and robust PV modules of 15% aperture-area efficiency, about $50/m^2 area cost, and thirty-year lifetimes. These goals are stated explicitly for thin films in the US DOE Solar Energy Technology Program's "Multi-Year Technical Plan, 2003-2007 and Beyond" (Table 4.1.1-1, page 50, http://www.eere.energy.gov/solar/about.html); and they are consistent with reaching the DOE long-term goal (2020) of cost-effective PV electricity at about 6 cents/kWh levelized energy cost. The purpose of this program is to make progress toward these objectives by achieving aggressive interim goals for thin film module efficiencies; cell and module processing; cell and module reliability; and the technological base that supports these key areas.

The three key technical elements needed to make thin film CdTe PV technology viable are to increased module efficiency, improved product reliability, and the development of robust processes that can be predictably duplicated at multiple manufacturing facilities. Efficiency gains are expected through improved photocurrent due to reduced optical losses in the window layers, increased fill factor due to improvements in uniformity and the back contact, and improved voltage due to process optimization of the junctions. Reliability gains are expected to result from packaging improvements as well as increased robustness of the device itself.

This program is designed to address the issues surrounding efficiency improvement, product reliability, and production capability through:

The purpose of this statement of work is to address the following research topics given below:

1) development of production compatible front contact window layers
2) continued development of our unique high-rate vapor transport deposition process for the semiconductor layers
3) systemic optimization and refinement of post-deposition processing
4) development of in process diagnostics, and
5) reliability improvement through testing and packaging alternatives

This program, as designed, was to be three-phase program with the duration of each phase being one year. However, because of the accelerating evolution of the industry, Phase II of the program will be abbreviated to three quarters and there will be no Phase III. The ultimate goal of this program is the delivery of full-modules that exhibit aperture efficiencies greater than or equal to 11% by the end of Phase I and greater than or equal to12% by the end of Phase II. The deliverables for Phase I of this program have already exceeded the requirement for Phase II with aperture efficiency of 12.2% (as measured by NREL). This result establishes the mark for the champion CdS/CdTe thin-film module performance and is a direct result of work performed on this program, additional NREL programs (“PVMAT” - ZAX-4-33628-04 & “Expanding the Limits” - ZXL-6-44205-07).

PROGRAM TASKS & MILESTONES FOR PHASE I AND PHASE II

3.1.0 Advanced Front Contacts and Window Layers

The first task involves continued development of advanced front contact and window layers (AFCW). Included in this category are the glass superstrate, a transparent conductive oxide (TCO) layer, an oxide buffer layer, and a sputtered CdS-based window n-layer. The Subcontractor is currently exploring analogous elements of a process used at NREL to make record efficiency cells for use in our production line. The NREL process employs a transparent conductive layer of cadmium stannate (Cd_2SnO_4), a buffer layer of zinc stannate (Zn_2SnO_4), and an n-layer of amorphous oxygenated CdS (a-CdS:O). (Films in the Cd-Sn-O and Zn-Sn-O systems shall be referred to as CTO and ZTO, respectively.) The role of the buffer layer is particularly important as it enables the use of thinner CdS resulting in higher photocurrent without compromise of other device parameters. Current tasks are focused on using a base layer of commercially available SnO_2 as the transparent conductor, a buffer layer (deposited by CVD, sputtering, or VTD), either sputtering a-CdS:O or depositing CdS with VTD, followed by CdTe formation using VTD. The initial results involving the use of sputtered ZTO buffer layers are promising, but benefits of this buffer layer have not been realized. Alternative buffer layer materials and methods remain under evaluation. To proceed to production the Subcontractor shall demonstrate compelling gains in module performance with a production capable process in order to justify the capital expenditure for a production sputter coater.

The Subcontractor has also deposited a-CdS:O by sputtering onto full size plates. The early results are promising, but the benefits are yet to be realized. Development of both deposition options for CdS (sputtered a-CdS:O and VTD CdS) shall continue .

Subsequent tasks focus on the replacement of the purchased SnO_2 with a better transparent conducting oxide. The NREL team has demonstrated that CTO on borosilicate glass can have clearly superior electronic properties compared to SnO_2 films, and the Subcontractor has been able to duplicate some of the laboratory results for CTO on borosilicate glass (in fact our record cell was made with these advanced front contacts). However, the advantages of CTO remain to be demonstrated at the module-scale on soda-lime glass using a manufacturing capable process. The high-efficiency cell processing conditions employ a lengthy high temperature anneal of the CTO in the presence of CdS which may not be compatible with soda-lime glass and our production line.

Sputter deposition rates of these front contact layers are also a concern. The Subcontractor has demonstrated higher deposition rates with some pulsed sputter modes using ceramic compound targets. However, significantly higher rates are possible using reactive sputtering from metal alloy targets. Reactive sputtering is potentially an enabling technology that shall remove manufacturing constraints and broaden the range of film properties possible. Thus some exploration of these options is warranted.

The inclusion of any of the possible layers into the device structure would constitute a dramatic change. Thus a very comprehensive level of testing is required.

If all the front contact layers were produced in house, the Subcontractor would employ the use of low-iron soda-lime glass as the near IR transparency is greater with an expected ~5% increase in photocurrent.

The proposed research focuses on continued development, optimization and testing of the front contact layers. This includes testing alternative deposition methods, combinations of layers, and rigorous stability and durability testing. It is expected that efficiency increases shall be achieved in steps of decreasing CdS thickness. Thus a number of optimization and testing iterations are expected. The Subcontractor shall also improve film characterization equipment.

Task 1.1 Advanced Front Contacts and Window Layers (Phase I)

a) The Subcontractor shall develop advanced front contact structure that may include TCO, buffer layer, and window layer (CdS).
   i) The Subcontractor shall evaluate type and deposition method for buffer layers in cells and modules. Evaluation shall include device processing.
   ii) The Subcontractor shall evaluate alternative CdS-based window layers in devices fabricated with the Subcontractor's processes.
   iii) The Subcontractor shall investigate sputtered transparent conductive oxide AFCW process (small area).

b) The Subcontractor shall evaluate benefits of using low iron soda lime glass superstrates.
   i) The Subcontractor shall fabricate cells on commercially -available low iron glass/TCO superstrates.

c) The Subcontractor shall develop diagnostic/characterization techniques for evaluating AFCW layers.
   i) The Subcontractor shall develop protocol for rapid, in-house characterization of AFCW material. Parameters of interest would be carrier concentration, mobility, optical transmission, band gap etc.

Task 1.2 Advanced Front Contacts and Window Layers (Phase II)

a) The Subcontractor shall develop advanced front contact structures which may include TCO, buffer layer, and window layer (CdS).
   i) The Subcontractor shall optimize performance of module made using AFCW layers.
   ii) The Subcontractor shall evaluate advanced TCO options.

b) The Subcontractor shall evaluate benefits of using low iron soda lime glass superstrates.
   i) The Subcontractor shall optimize modules made on commercially available low iron/TCO glass superstrates (if material is available).

c) The Subcontractor shall develop diagnostic/characterization techniques for evaluating AFCW layers.

   i) The Subcontractor shall identify techniques for diagnosing AFCW films online for deposition process control.
   ii) The Subcontractor shall develop prediction capability of gain in performance based on measured opto-electronic parameters of AFCW films.
   i) The Subcontractor shall perform work to cost effectively integrate advanced TCO coated low iron glass superstrates to a high throughput manufacturing environment.

b) The Subcontractor shall develop diagnostic/characterization techniques for evaluating AFCW layers.
   i) The Subcontractor shall identify/specify equipment needed for online and offline characterization of AFCW films in a manufacturing environment.

3.2.0 Semiconductor Deposition

Central to the manufacturing technology is the unique high-rate deposition technique called vapor transport deposition (VTD). This method is used for both CdS and CdTe. Essentially powdered source material is continuously injected into a high temperature zone where it is vaporized and distributed into a sheet of vapor that is directed toward a moving web of glass. The vapor cloud is dense and it condenses on the glass forming films at high rates. Material input rates directly control film thickness.

The Subcontractor has developed a significant improvement to the original method that shall be referred to as VTD-2. The VTD-2 technique is simpler to control and opens access to a broader operation parameter space. The larger parameter space translates into the ability to deposit CdTe films with a greater variety of microstructures. VTD-2 type distributors shall also be used for CdS, although the exact design may differ from that used for CdTe. The Subcontractor is currently narrowing the field of VTD-2 designs and has just begun to explore the factors that affect CdTe microstructure. Thus optimization of the physical and thermal geometry of the VTD-2 distributor designs is expected to continue for some time.

The VTD technique is well suited to the task of continuously converting source material into the relatively thick CdTe absorber layer (currently the absorber layer is about 10x thicker than the next thickest layer). Material utilization is an important consideration with respect to equipment uptime. It will be possible to operate the production system continuously for a week ($\sim 10^4$ plates) between cleaning operations. However this shall likely necessitate some further changes in the distributor system.

In contrast, VTD of CdS presents a different set of challenges. For high efficiency modules increasingly thinner CdS is required. This imposes increasingly stringent demands on uniformity and control. One shall not only manage the transverse vapor distribution, but also precisely control extremely low material input rates (~5mg/s). The Subcontractor shall develop custom material feed equipment and on-line film thickness sensors, but improvements shall be necessary for very thin films. As stated above, there is an alternative path to CdS formation and the Subcontractor shall be working to choose the best option.

The Subcontractor has developed very sophisticated numeric models for distributor operation through a subcontract with the Colorado School of Mines. The models have concentrated primarily on conditions within the vaporizer and distributor and on material and energy transport between the distributor and the glass. Insights into uniformity and edge effects, utilization and build-up control shall result from this effort.

VTD has proven very successful for large-area, high-throughput deposition; however, it remains a relatively immature deposition technique with a knowledge base that is largely internal. The Subcontractor's films are deposited at very high rates so quite unlike other methods and new distributors, feeders and sensors are in use. Thus a myriad of variations on the central theme remain unexplored.

The proposed research focuses on continued VTD development for both CdS and CdTe. Included shall be 1) continued process and distributor equipment optimization for both CdTe and increasingly thinner CdS and 2) improved sensors for thin CdS.

Task 2.1 Semiconductor Layers (Phase I)

a) The Subcontractor shall optimize the best VTD-2 distributor design for CdTe deposition including distributor geometry and process parameters to produce high efficiency, stable modules.
b) The Subcontractor shall optimize the best VTD-2 distributor design for CdS deposition (<800Å) including distributor geometry and process parameters to produce high efficiency, stable modules.
c) The Subcontractor shall improve on-line sensors for real time CdS thickness monitoring.

Task 2.2 Semiconductor Layers (Phase II)

a) The Subcontractor shall modify and optimize the CdTe deposition system that can operate continuously for 120 hours and produce higher efficiency junctions.
b) The Subcontractor shall modify and optimize the CdS deposition system to produce higher efficiency junctions with effective CdS film thicknesses <500Å.
c) The Subcontractor shall improve on-line sensors for CdS thickness.

3.3.0 Post Deposition Processing

Subsequent to the deposition of the front contact and semiconductor layers are a series of processing steps that result in a completely functional interconnected but un-encapsulated sub-module. This sequence of steps includes a re-crystallization anneal, back contact application, and the interspersed laser scribing operations. Collectively, the Subcontractor refers to this sequence as post-deposition processing (PDP). For this statement of work, the laser scribing operations, required to form an interconnected module, shall not be addressed per se unless the Subcontractor finds that altered TCO layers require major changes in scribing conditions. However, post-deposition processing steps that the Subcontractor shall address shall be compatible with the overall interconnection scheme.

The re-crystallization / activation process is done by a wet $CdCl_2$ application followed by a high-temperature air-annealing step. CdS/CdTe interdiffusion, grain boundary passivation, doping, and structural defect reduction occur during this step. Film properties subsequent to the activation process depend strongly on the material properties of the incoming front-contact and semiconductor layers. For example, the addition of a front contact buffer layer, a reduction in CdS thickness, or a change in microstructure of CdTe are all necessitate adjustments in the $CdCl_2$ activation process.

In turn, the $CdCl_2$ activation step influences the back contact application process. Oxide residues that impact the back contact properties form on the CdTe surface during the activation process. Variations in $CdCl_2$ processing lead to different mixes of residue species. Consistent formation, removal, or conversion of the residues is required to ensure consistent contact performance. A variety of etches with cleaning, oxidizing or reducing properties shall be evaluated in order to optimize the back-contact application procedure.

The CdTe surface and microstructure also affect the doping step that is required for consistent contact and device operation. Doping interacts strongly with the activation step. Together they are major factors that determine device stability. Continued integrated studies are required to improve module stability.

Contacting structures to CdTe thin film solar cells typically employ an interfacial layer (IFL) between the CdTe surface and the back electrode. Chemical and electronic properties of the IFL are a major factor governing device performance however they remain poorly understood. The IFL can also interact with the electrode metallization, and this shall be considered when optimizing contact structures. Thus evaluating material combinations are central to development of stable back contact structures. In addition, the Subcontractor has found that electrode deposition conditions can also affect device performance and stability.

Improving and optimizing the post deposition process involves an integrated systemic approach that considers the incoming layers, the activation, doping, IFL and metallization processes and always judges the outcome with both initial and long term performance criteria. This approach shall be iterative, as continued changes and improvements shall occur in many places.

The proposed PDP development work includes 1) optimization of activation and doping steps for new incoming layers, 2) evaluation and optimization of surface etches and treatments, and 3) evaluation and optimization of promising IFL material combinations, and 4) optimization of metal electrode deposition.

Task 3.1 Post Deposition Processing (Phase I)

a) The Subcontractor shall optimize activation processing – Phase I.
b) The Subcontractor shall establish relationship between doping and activation processes.
c) The Subcontractor shall evaluate candidates for compound and alternative IFL.

d) The Subcontractor shall evaluate pre-contacting treatments.

Task 3.2 Post Deposition Processing (Phase II)

a) The Subcontractor shall optimize activation processing – Phase II.
b) The Subcontractor shall demonstrate improved module stability with optimized doping/activation processing.
c) The Subcontractor shall establish procedure for IFL formation.
d) The Subcontractor shall optimize IFL application procedure.
e) The Subcontractor shall evaluate IFL / back-electrode interaction.
f) The Subcontractor shall down-select pre-contacting treatment.

3.4.0 Third Level Metric Diagnostics

Diagnostic measurements enable process development as well as signal, locate and identify process deviations. Each process step accomplishes one or more specific functions, and some measure of the effectiveness of each step should be possible. The Subcontractor's engineers are well versed in using process improvement tools such as Taguchi and 6 Sigma. These process improvement methods involve mapping the important functional steps, identifying vital metrics, and applying robust engineering principles to optimize product performance and process yield. The key constraint in the sequence is the limited knowledge of what to measure and how to measure it.

The Subcontractor shall analyze production line module performance in a sequence of increasing levels of sophistication. Module power conversion efficiency, the essential function of a PV module, is designated as the first level metric. The light IV curve can be resolved into more fundamental components such as short circuit current density (Jsc), open circuit voltage (Voc), and fill factor (FF), which are designated as second level metrics (2LM). Collectively these second level metrics determine the module efficiency and to a large degree are independent.

Similarly, third level metrics (3LM) are defined as measurable quantities that directly impact second level metrics. Third level metrics are typically physical, chemical, optical or electrical properties of films or devices. A useful 3LM shall be traceable to device performance, sensitive to process variation, stable, repeatable, and reproducible. Ideally the property should be independent of other metrics and be measurable on-line. The ideal metric enables each process step to be optimized and controlled independently. If a key property can only be measured later, it is desirable that it be determined by a specific process step.

At present the Subcontractor primarily measures light IV performance and relies on the second level metrics to analyze process variation and to locate problems. Reliance on 2LM has several shortcomings. 2LM occur late in the process and typically are not capable of distinguishing the source of most variations. Thus it is generally not possible to identify the process step responsible for a given variation in performance. For example, a low short circuit current may be due to high CdS absorption or low red response.

To accelerate improvement in product performance, The Subcontractor's engineers require detailed knowledge of the physics of device operation and of the key physical, chemical, and electrical properties of the materials. The Subcontractor shall measure the vital properties, how the properties are affected by process variables, and how the properties affect device efficiency and stability.

Working independently and with the National CdTe R&D Team over the past few years, the Subcontractor has begun to identify some 3LM. The initial set of metrics involved IV measurements as a function of temperature (IVT) and quantum efficiency (QE) with bias. While these measurements provide insight, both cannot be conducted until late in the process, and IVT measurements of many real devices cannot be interpreted unambiguously.
National CdTe R&D Team members can help (and often lead) the process by identifying the key properties, by defining the equipment and procedures to obtain the data, and by recommending how to quantitatively interpret the data.

The Subcontractor shall develop 3LM methodology through an ongoing process of identification and evaluation of WIP metrics. Planned activities are to use designed process variation experiments to create sample sets that shall benchmark the capability of selected measurements to effectively resolve process differences.

Task 4.1 Diagnostics (Phase I)

a) The Subcontractor shall evaluate first round set of in-process metrics.
    i) The Subcontractor shall select a first round set of key measurements.
    ii) The Subcontractor shall fabricate sample sets with process variation and evaluate measurements.

Task 4.2 Diagnostics (Phase II)

a) The Subcontractor shall evaluate second round set of in-process metrics.
    i) The Subcontractor shall select a second round set of key measurements.
    ii) The Subcontractor shall fabricate sample sets with process variation and evaluate measurements.

3.5.0 Product Reliability

Product reliability is a key customer requirement. Central to assuring product quality are a variety of accelerated life testing (ALT) procedures. Development of rapid ALT protocols is critical to all of our development work as process changes anywhere in the production line cannot be implemented unless the impact to customers is known with high confidence. Historically much of our focus has been on the development of ALT procedure involving light exposure with durability testing (thermal cycling and humidity/freeze, and damp heat) limited to the standard IEC-61646 qualification protocol. More recently the Subcontractor has begun to employ a wider array of more stressful durability testing including the simultaneous use of electrical stress. These tests have already demonstrated rapid discrimination between process alternatives. Continued development of test protocols shall ensure increased field reliability.

The Subcontractor has focused on developing a more rapid light exposure test than the eight week test that had previously been adopted. Ideally any test would be correlated to field testing, such that an acceleration factor could be determined, and would not cause a failure mode that would never be observed in the field. In practice, a protocol becomes useful if it can differentiate behavior under stress based upon module architecture or module fabrication process.

The Subcontractor shall deploy and track a much larger number of modules in the field. Consequently, the Subcontractor shall have more examples of potential problems and shall be able to conduct a number of cases of failure analysis. As a result of weaknesses found, the Subcontractor shall begin testing some alternative packaging options. Current work includes the addition of edge seals that are more resistant to moisture ingress and leakage, study of performance changes that occur during lamination, and alternative busbar configurations. The Subcontractor has not yet explored in detail alternative encapsulants. Since the device is a superstrate structure, the Subcontractor does not have any requirement for optical transmission, and thus the number of potential candidate materials is larger.

The proposed activities focus on 1) continued development of ALT including durability tests with electrical stress, 2) analysis of field failures, and 3) evaluation and optimization of alternative packaging.

Task 5.1 Product Reliability (Phase I)
a) The Subcontractor shall monitor field test sites.
b) The Subcontractor shall continue cross-correlation between rapid ALT light exposure protocols and field testing.
c) The Subcontractor shall analyze modules returned from the field due to anomalous behavior.
d) The Subcontractor shall develop damp-heat with bias testing protocol.
e) The Subcontractor shall evaluate and select packaging alternatives – Phase I.

Task 5.2 Product Reliability (Phase II)
a) The Subcontractor shall monitor field test sites.
b) The Subcontractor shall continue cross-correlation between rapid ALT light exposure protocols and field testing.
a) The Subcontractor shall analyze modules returned from the field due to anomalous behavior.
b) The Subcontractor shall evaluate and select packaging alternatives – Phase II.

4.0 MILESTONES

Following are the milestone for each of the three phases:
Phase I:

- Demonstrate 11% module with < 5% loss in ALT protocol.
- Select best material and method for buffer layer formation.
- Select CdS deposition method (VTD or Sputtering).

- Select best IFL candidate for optimization.
- Select one new in-process metric to be implemented in production.
- Select ALT protocol.

Phase II:

- Demonstrate 12% module with < 5% loss in ALT protocol.
- Select best pre-contact treatment for optimization.
- Select additional in-process metric to be implemented in production.
- Select advanced packaging material and module architecture.

TECHNICAL APPROACH

The main effort to develop the AFCW was performed under the aegis of the PVMAT program. This included all deposition and processing work. The TFPPP contribution to the AFCW took the form non-standard optical measurement and modeling work. This decision was made specifically to avoid duplication of effort as well as most effectively using the funding and resources available to both programs. The benefit to the TFPPP program was in the form of the fully-developed superstrate used in successfully achieving the Phase I deliverables.

Similarly, the semiconductor deposition work in the VTD systems was being developed under PVMAT as well as First Solar internal R&D. These efforts fully cover all of the tasks that were proposed under the TFPPP. The TFPPP derives the benefit from both of these programs. This allowed the semiconductor deposition resources of the TFPPP to be used in testing material deposited by other techniques – specifically, sputtering. The benefits of using multiple deposition techniques for this work are expanding the deposition temperature range and the precursor chemistries available. This goal of this effort, which will continue throughout the program, is to provide the means of improving the semiconductor transport properties in the bulk and improve interfacial quality.

The goals of this work are to improve the electronic transport properties of the semiconductor layers, improve the back contact properties. Efforts to improve the device structure and material properties will continue throughout all phases of this program. The more long-term effort in the deposition task of this program is required by the time-consuming need to optimize the PDP process for each change in the structure or material composition; the long lead time of some of the materials; and the lengthy time required for stability testing.

From its inception, this program was considered to be a three year effort with each successive year building on the accomplishments of the previous year. Consequently, the work early in the program was heavily weighted towards making progress in the areas that would enable the successful completion of subsequent work. For Phase I, this meant concentrating the work in the area of selecting and developing the diagnostic tools that would be necessary for the PDP and reliability improvement work.

The ultimate objective in selecting a suite of characterization techniques is to uniquely determine where the deficiencies (deviation from maximum efficiency) in the device occur and to quantitatively relate this to a process control variable in the manufacturing line. Each member of the characterization suite would ideally be non-contact, non intrusive, and applicable to the device at any point in the manufacturing procedure as well as in the field. Further, these characterization tools would have mapping capability – for the evaluation of uniformity across an entire module. Finally, the time to perform the analysis would have to be no greater that the production time per module (much less than one minute per module). From these criteria, we establish the hierarchy of characterization (from highest desirability to lowest):

a) Optical characterization (most general)
b) Electrical characterization (generally requires electrical contact)
c) Opto-electronic characterization (combination of the above)
d) Structural characterization (grain size, orientation, layer thickness, etc.)
e) Surface/interface characterization
f) Chemical analysis (sampling methods)

The first two quarters of Phase I were dedicated to the determining and procuring the characterization tools required to further the efficiency and reliability improvement efforts.

Development in the 3LM task has be hindered by the unavailable or inappropriate, commercially available characterization tools. Further, the tools that are available yield data that, taken by themselves, have ambiguous interpretations. Therefore, as the leader in thin film technology for photovoltaics, First Solar's approach to this industry-wide problem is to identify the necessary characterization tools, understand the consequences of the measured properties for module performance, and work with vendors to provide tools capable of in-line measurements on full modules. Identifying and understanding the 3LM techniques is being done in cooperation with NREL under this program and others. Working with vendors to expand existing tools or develop new tools is the purview of First Solar as the industry leader.

The deficiency of commercial tools has been an issue for three of the more promising characterization techniques – TRPL (Time Resolve Photoluminescence), MCSE (Multichannel Spectral Ellipsometry) & SKP (Scanning Kelvin Probe). The difficulty with implementing these techniques is due to unsatisfactory results from vendor qualification tests. These results do not necessarily mean that the commercially available instruments are unsuitable for First Solar; it only means that the vendor interpretation of the test results is too ambiguous to justify purchase. To circumvent the vendor issues, First Solar increased interactions with NREL, specifically the Measurements & Characterization Group. First Solar worked actively with NREL's Wyatt Metzger for the TRPL and Helio Moutinho for the SKP in Phase I. It is hoped that, in the future, the work with the NREL experts will allow First Solar to successfully cause the commercial vendors to improve their response to the thin-film solar industry.

The PDP improvement efforts accelerated during the latter half of Phase I due to progress in defining the characterization set need for this program. The PDP work consists of four parallel efforts: overall optimization of the baseline PDP process, improvement of the electronic transport properties in the CdTe (including the effects of interfaces), improvement in the back contact (reduce series resistance and improve stability), and optimize the design of the cell and module to achieve higher efficiency. The first three efforts are coupled and iterative. Work in these areas will continue throughout the lifetime of this program and beyond. The last effort, optimized cell/module layout, can happily be performed completely parallel to the other PDP efforts. The early PDP efforts in Phase I concentrated entirely on realizing the efficiency improvement derived from an optimized module layout. This resulted in the champion CdS/CdTe module delivered under TFPPP Phase I. The efforts to improve the electronic transport characteristics of the device began in the latter half of Phase I. Although not a specific task, work to develop more environmentally benign process chemistries is included with these efforts.

Two important reliability efforts were initiated in Phase I Q2 that will provide greatly improved ALT capabilities. The first effort was the dedication of personnel to acquire and analyze reliability and stability information for full modules (in-house and in the field). This effort combines the work of the reliability and test groups to correlate efficiency losses to root cause in the process line(s). The second effort was the improved accuracy for the measurement of activation energies associated with elevated temperature light soak. This has been an in-house effort to expand the temperature control for full modules (a task that had to be done in-house because of the industry-wide lack of infrastructure for such testing). This effort was augmented by "dot" cell temperature controlled light soak measurement. The use of dot cells facilitated the testing.

Previous activation-energy studies have been at the dot-cell level, with only limited data from full modules. In Q2 results have been obtained for the first time, which provided activation energies for light soak with full modules. The results are roughly similar to results published in the literature. However, this initial test underscores the need to obtain better control of light soak conditions during testing as well as the need to employ 3LM: Temperature-control in commercially-available light soak units remains a major challenge for the industry. Additional work has already begun. This continuing work will involve testing of full modules as well as individual cells with far more extensive characterization.

TASK DETAILS: PHASE I

Task 1.1 Advanced Front Contacts and Window Layers (Phase 1)

a) The Subcontractor shall develop advanced front contact structure that may include TCO, buffer layer, and window layer (CdS).

   i) The Subcontractor shall evaluate type and deposition method for buffer layers in cells and modules. Evaluation shall include device processing.

   ii) The Subcontractor shall evaluate alternative CdS-based window layers in devices fabricated with the Subcontractor's processes.

   iii) The Subcontractor shall investigate sputtered transparent conductive oxide AFCW process (small area).

The development of TCO/CdS alternatives was performed using VTD and other deposition techniques under the PVMAT and ETL programs. The results are reported in the respective programs

b) The Subcontractor shall evaluate benefits of using low iron soda lime glass superstrates.

   i) The Subcontractor shall fabricate cells on commercially - available low iron glass/TCO superstrates.

The primarily advantage of superstrates incorporating low-iron soda lime glass is the increased transmission in the near infrared. Calculations based on reported n & k values as well as experimentally measured n & k values for standard and low-iron soda lime glass show a potential increase in efficiency of 4.7% (relative). The increase in efficiency is due to an increase in J_{SC}. This benefit has been confirmed in samples fabricated with commercially available soda lime glasses. ALT measurements performed on modules produced with low-iron soda lime glass show equivalent stability to standard production material.

c) The Subcontractor shall develop diagnostic/characterization techniques for evaluating AFCW layers.

   i) The Subcontractor shall develop protocol for rapid, in-house characterization of AFCW material. Parameters of interest would be carrier concentration, mobility, optical transmission, band gap etc.

Three characterization methods have been chosen to characterize the incoming TCO layer and their changes through processing:

- Optical characterization by transmission/reflection (layer structure, band gap, n & k values, surface roughness)
- Contactless resistivity measurements (based on eddy currents and confirmed by 4-point probe measurements)
- Hall measurements by the method of van der Pauw (for carrier concentration and carrier mobility

These characterization tools are in-house and operational.

Task 2.1 Semiconductor Layers (Phase I)

a) ***The Subcontractor shall optimize the best VTD-2 distributor design for CdTe deposition including distributor geometry and process parameters to produce high efficiency, stable modules.***
b) ***The Subcontractor shall optimize the best VTD-2 distributor design for CdS deposition (<800Å) including distributor geometry and process parameters to produce high efficiency, stable modules.***
c) ***The Subcontractor shall improve on-line sensors for real time CdS thickness monitoring.***

Again, to most effectively make use of resources this work was done under the PVMAT program. The work benefited the TFPPP in the form of the optimized structure that was used to produce the Phase I deliverable, champion module.

There was some non-VTD deposition work done under the TFPPP. The deposition work begun in Phase I Q2 included screening tests to determine the viable combinations of deposition techniques and chemistries that show potential to achieving the first year program goal of greater than 11% aperture efficiency. Deposition test being explored include sputtering and reactive sputtering as well as chemical techniques in combination with VTD. Interfacial layers both above and below the main VTD absorber layer were explored using full modules.

Task 3.1 Post Deposition Processing (Phase I)

a) ***The Subcontractor shall optimize activation processing – Phase I.***
   The work to optimize the standard PDP process was completed primarily under the PVMAT program with input from TFPPP in the form of advanced characterization. On-going work will be performed as part of First Solar's continuous improvement program.

b) ***The Subcontractor shall establish relationship between doping and activation processes.***
c) ***The Subcontractor shall evaluate candidates for compound and alternative IFL.***
d) ***The Subcontractor shall evaluate pre-contacting treatments.***
   Tasks 3.1 b, c, & d were primarily performed on the single cell level under the ETL program. This work was undertaken by the ETL program to develop a short list of viable candidates to apply to full modules. By separating the work in this way, the TFPPP was able to devote production line, module level resources to the task of optimizing the module layout and applying the synergistic efforts of all three programs (TFPPP, PVMAT, and ETL) to achieve the TFPPP goal of achieving an 11% aperture efficiency module.

   As part of this work, an effort was undertaken to model the benefits of optimizing the cell layout in a panel. Specifically, optimizing the number of cells per panel and maximizing the active area per panel. A linear, distributed resistance model was used in the optimization (this represents the most conservative estimate for evaluating the calculated improvement in efficiency). Calculations show that by optimizing the layout of the cells within the panel the gain in efficiency is sufficient to halve the difference between the 11% goal for the first program year and the baseline efficiency at the beginning of the program. Taken together, improvement in the module layout and improvement derived from the other NREL programs should increase efficiency by a factor of 7-8% over the current production efficiency (based on experiments undertaken in Q3). This was confirmed with the 12.2% aperture efficiency module delivered under TFPPP Phase I.

Task 4.1 Diagnostics (Phase I)

a) The Subcontractor shall evaluate first round set of in-process metrics.

- ***i) The Subcontractor shall select a first round set of key measurements.***
- ***ii) The Subcontractor shall fabricate sample sets with process variation and evaluate measurements.***

The protcol for down-selecting the characterization tools to be used in Phase I and future work was

1. Can the measurement be related to the 2nd level metrics in a module or test cell
2. Is there a path for integrating the measurement into the process line
    a. Non-invasive, non-contact techniques are preferred
    b. Destructive techniques can be used, but only if the sampling rate is very low and the test is not labor intensive
3. Availability of the test
    a. Commercially available (preferred)
    b. Test performed by outside vendor under contract (specialized or capital intensive techniques)
        i. If proven useful, then there must be a path to bringing the technique in-house
        ii. Continue using an external vendor only if no other option exists
    c. Vendors accept & respect First Solar's IP rights and confidentiality
    d. In-House development
        i. Can be developed at a systems level with off-the-shelf components
        ii. Develop from scratch (this is the least preferred embodiment)

The following are the Phase I efforts to develop the suite of third level metrics (3LM) to be used to facilitate efficiency improvement and study the root cause of efficiency degradation mechanisms in individual cells and laminate modules.

- Semiconductor temperature measurement (actual measurement of thin film temperature)
  Commercially available temperature monitors based on band gap shift with temperature demonstrated very poor accuracy with thin films. More traditional

pyrometry techniques are not being investigated under First Solar's internal R&D. No additional work will be done under the TFPPP.

- The optical spectrometry tool
  The system arrived in Q2 has been set up off-line. It has been used for development across all of the NREL programs, but is used most heavily for PVMAT's Advanced Contact Window Program. This system also calculates surface roughness as part of its advanced modeling software. Once installed, the system has proven its effectiveness in measuring the device structure through CdS deposition. With the CdTe layer on, measurements are possible, but assumptions must be made about critical structure parameters to circumvent the transmission/reflection data lost to heavy absorption in the CdTe. Nevertheless, the system will has proven its worth as an off-line tool for development and production sampling.

- Contactless Sheet Resistance Measurements
  Contactless sheet resistance measurements are now being performed on full panels using an instrument test bed adjacent to one of the Perrysburg sites process lines. The best evidence of the success of this technique is that additional unit has been procured specifically for TCO development. The non-contact sheet resistance measurements have been implemented as an off-line quality check. The system is being used as to test the conductance of the TCO on as-received superstrates and after semiconductor deposition.

- Hall Measurements by the method of van der Pauw
  A commercial unit was purchase and is now used for TCO development and qualification. The system is used to measure the TCO free carrier concentration and majority carrier mobility.

- J-V measurements as a function of light wavelength and intensity
  A test set is in operation for individual cell measurements. With this technique, the data will require extensive analysis based on a device model to extract reliable electrical transport parameters and is still being developed. However, this techniques has shown great promise in its present form as a way of quantitatively (albeit relative) evaluating changes in the back contact.

- Development of PL consisted of two parallel efforts: detailed PL as a function of wavelength measurements and the design and fabrication of a simple, robust PL system suitable for use in a production environment. Dr Wyatt Metzger of NREL has kindly been providing support with the detailed PL measurements. The robust PL measurements system was design and fabricated entirely in-house at First Solar's Perrysburg, Ohio facility. First Solar's robust PL system actually consists of two PL systems in tandem. One system to detect the CdS PL signal and the other system to detect the CdTe PL. Phase I efforts concentrated on the development and evaluation of the PL(CdS) system with the final embodiment of the equipment capable of mapping the PL(CdS) intensity of entire modules.

Extensive testing was done with this system to determine the correlation of CdS(PL) signal with efficiency and stability. The results of this evaluation showed no correlation with the CdS(PL) with either efficiency or stability. Consequently, there will be no further development of this technique as a diagnostic tool in Phase II.

- Time Resolved Photoluminescence (TRPL) for carrier lifetime measurement
  FS is currently qualifying a commercial vendor for this technique. The process has been slow and the results are questionable. First Solar will enter into an agreement with NREL to provide TRPL measurements for verifying the analysis of the commercial system and help with interpreting the results in Phase II of the program. A commercial system will be procured in Phase II to be used as the platform for First Solar's in-house TRPL development

- Electroluminescence
  Work with electroluminescence (EL) as a diagnostic tool began at the end of Phase I. EL is attractive because it could be used for analyzing efficiency degradation in the field. Further an imaging variant of this technique could provide a way of monitoring the effects of non-uniformity in production and in the field. There are two problems with this technique. The first problem is that there is no vendor producing such a system capable of capturing the EL image at low current densities in a reasonable time. Typically, the time for a single measurement is on the order of one hour. The second problem with EL is the interpretation of the data. A great deal of development needs to be done to make this technique useful. The EL development will continue during Phase II with the goal of determining if the technique is worth contracting a vendor to develop a system that would be suitable for use on the production line and in the field.

- Electron Back Scatter Diffraction (EBSD)
  EBSD measurements to obtain grain size and orientation have been implemented and data are now being collected on "production-pulls." These data are being collected for analysis to determine if these measurements are a valid predictor for efficiency; however, there is no strong correlation between the EBSD data and efficiency.

- Multi-Channel Ellipsometry
  Initially, FS was dealing with two potential vendors. Only one vendor now remains as being viable – for measurement and analysis of the data. Work with the remaining vendor will continue; however, much of the data obtainable by ellipsometery is available from optical spectroscopy. First Solar will not pursue this characterization method under this program.

- Scanning Kelvin Probe (Work Function Monitor)
  In-house development and application will require a large effort. The commercial system acquired initially for this work proved failed to demonstrate sufficient reliability and reproducibility for monitoring surface conditions or for back

contact development. This technique has far too much potential for process control and diagnosis to give it up easily. As a result, First Solar will procure another system for evaluation in Phase II of TFPPP

- Inductively Coupled Plasma (ICP) for chemical analysis (sample-based, off-line, destructive technique for chemical analysis)
  Unit is in house and operational. It has been qualified for use with liquids (chemical digestion). The system also incorporates a laser ablation sampling option. The laser ablation technique will greatly speed the total analysis time (and could be incorporated in-line), but is still in development and will continue to be developed (at reduced priority) throughout the remainder of this program.
  The ICP-MS has proven itself to be a reliable and valuable SPC tool as well as an indispensable diagnostic tool. The ICP-MS is still being used heavily in the mode where the samples are chemically digested and input into the ICP as a liquid. The use of laser ablation is still under development albeit at a slower than anticipate rate because of the ease and usefulness of the chemical digestion technique. Development of laser ablated ICP measurements for depth profiling is beginning. This technique has the promise of provided an in-house, rapid turnaround substitute for SIMS.

- IV and CV as a function of temperature
  Development of the tool for measuring IV(T) & CV(T) was completed in Phase I, Q3. This tool is being used exclusively as a diagnostic tool for determining deep levels in the semiconductor layers. There is no plan to develop expand this system as a production tool.

Task 5.1 Product Reliability (Phase I)

a) The Subcontractor shall monitor field test sites.

Data are monitored continuously. Modules from test arrays are periodically brought back to the Perrysburg facility for more extensive characterization than is possible in the array then returned to the field.

b) The Subcontractor shall continue cross-correlation between rapid ALT light exposure protocols and field testing.

In addition to monitoring field test sites, sister modules to those fielded in the arrays are subjected to ALT. In this way, a direct correlation between field results (over a period of years) and the ALT results are obtained. All testing is performed on laminated modules.

A parallel effort to determine the activation energy of the efficiency degradation mechanism(s) began in Phase I. This initial work gave rise to a plan to perform extensive ALT and characterization on a full modules utilizing different stressors – heat, light, and electrical bias. This test will be begun under Phase II of this program

c) ***The Subcontractor shall analyze modules returned from the field due to anomalous behavior.***
Field returns that exhibit low efficiency that is not attributable to some mechanical damaged are subjected non-destructive characterization to determine the cause

d) ***The Subcontractor shall develop damp-heat with bias testing protocol.***
This task is complete. This is a screening test to determine the resistance efficiency degradation with damp heat in forward bias.

e) ***The Subcontractor shall evaluate and select packaging alternatives – Phase I.***
Several different packaging schemes were examine that were intended to complement the optimized module layout. However, the decision was made to use the standard packaging scheme to reduce any risk associated with using the optimized cell design .

SUMMARY OF PHASE I

The primary milestone of Phase I was the demonstration of a module with 11% efficiency. This was achieved and greatly exceeded. The champion module delivered to NREL under this program had a confirmed aperture efficiency of 12.2% and exhibited stability with ALT.

The baseline ALT protocol has been established and is compatible with the 3LM characterization suite when applied to a combination of laminated modules, sub-modules, and individual cells. In addition to the baseline ALT, the protocol and stressors for a more extensive ALT that will result in the determination of the efficiency degradation activation energies. Once the activation energies are determined the response to the stressors should give quantify the ALT to field data.

The down-selects for the planned process improvements (buffer layer, CdS deposition method, IFL) have been determined. In each case at least two candidates are designated to mitigate the risk involved with committing to a single candidate.

PLANS FOR PHASE II

Phase II of this program has been abbreviated to three quarters and there will be no Phase III. We at First Solar are committed to achieve as many of the Phase II milestones as possible; however, with the shortened period of performance we must be selective in the priorities of the program. In the time remaining, we will produce the 12% aperture efficiency module for delivery to NREL as well as undertake the very extensive ALT reliability testing. The correlation of field data to ALT through activation energy determination cannot be completed in the time remaining in the program, but we will nevertheless continue with this effort.

Finally, the work to obtain increased efficiency through improved PDP and back contact, begun under this program and the ETL program, will continue at a level to leverage the results of the previous phases. It must be understood that these efforts will continue on a "best effort" basis and that completion by the termination date of the program is unlikely.

REPORT DISTRIBUTION

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14. ABSTRACT *(Maximum 200 Words)*

The primary milestone of Phase I of First Solar's subcontract was to demonstrate a cadmium telluride module with 11% efficiency, which was achieved and greatly exceeded. The champion module had an NREL-confirmed aperture efficiency of 12.2% and exhibited stability with accelerated life testing (ALT). The baseline ALT protocol was established and is compatible with the 3LM characterization suite when applied to a combination of laminated modules, sub-modules, and individual cells. In addition, the protocol and stressors for a more-extensive ALT will result in determining the efficiency degradation activation energies. Once the activation energies are determined, the response to the stressors should quantify the ALT to field data.

15. SUBJECT TERMS

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