October 1999 • NREL/SR-520-26948

Subcontractor Report

Thin-Film Photovoltaic Partnership — Apollo® Thin-Film Process Development

Phase I Technical Report
May 1998 — April 1999

D.W. Cunningham and D.E. Skinner
BP Solar Inc.
Fairfield, California

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Contract No. DE-AC36-98-GO10337

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Prepared under Subcontract No. RAK-7-17619-27

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Acknowledgments

Acknowledgments are due to the following people and organizations.

BP Solar Apollo® Team:
R. Bernardi, D. Cunningham (Principle Investigator), K. Davies, S. Delp, L. Grammond, S. Harrar, J. Healy, E. Mopas, M. Rubcich, M.Sadeghi, D. Skinner (Program Manager), T. Trumbly

BP Solar Inc. Systems Group:
D. Dunham, T. Murphy

National Renewable Energy Laboratory
BP Solar Ltd.
Brookhaven National Laboratory
Institute of Energy Conversion/University of Delaware
Radian International

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EQUIPMENT DESCRIPTION FOR CdS AND CdTe DEPOSITION

NREL Thin Film Partnership Project

Phase 1 Report

1. Introduction

BP Solar first started investigative work on CdTe photovoltaic in 1986. The module product name chosen for the CdTe devices is Apollo®. The deposition method chosen was electro-chemical deposition due to its simplicity and good control of stoichiometric composition. The window layer used is CdS produced from a chemical bath deposition. Initial work focused on increasing photovoltaic cell size from a few mm^2 to 900 cm^2. At BP Solar's Fairfield plant, work is focused on increasing semiconductor deposition to $1m^2$. The primary objective of this subcontract is to establish the conditions required for the efficient plating of CdS/CdTe on large area transparent conducting oxide coated glass superstrate.
The initial phase concentrates on superstrate sizes up to $0.55m^2$. Later phases will include work on 0.94 m^2 superstrates.

The tasks in this subcontract have been split into four main categories.

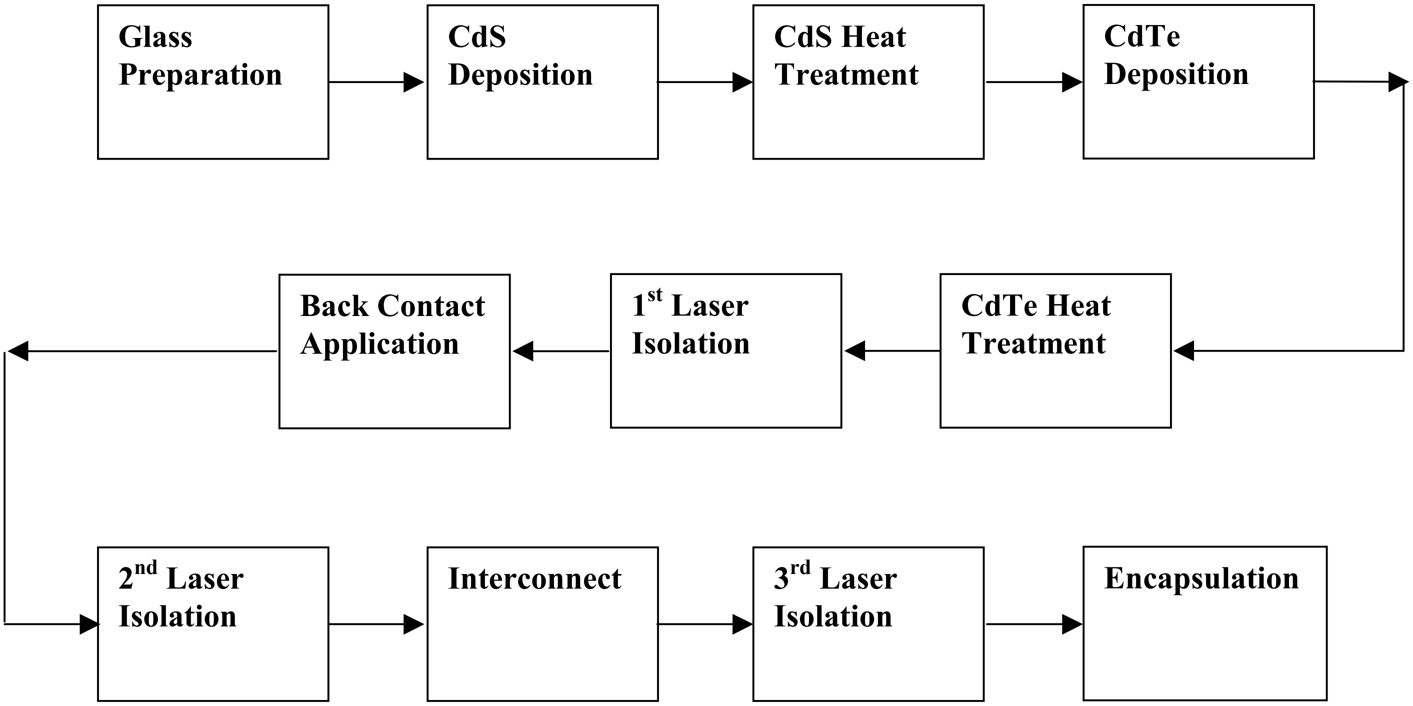
- CdS and CdTe Film Studies.
- Enhanced Laser Processing.
- Outdoor Testing Program for the Apollo® module.
- Production Waste Abatement and Closed Loop Study.

The first task is seen as critical in the characterization of the semiconductor's performance because it defines a baseline for the first devices from the large area reaction chambers. The second task will concentrate on optimization of the high volume laser processing techniques required for production. The third task, outdoor testing, is essential for any new thin film product and not only provides confidence in the device, but also may identify any improved performance over traditional crystalline silicon technology, such as low light level "switch on" effects. The last task is important for the technology since it is based on wet chemical reactions. This builds on work performed under a previous NREL contract # AFF-8-17619-27.

2. CdS and CdTe Film Studies

2.1 Process Schematic

The schematic shows the process sequence for CdS, CdTe deposition and back contact application.



2.2 Reaction Sequences for CdS and CdTe

CdS

CdS is deposited from an aqueous solution reaction. The reduction/oxidation reaction is as follows:

$$Cd^{2+}(complex)(aq) + (NH_2)_2CS(aq) + 2OH^-(aq) \rightarrow CdS(s) + H_2NCN(aq) + 2H_2O(l)$$

Excess CdS is removed from the plate using HCl. The resulting byproduct is $CdCl_2$, which is easily treated/removed in BP Solar's wastewater treatment system.

$$CdS(s) + 2HCl(aq) \rightarrow CdCl_2(aq) + H_2S(g)\uparrow$$

The H_2S gas is scrubbed using a activated carbon scrubbing system.

CdTe

CdTe is deposited by electrochemical deposition. The cathode in the reaction is a TCO coated glass substrate. The substrate is commercially available. The reaction for the reduction of Cd and Te at the TCO surface is as follows:

$$Cd^{2+}_{(aq)} + HTe0_2{}^{+}_{(aq)} + 3H^{+}_{(aq)} + 6e^{-} \rightarrow CdTe(s) + 2H_2 0_{(l)}$$

2.3 CdS Equipment and Operation

The window layer, CdS, is deposited in high volume equipment that has four in line process tanks. The equipment configuration comprises of a pre-clean DI water tank that is used to clean the glass surface, two identical process vessels and a heated DI rinse tank.

The final tank (heated DI) acts to clean and quench the deposition reaction and also aids rapid drying of the glass plate. The two process tanks are worked in parallel and are identical. Process chemicals are supplied from two reservoirs. The first reservoir contains the cadmium compound and chelating agent, aqueous ammonia. The second reservoir contains the thiourea aqueous solution. The metering/mixing of these compounds is computer controlled, as is the sequence in which they are added. This needs to be precise, as the plates must be added at the moment the compounds are placed in the tank. Also, the components must be sufficiently mixed to initiate the reaction. A typical reaction time is 15 minutes. The CdS deposition follows an exponential decay, with the fastest deposition rates occurring in the first 5 minutes. After the deposition is complete, the bath waste is sent to the waste treatment and recycling system.

The next step of the CdS process is the removal of residual CdS from the front of the glass and along the edges. The edge removal is performed so that electrical contact can be made to the tin oxide surface for electroplating. The contact is made on the exposed tin oxide surface on both long (61") edges of the plate.

The excess CdS is removed using HCl. This has been found to be a very efficient method for CdS removal. The reaction is very rapid, affording byproducts of $H_2S_{(g)}$ and $CdCl_{2(aq)}$. Both byproducts are easily abated and controlled. These abatement technologies were described in detail in BP Solar's DOE funded project that was completed July 1998.

The final CdS process step prior to CdTe deposition is a 400C heat treatment that recrystallizes the CdS, modifying its band gap.

2.4 CdTe Equipment and Operation

Three plating systems were used in Phase 1 work as follows.

Single Plate Tank

During the first quarter of Phase I considerable emphasis was placed onto Task 1.0 with respect to equipment design. It was decided to build a dedicated single plate, large area tank to be used exclusively for the NREL funded program. This way specific tests could be performed under the program without affecting production activities at Fairfield.

The equipment design was based on a single plate bath capable of accommodating 61” by 14”; tin oxide coated glass substrates. For ease of operation in a manual mode, the plate was orientated with the 61” length parallel to the horizontal. Bath details are as follows:

Solution volume:	200 litres
Maximum cathode size:	14” x 61”
Heating capacity:	8 kW (Electric)
Control:	Autostat (Potentiostat)
Construction materials:	All natural or heat stabilized polypropylene Exposed metals are Teflon™ coated
Solution components:	Cadmium sulphate Tellurium oxide Sulphuric acid 18 MΩ DI water

On installation of the bath, activities included solution purification by electrolysis and impurity analysis. Impurity concentration was determined using BP Solar’s in-house ICP-AES.

Pilot Line Tank

In addition to the single plate tank BP Solar also constructed a full scale, single production unit utilized specifically for scale-up issues. The tank is capable of accommodating forty (40) 61” x14” substrates and uses a standard production potentiostat controller. This tank stands alone from the main production line, so process experiments can be performed independently. The volume of the tank is 4,000 lites, and heating is provided by a Teflon heat exchanger served with 250°F process water from an external circuit. The process water is heated using natural gas. We believe this is a unique method of process heating for semiconductor material fabrication and significantly reduces energy costs for the Apollo® process.

Main Production Tank

The main production system is independent of the prototype tank, but is comprised of the same basic forty (40) plate unit used in the pilot line, replicated eight (8) times. The equipment has a high level of automation especially with respect to plate handling. For each forty (40) plate tank there are two (2) recirculation pumps which supply Tellurium replenished solution to the plate cathodes. These pumps are standard Teflon based, magnetic drive systems. The computer-controlled potentiostat is used to administer the applied voltage to the cathode plate. It is also used to determine the total charge applied to the plate by integrating the plating current with time. The target charge is 1200C/sqft and the charge produces approximately 1.6μm of CdTe film.

Figure 1. Main Production Tank

2.5 Material Characterization

In addition to the CdS and CdTe characterization, the Fairfield team also conducted characterization studies on tin oxide.

10Ω/□ tin oxide optical characterization.

BP Solar uses nominal 10 ohm/sq (sheet resistivity range 9 to 11Ω/sq.) tin oxide coated glass as a primary substrate for the deposition processes. We have studied the optical properties of recent tin oxide coated glass (made April 1998) versus older generation materials (circa 1992). We wish to study the morphology of the material in more detail but so far have used only optical methods to characterize the material. We plan to expand the work on TO during the next phase.

The optical characterization has shown a difference between the old and new 10-ohm/sq materials. The transmittance is normal transmittance corrected to AM1.5 and as measured in air. The integration range was 350nm to 850nm.

There appeared to be a 10% higher transmittance of light in the above range comparing old tin oxide glass to new. Continuing work will determine if this has an effect on the device performance.

Table I. Transmittance

Substrate	Transmittance (%)
Old 10 ohm/sq	70%
New 10 ohm/sq (low haze & high transmission)	77%
Old 10 ohm/sq haze value	5%
New 10 ohm/sq haze value	1%

CdS Optical properties

The band gap and transmittance measurements are shown for various CdS thickness is in the table below. All CdS depositions are on new 10 Ohm/sq TO except where stated.

Table II. Band Gap and Transmittance Measurements for CdS

Sample	*Thickness (Å)*	*Bandgap uCdS (eV)*	*Transmittance uCdS (%)*	*Bandgap hCdS (eV)*	*Transmittance hCdS (%)*	*Comment*
a	700	2.43	57			UK
b	749	2.38	51	2.15	47	UK
c	595	2.42	58			Fairfield
d	623			2.32	55	Fairfield
e	666			2.28	55	Fairfield
f	679	2.41	57			Fairfield
g	897			2.26	53	Fairfield

NOTE: u stands for un-heat treated, and h stands for heat-treated.

In the above table, the transmittance measurements show the CdS made on production equipment at Fairfield is comparable to the CdS made by the UK team on 1 square feet TO plates. An example of the transmittance versus wavelength for preheat treated and post heat-treated CdS is shown below.

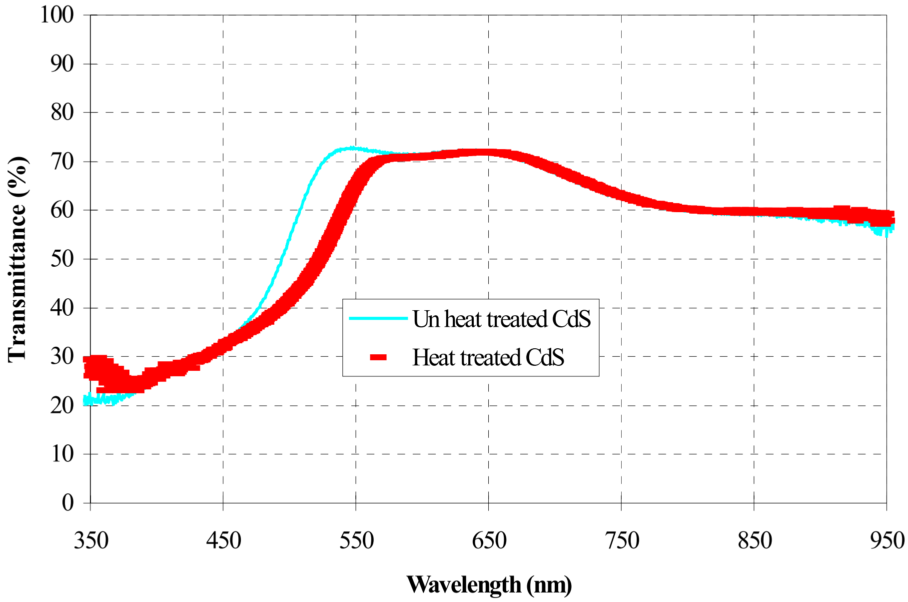


Figure 2. CdS Comparison: Unheat-Treated & Heat Treated

CdTe Optical properties

All CdTe depositions are on new 10 ohm/sq except where stated. The thickness and band gap measurements were determined optically using the same software controlled equipment (Oriel spectrophotometer) used in the CdS analysis. Note that although these results & CdTe thickness are on early devices from the plating system, there is good correlation with the equivalent test samples (1sqft) from the UK group.

Substrate size: BP Solar has been performing the engineering trials on both 14” x 61” and 14” x 48”size substrates. While the main plating has been on the 14” x 61” substrates, the substrate is often cut down to 48” in length so that 1sqft can be used for characterization off line from the device processing.

Table III. Band Gap and Transmittance Measurements for CdTe

Sample	***Bandgap uCdTe (eV)***	***Bandgap hCdTe (eV)***	***Comment***
a	1.518	1.499	UK made &measured.
b		1.474	UK made, Fairfield measured.
c		1.472	UK made, Fairfield measured.
d		1.474	Fairfield made & measured.

In summary, initial characterizations of the tin oxide coated glass, CdS and CdTe deposits have shown good correlation with the small area samples from the UK group. Tin oxide plates from the glass manufacturer made in 1998 have shown better transmittance (about 10%) than earlier production (circa 1992). The effect on device performance of this is yet to be quantified.

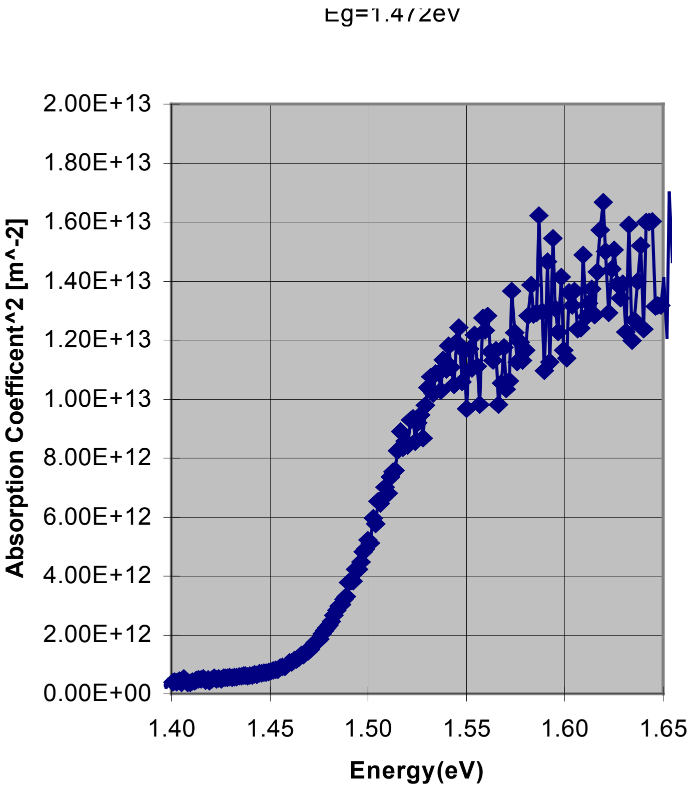


Figure 3. Heat Treated CdTe

2.6 Optimization of CdS/CdTe Bath Operations

CdS:

An improvement in device quality with increasing CdS thickness was observed in terms of an improvement in the integrity of the CdS layer. The thicker layers that are less prone to pinholes and this is reflected in the observed improvement in fill factor and Voc. Thicker CdS layers have not affected Isc over the range studied.

Figure 4 shows the effect of cadmium sulphide thickness on plate efficiency. The average efficiency of plates with cadmium sulphide thickness below 875 angstroms is approximately 5%. Above 875 angstroms the average efficiency was greater than 6%. The origin of this improved efficiency can be identified as coming from primarily Voc and fill factor.

CdTe:

There has been also been an improvement in device performance with increasing CdTe thickness. The reasons for this improvement are less clear, but there is an obvious increase in both fill factor and Voc. Such an increase in these properties would not be caused by deposit thickness alone. It is believed that CdTe thickness also effects recrystallization and final crystal size. The effect on larger grain sizes has contributed to the improvement. On the other hand, an expected improvement in Isc, with increasing CdTe thickness, has not been observed.

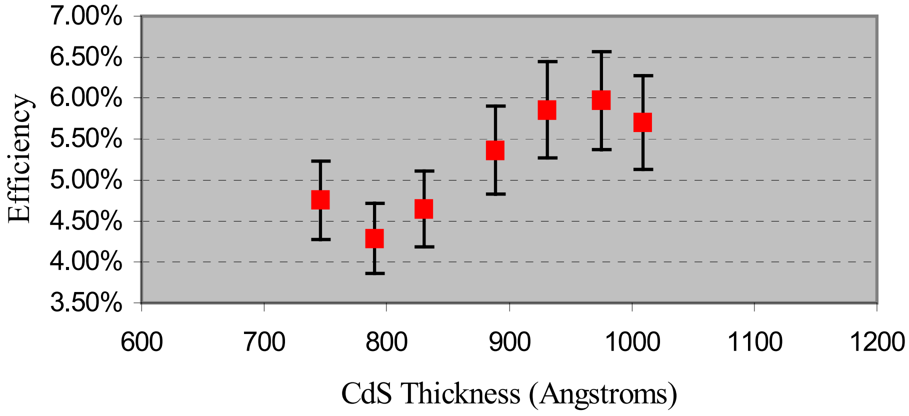


Figure 4. CdS Thickness versus Average Efficiency

Figure 5 shows the effect of CdTe thickness on plate efficiency. A trend of increasing efficiency with CdTe thickness is observed between approximately 1.0 and 1.8 microns. After 1.8 microns there appears, within measurement error, to be a plateau. Above 2.2 microns there is insufficient data to determine whether the plateau continues or whether performance actually changes.

Figures 6 and 7 show the relationship between CdTe thickness and Voc and Isc respectively. The Voc described here is for a 31 (active) cell plate. The Isc relates to a 119.4cm2 cell area. This area includes wasted width. The Voc increases by about 120 mV between CdTe thickness of 1.0 to 1.8 microns. Above 1.8 microns there appears to be a plateau. The relationship between CdTe thickness and Isc is less clear. However, there appears to be an improvement in Isc with increasing CdTe thickness over the range 1.0 to 1.5 micron. The difference is too small to accurately quantify. Fill factor improves over the CdTe thickness range of 1.0 - 2.2 microns.

Because of variations in CdS thickness, efficiency versus CdTe thickness was determined for all CdS thickness values over 870 angstroms. The same trend of increasing efficiency with CdTe thickness is observed. Again there is insufficient data above a 2.3-micron thickness to establish whether there is any effect on efficiency at even higher thickness.

CdTe Heat treatment:

Experiments on the heat treatment of CdTe are continuing. While initial results indicate that the optimum temperature for n-p conversion and recrystallization is higher than previously used there is insufficient data to accurately assess the effect of different temperatures on the conversion process.

Conclusions:

Initial correlations have been identified for CdS and CdTe films and electrical performance. Future work will continue to optimize the films with electrical properties.

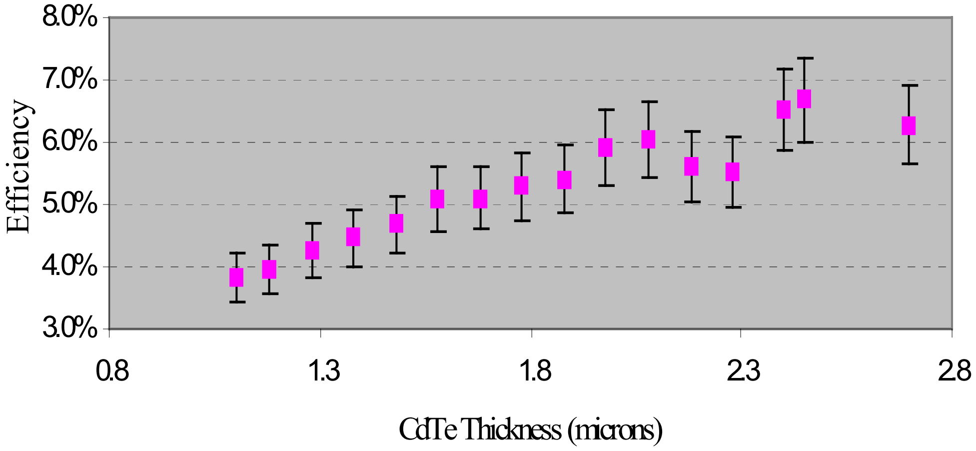


Figure 5. CdTe versus Efficiency

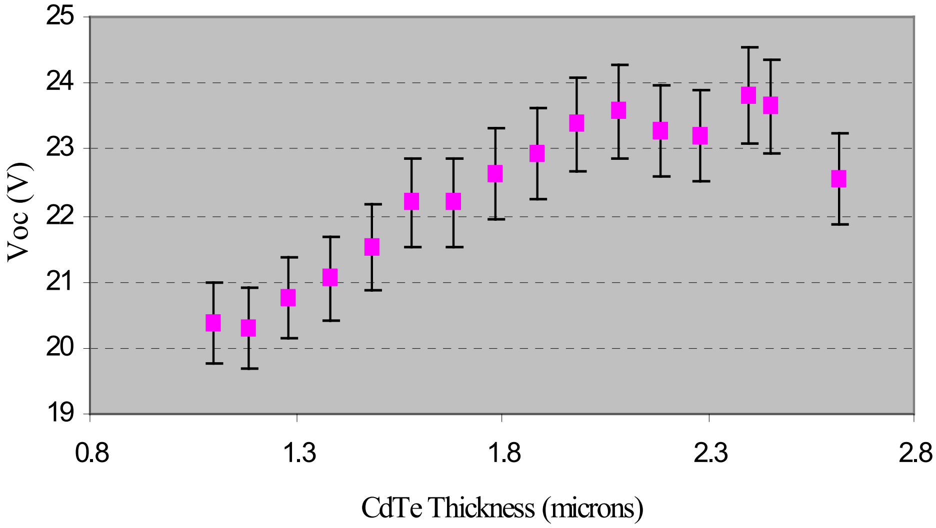


Figure 6. CdTe Thickness versus Plate Voc

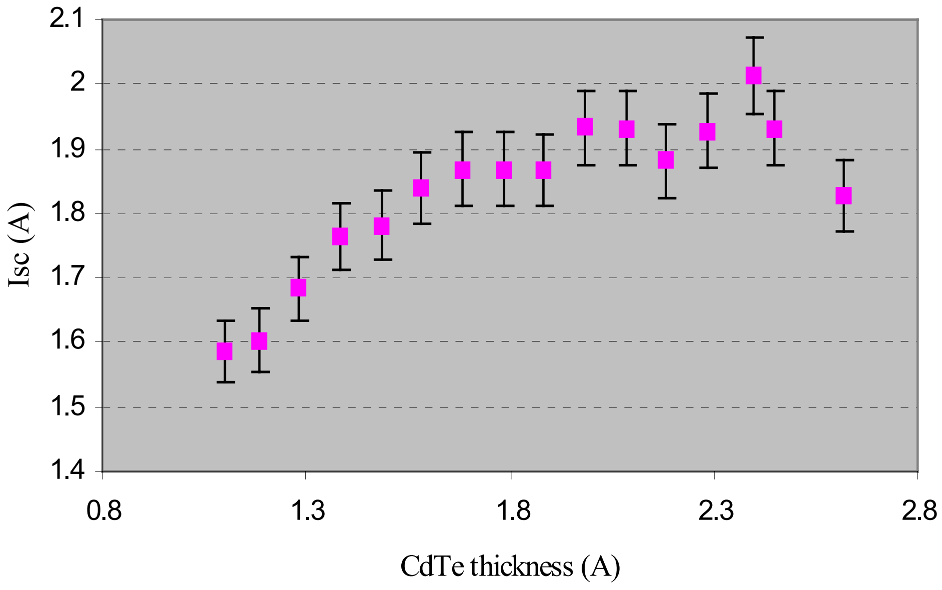


Figure 7. CdTe Thickness versus Plate Isc

3. Enhanced Laser Processing

The aim of this task is to optimize laser scribing and, therefore, optimize any aspects that affect device performance. BP Solar staff visited manufacturers such as U.S. Laser to perform trials on speeds and cutting frequencies. Various beam powers were utilized and cutting speeds up to 8 inches per second were investigated. Laser table travel speed is important to achieve high throughput and manufacturing economies. Laser scribing is critical in the BP Solar thin film process as it needs to be selective with respect to cutting the tin oxide in the first cut but, for the second and third cut, the tin oxide needs to be left untouched. Damaging the tin oxide during these scribes could lead to a high series resistance, device instability and, in the worst case, breakdown in the device series interconnect.

Higher frequencies and higher powers have been made possible more recently with the availability of LBO (lithium borate) crystals used as frequency doublers. It is hoped that this will allow BP Solar to use a single high power laser split six times to improve throughput at the laser station.

4. Outdoor Testing Program for the Apollo® Module

During Phase 1 of the project the BP Solar team set up two outdoor systems to determine reliability of the Apollo® modules. The objective of the outdoor systems was to place the modules in a real environment and evaluate the performance under load. Initially a small system was installed of just eighteen (18) modules, albeit grid connected. In the last quarter of Phase 1 a second, larger system was installed on the grounds of the BP Solar factory. A description and presentation of the initial results are given as follows.

4.1 0.5 kW Roof Mounted System

An important area for qualification of a new thin film process is outdoor testing. During the first quarter of Phase 1, an interim test structure was erected on the roof of the Fairfield building. Some of the first modules to be produced at Fairfield were placed into this structure. A total of 18, 25W modules were connected in 6 parallel strings of three modules. This configuration was chosen to fit the nominal 48V (Vmp) input requirement of the grid tied Trace inverter. The Trace inverter is a 4kW utility-tied device.

The modules on this system had been operational for one year starting April 1998 through the summer period at Fairfield. The data obtained from these modules has been averaged over the period and displayed on Figure 8. The stability of the array appears good over the extended period. There have been no operational problems with the inverter during this time. Within measurement errors (±2%), the module performance has been stable. The array will continue to be operational along side a second 2kW system, so that their performance can continue to be tracked and compared.

During February 1999, the inverter was removed and installed on the 2kW system. At this time, a passive load resistor was connected to each module on the roof system to keep them close to maximum power point.

The performance of the roof-mounted system over a one-year period is shown in Figure 8.

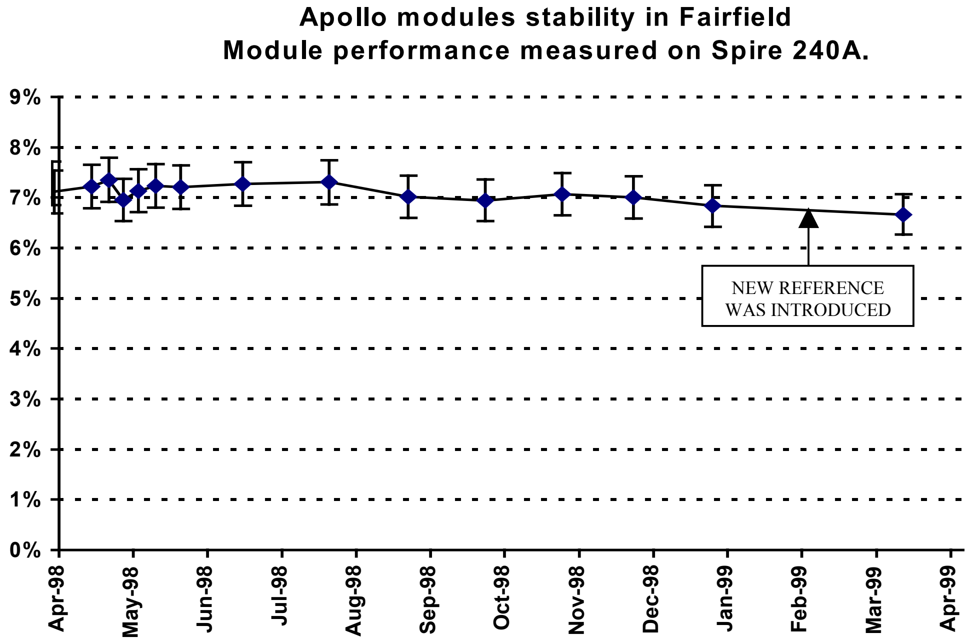


Figure 8. Outdoors performance on the 0.5kW system

The graph in figure 8 shows the performance of the modules after a twelve-month period of continuous operation. In order to measure the power and determine the efficiency of the modules, they needed to be removed from the array. The modules were measured on a spire 240A. Each data point represents average module efficiency for all the modules under test. The plot clearly shows continuing stability over the measurement period, with the average module efficiency at approximately 7%. The perturbation seen early in the measurements is due to a period where the system was being loaded with modules. As a result, the average efficiency appears to vary across the first few weeks of operation as the sample size changes.

It should be pointed out that on February 18th 1999, a new reference (measured by NREL) was introduced as calibration module for the 240A. A 2% (relative) lower efficiency was observed after the change. This explains the slightly lower value for the last measurement. In summary, after a year of operation, the first article Apollo® module shows good stability in a real environment.

4.2 2kW Ground Mounted system.

While the roof top system data was valuable, the design has a number of limitations. The main limitations of the roof top systems are as follows:

- The array needs to be dismantled for the module performance to be measured. No continuous data logging is installed.
- There is no continuous method to measure insolation, wind speed, or temperature.
- The roof was not designed to withstand structural loads. Therefore, the system cannot be expanded.

A plan was drafted in co-operation with the BP Solar systems engineering group to build a ground mounted 2kW system. Advantages of this approach are the incorporation of a data logger into the system design and greater outdoor testing capability for BP Solar. Also, the larger 2kW system means the inverter can operate more efficiently.

The CdTe team has worked closely with the BP Solar Inc.'s system group to develop a 2kW ground-mounted system adjacent to the factory. The 2kW system incorporated the 14" x 48" engineering size plates. This size was smaller than the commercial 14" x 61" plate. However, the behavior of the module will be very similar. The system grid is tied using a Trace inverter.

Figure 9. 2kW Beta Site System

Initially, the data will be saved to a 2MB-memory board in Fluke data acquisition system. Later the system performance data will down load, via modem, directly to the BP Solar server at Fairfield. We hope to implement this change in Phase 2.

From the picture, the data logger and inverter station can be seen below the array, in a central location. The data logger is contained in a weather proof, NEMA enclosure. The mounting structure used for the system is a standard design used in BP Solar. The lowest point of the array is 6 feet off the ground and allows for easy maintenance of the electronic equipment as well as providing shade from direct sunlight.

The final installation included a certification from the local utility, PG&E. All the modules are covered with a protective film during the installation period. Once fully installed, they were uncovered at the same time and data logging started operation. The system was put in operation on March 18th1999.

The following highlights the system's functionality in detail:

- 3 modules are put in series to form a **string**.
- 4 strings are put in parallel to form a 12-module ***sub-array***.
- 6 sub-arrays are put in parallel to form ***array***.
- Total: (3x4x6) 72 modules

An array junction box contains the inputs from the 6 sub-arrays. The junction box was configured so that load voltage and load current could be measured on each sub-array. Also, the sub-arrays can be individually set at an Isc and a Voc mode independently of the other sub-arrays.

The array is connected to the grid by a TRACE inverter SW5548PV. This TRACE inverter has a power point tracking system built in. At the moment the inverter is tracking every minute looking for a 1A increase in an AC current. When the system is in this mode, we can assume that it is operating at Imp and Vmp. A Fluke Hydra series II 2635A data logger with 24 channels is use for data acquisition. The channels are designated for recording the following variables:

- Insolation: Measured by a LI-COR pyranometer. This provides a variable voltage signal. The intensity is determined in W/m2 using a conversion factor, y=mx+b (m=76.4643E03).
- Current in each sub-array: All the currents are measured using a 50mV/10A Shunt resistance.
- Voltage in each sub-array is measured, just before the shunt resistance.
- Temperatures of modules are measured at different localizations on the array bottom, middle, top, front, and back of the module.

- Ambient temperature: Measured by a thermocouple fixed on the electrical box sitting in the air. The thermocouple is shaded from direct sunlight.
- Wind speed: Measure with a Young Gill microvane & 3-cup Anemometer model 12002/12005

The data are stored in a SRAM memory card that is inserted into a PCMIA slot in the Fluke data logger. The data logger is set up to perform a sweep every 2 minutes. Each week, the card is downloaded to an ACCESS database. Graphics have been set up to show for a specific day the current, voltage (Figure 10), power, intensity (Figure 11), temperature and wind (Figure 12) on a *two minute* basis or on *hourly* basis.

The following graphs show some of the initial data obtained from the system. The first figure shows the voltage and current output for sub-array 1. The inverter load sets the DC voltage at 48V. While the DC current follows insolation fluctuations, an affect of the inverter operation is apparent at light intensities below 100W/m^2 that affect the V load voltage. If the array current is below 1A(DC), the inverter has difficulty determining maximum power point. This is manifested as poor load voltage control and is evident at the beginning and end of the day. Trace is investigating a new inverter range that starts maximum power point tracking in the mA current range rather than amp range. This will give the inverter much better low light level performance. When available, this inverter will be installed in place of the current model.

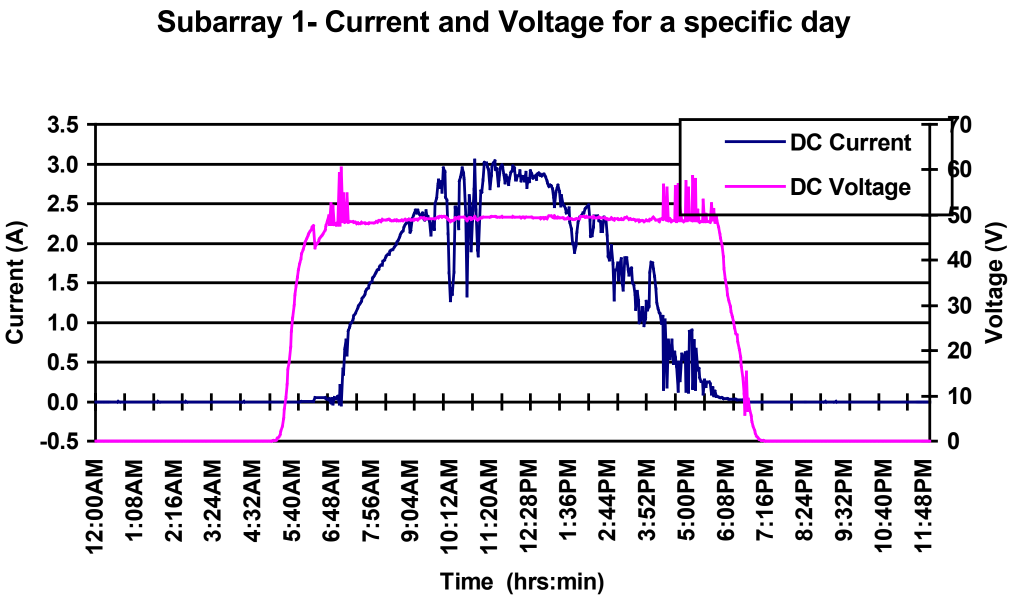


Figure 10. Example of current and voltage graph for one sub-array for a specific day 03/28/99.

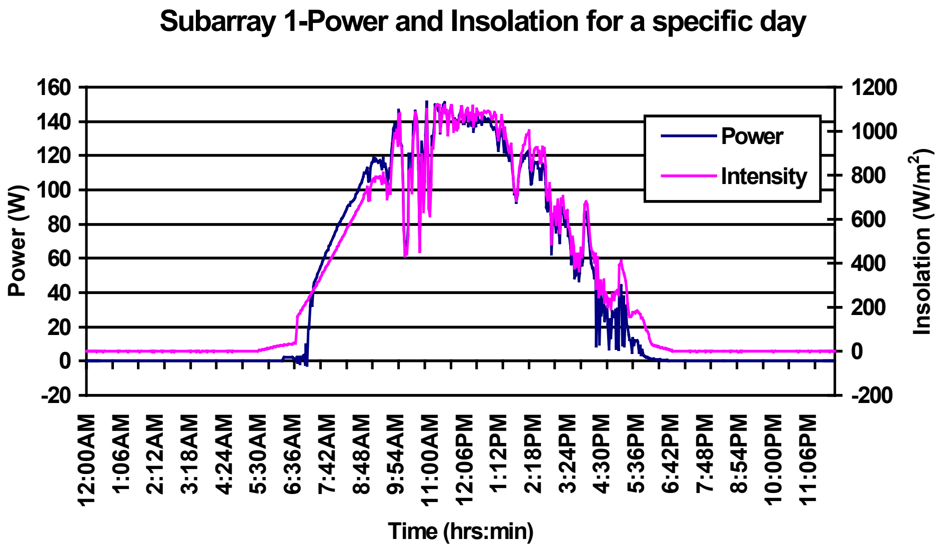


Figure 11 Example of power and insolation graphs for one sub-array for a specific day 03/28/99.

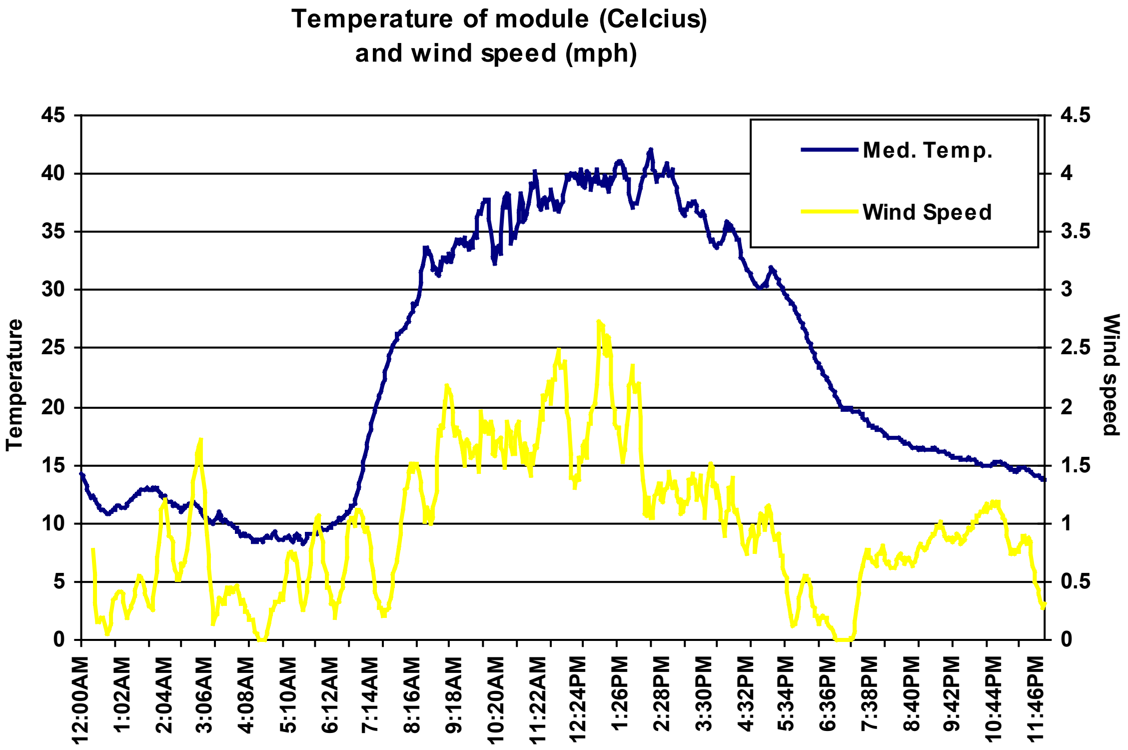


Figure 12. Example of temperature and wind speed graphs for one sub-array for a specific day 03/28/99.

Normalized power is calculated for each sub-array each day. The current and voltage readings are normalized to 25°C and an average power is calculated for values that are recorded when the insolation varies between 975 and 1025 W/m^2. Therefore, within error, no normalization is required for light intensity.

In summary, BP Solar has constructed two outdoor systems for measurement and evaluation of Apollo® module performance. The initial data is very encouraging for the Apollo® technology, showing good stability in a grid-connected application

5. Production Waste Abatement and Close Loop Study

Introduction:

BP Solar worked with its contractor, Radian International, to research improvements to the production waste abatement processes at the BP Solar Fairfield facility. The objectives of this program are to enhance the performance of the current waste abatement processes, make progress toward the closed-looping of the wastewater streams, and maximize reclamation of cadmium and other materials. The results are described in this section.

5.1 Characterization to Determine Feasibility of Closed-Loop Treatment

Characterization efforts included further analyzing and estimating waste stream composition, developing process flow diagrams for waste streams, and defining the specifications of the reverse osmosis system.

5.1.1 Analyzing and Estimating Waste Stream Composition

Waste stream characterization efforts focused on understanding the nature of the major waste streams generated by the Apollo® process, the cadmium sulfide (CdS) bath discharge and combined plant rinse waters, and the spent solution and rinses from downstream processes.

Sampling and analysis was performed on the CdS bath discharge and combined plant rinse waters at various locations through wastewater treatment. The objective was to determine if the wastewater generated by the various Apollo® manufacturing steps is consistent with the wastewater characterization that formed the basis for the equipment design and the treatment process performance guarantees. There was speculation that waste may contain more particulate CdS than originally predicted. The analysis shown below in Table III verifies that the wastewater (post-filtration, as introduced to the treatment system) is in fact within specifications for total and dissolved cadmium and total suspended solids (TSS).

Table IV. Analysis of Wastewater from CdS Bath and Plant Rinse Waters

Sample Location	Analysis Results (mg/L)				
	Total Cadmium	Dissolved Cadmium	Total Sulfides	Dissolved Sulfides	TSS
CdS bath	210	120	23	1.6	87
Bath discharge post-1.0 µm filters	79	66	6.4	1.2	nd
Collection tank	310	280	3.6	1.2	nd
Waste treatment influent tank (T1A)[1]	17	18	1.2	nd	nd
Post-ion exchange 1.0 µm filters	13	14	1.6	1.6	nd
Post-ion exchange	nd	0.04	1.6	1.2	nd

[1] Specifications for waste treated by ion exchange/electrowinning system are determined at this point. Wastewater specifications for Cd = 250 mg/L, and for TSS = 34 mg/L.

CdS = cadmium sulfide
mg/L = milligrams per liter
nd = nondetect.
µm = micrometers
TSS = total suspended solids

Characterization of the waste generated from downstream processes relied on material balance and spot analysis of cadmium rather than field sampling and analysis. Table IV summarizes the key attributes of the three waste streams coming from downstream processes.

Table V. Waste Stream Components from Downstream Processes

	Spent Solution	First-Stage Rinse	Final-Stage Rinse
Average service flow rate at full production[1]	50 gallons/shift	160–240 gallons/shift	240 gallons/shift
Total cadmium	150–300 ppb	75–150 ppb	15–50 ppb
Organics[2]	870 ppm	4790 ppm	120 ppm
pH	10.5–12	6–9	6–8

[1] Flows are based on changing the tanks every six hours at a full-production rate of 40 plates/hour.
[2] A mixture of compounds consisting of large organic molecules.

ppb = parts per billion
ppm = parts per million

5.1.2 Developing Process Flow Diagrams for Waste Streams

Radian worked with the BP Solar team to prepare 12 process flow diagrams (PFDs) illustrating waste flows and piping details. The investigation of waste stream piping that generated these PFDs served to clarify sources of waste and identify any sources of "uncharacteristic" waste or city water that might be entering the treatment systems.

Actions taken by BP Solar as a result of this investigation will reduce the potential for discharges to the wastewater treatment process that could make the waste difficult to treat by the current treatment processes. These PFDs will be used throughout the closed-looping evaluation to:

- Refine waste stream content and quantities based on as-built design information;
- Rank waste streams for closed-looping potential; and
- Further identify opportunities for segregation or process improvements.

5.1.3 Defining the Specifications of the Reverse Osmosis System

BP Solar uses reverse osmosis (RO) system to provide all the deionized water needed for the Apollo® processes. The influent specifications of the RO system dictate the treatment objectives for closed-looping. Radian investigated the possibility of recycling treated wastewater as deionized water makeup. Any treated wastewater recycled to the RO would need to be carefully pretreated for removal of the following:

- Particles: Particles greatly affect pressure drop and could render the membrane unusable;
- Organics: Because of biofouling and/or surfactants (cationic or anionic), organics attach to the highly charged surface of the membrane and render it unusable; and
- Oxidizing agents:. These include H_2O_2, Cl_2, etc. Oxidizing agents are not likely an issue for BP Solar's wastes.

Emphasis has been placed on treatment or removal of particulate and organic material to support BP Solar's objectives for closed-loop reuse of wastewater as potential deionized water makeup.

5.2 Technologies for Organic Material and Particulate Removal

Radian investigated technologies for removing organic material and particulate from the two major waste streams generated by the Apollo® process: (1) the spent process solution and rinses from downstream processes and (2) the CdS bath discharge and combined plant rinse waters. Using these investigations, BP Solar is undertaking the treatability tests described further in this section.

5.2.1 Treatment Alternatives for the Downstream Process Waste Streams

The downstream processes involved in the manufacture of Apollo® thin film modules generate waste streams contaminated with organic material and cadmium. These large-volume waste streams include a spent process solution and two rinse streams. The objectives of the waste treatment evaluation for downstream process waste streams are as follows:

- Determine the waste volume reduction capabilities;
- Determine the economics for recycling the spent process solution;
- Determine total organic compound (TOC) and cadmium removal capabilities; and
- Identify the chemical or other limitations of the treatment systems.

The organic material present in the downstream process waste streams tends to agglomerate into a scum layer on the surface of the water and is therefore not suited for treatment with several technologies that are commonly used to remove organic compounds from wastewater (e.g., carbon adsorption or chemical oxidation). One possibility is to chemically pre-treat the water to flocculate the organic material and particulate cadmium. Also, some specialized membrane filtration systems appear to be capable of removing organic material and particulate cadmium. Most membrane systems would not concentrate the waste to an acceptable degree because they would be fouled by organic material. Table V shows technologies that Radian has identified for evaluation.

Table VI. Technologies for Removal of Organic Material from Downstream Process Waste Streams

Technology	Priority	Comments	Capital cost[1]
High-shear membrane treatment	High: begin laboratory investigation	Waste stream was reduced by 90% before running out of sample in concentration study. Vendor predicts waste stream reduction of >95%, based on experience.	$90,000 per unit
Cross-flow membrane filtration	Low: pending results of initial tests	Waste stream is reduced by an estimated 95%. Believed to be more subject to fouling than high-shear membrane	$84,000 per unit
Chemical pre-treatment/flocculation	High: begin laboratory investigation	Concentration study needs to be conducted.	$30,000

[1] Capital costs are approximate and vary based on the volume of influent into the unit and the degree of waste stream reduction. Annual operating costs and installation are not included in the estimate.

5.2.1.1 High-Shear Membrane Treatment

This treatment process utilizes an innovative high-shear technology that provides the efficiency advantages of a flow-through membrane but prevents fouling by minimizing the buildup of particles on the surface of the membrane. The membrane filtration system also removes particulate cadmium. The organic material found in the downstream process waste streams has been successfully separated by this technique in laboratory screening tests. The equipment manufacturer predicts a waste volume reduction of 98% to 99.5% (significantly greater than that of any competing technology). Concentrating the solids to this degree would eliminate the need for additional de-watering equipment (e.g., filter press). BP Solar is currently conducting a concentration study with the equipment manufacturer to determine the treatment capabilities of this technology.

5.2.1.2 Cross-Flow Membrane Filtration

Inquiries into ultrafiltration systems suggest that the organic material that was found in the downstream process waste streams would foul most cross-flow membrane systems. One of the downstream process equipment manufacturers has experience in treating the spent solution and rinse streams generated by BP Solar with a cross-flow membrane system. From this experience, the manufacturer expects a waste stream reduction of 95%. Additional dewatering equipment would likely be needed to reduce the sludge volume.

5.2.1.3 Chemical Pretreatment/Flocculation

One supplier of wastewater treatment systems has developed a system to treat wastewater contaminated with organic material from processes in the microchip industry. The processes on which the system is bases are similar to BP Solar's downstream processes.

The organic material is first chemically treated to convert it into a granular material that settles out of solution under alkaline conditions. Particulate cadmium is also removed during this process. This technology has a lower capital cost than the other two alternatives. Also, the supplier of this system has already provided the reverse osmosis, media filtration, and disinfection systems at BP Solar. BP Solar is currently conducting a concentration study with this supplier to determine the treatment capabilities of this technology.

5.2.2 Treatment Alternatives for CdS both Discharge and Plant Rinse Waters

The approximate characteristics of the spent cadmium bath and collection tank waste streams are shown in Table VI. Several feasible alternative technologies exist for treating particulate from CdS bath discharges. Table VII shows the most promising technologies.

The objectives of the particulate removal evaluation are as follows for each technology:

- Determine the waste volume reduction capability;
- Determine the TSS, TOC, and cadmium removal capability; and
- Identify the chemical and other limitations of the system.

5.2.2.1 High-Shear Membrane Treatment

The high-shear membrane treatment technology described previously for removal of organic material from the downstream process waste may also be a feasible technology for particulate removal. Treating both streams simultaneously could reduce the capital cost of equipment to address the downstream process waste streams and CdS bath particulate wastes. However, it has not yet been demonstrated how effective this technology can be at treating either of these streams independently or both streams combined. The characteristics of the treated wastewater and residual sludge will be important aspects of evaluating the overall cost of the combined treatment. BP Solar is currently conducting a concentration study with the equipment manufacturer to determine the particulate removal capabilities of this technology on the CdS bath discharge waste. A concentration study on the combined downstream process waste streams and the CdS bath particulate wastes will also be performed.

Table VII. Components of the Spent Cadmium Sulfide Bath and Collection Tank Waste Stream

	Cadmium Sulfide Bath	Collection Tank[2]
Peak service flow rate	NA	16–18 gpm
Dissolved cadmium[1]	120 mg/L	70 mg/L
Total cadmium	210 mg/L	80 mg/L
pH	10–11	10–11

[1] Dissolved cadmium was determined using a 0.45 µm filter
[2] After 1.0 µm filtration

µm	= micrometer
gpm	= gallons per minute
mg/L	= milligrams per liter
NA	= not applicable

Table VIII. Technologies for Particulate Removal from Cadmium Sulfide Bath Discharges

Technology	Priority	Comments	Capital Cost[1]
High-shear membrane treatment	High: begin investigation	Vendor predicts waste stream reduction of 98% to 99.5% (estimate based on experience).	\$160,000
Centrifuge	Medium	Waste stream can be reduced by >95% (estimate based on experience).	\$200,000
Cross-flow membrane microfiltration	High: begin investigation	Waste stream can be reduced by an estimated 95%.	\$100,000
Dissolve CdS in the presence of surrogate metal	Medium	Could produce sulfur or H_2S. Approach needs to be revisited.	\$95,000

[1] Capital costs are approximate and vary based on the volume of influent and the degree of waste stream reduction.

5.2.2.2 Centrifuge

A decanter centrifuge capable of removing particles as small as 1 micrometer (μm) was proposed by one equipment manufacturer for removal of particulate from the CdS bath discharge waste. The preliminary concentration studies by this manufacturer predicts waste reduction of at least 95%, and possibly as high as 98%, with the potential to form a solid sludge requiring no further dewatering equipment. However, the wastewater sample they tested may not have been representative, as the particles in the sample were all greater than 1 μm; other analysis indicates that 52% of the particulate in representative CdS bath discharge is between 0.5 μm and 1 μm. This equipment manufacturer has a solids-ejecting separator technology that is capable of removing submicron particles that could be investigated further. Due to these uncertainties, mechanical complexity and higher cost, this technology was not chosen for BP Solar's initial treatability testing.

5.2.2.3 Cross-Flow Microfiltration

Because most of the particulate matter in the CdS bath discharge stream is larger than 0.5 μm, it is feasible to use microfiltration technology to remove particulate. Several equipment manufacturers have recommended microfiltration technology for particulate removal. One unit under evaluation is a 0.1 μm cross-flow microfilter that includes a filter press for dewatering the solids in the reject stream. BP Solar is currently conducting a concentration study with the equipment manufacturer to determine the particulate removal capabilities of this technology.

5.2.2.4 Dissolve CdS in the Presence of Surrogate Metal

Radian has been developing a technology that may be suitable for treating the CdS bath discharge. This technology works by disengaging the cadmium from the sulfide, forming a complex of the cadmium with an organic material, and precipitating the sulfide with a surrogate metal that has a high affinity for sulfur and a low affinity for the organic material. This technology leaves cadmium in dissolved form, where it is recovered by the existing ion exchange/electrowinning process. This technology would also allow recovery of cadmium presently removed as particulate CdS on filters (estimated to be 70% to 75% of the total cadmium discharged). The required equipment for this technology is a flocculation tank and a settling vessel. A filter or filter press may be required for dewatering, but the ferrous sulfide waste produced may be non-hazardous. A laboratory feasibility study needs to be conducted to investigate this option further.

5.2.3 Treatability Test Plans and Status

BP Solar has initiated treatability tests with two suppliers to evaluate the effectiveness of their technologies in removing organic material from the downstream process waste streams and particulate from the primary wastewater stream. Treatability testing is designed to provide the information necessary to determine which of the alternatives are most capable of meeting treatment and waste reduction goals, and which are most economically desirable.

The high-shear membrane treatment system unit offers several alternatives for treatment of BP Solar's waste streams. For example, this process may be capable of treating a spent solution from a downstream process (separate from other streams) for potential to recycle this material. The process may also be capable of treating both the downstream process wastes and the CdS bath discharge wastewater stream combined for removal of both particulate and organic material. BP Solar has collected samples of process wastewater and CdS bath solutions and sent these to the supplier. The supplier will mix the samples to make the desired testing solutions. The attributes of these sample streams and the treatment goals are presented in Table VIII.

Another treatment system supplier proposes two different processes for the treatment of the downstream process waste streams and the CdS bath discharge wastewater streams.

They propose treating the CdS bath discharges by cross-flow membrane microfiltration and the downstream process waste streams by chemical pretreatment and flocculation.

Their processes are not capable of combined treatment of these waste streams. Therefore, only two test solutions are identified for treatability testing. BP Solar has collected samples of process wastewater and bath solutions and sent these to the supplier. The supplier will mix the samples to make the desired testing solutions. The attributes of these sample streams and the treatment goals are presented in Table IX. The results from this study will be determined during Phase 2.

Table IX. Treatability Test Solution Attributes and Treatment Goals for the High-Shear Membrane Treatment System

Test Sol’n	Solution Contents	Process Flow Rate	Treatment Goal	Waste Stream Reduction Goal
1	50 gallons of spent solution	50 gallons/shift	Remove organics for potential recycle of process solution	>50 times reduction
2	50 gallons of combined rinse streams	440 gallons/shift	Remove organics.	>50 times reduction
3	5 gallons of spent developer solution and 45 gallons of rinse streams	490 gallons/shift	Remove organics.	>50 times reduction
4	50 gallons of initiated bath solution	16 gpm	Remove cadmium particulate >0.3µm.	100–200 times reduction
5	0.5 gallons of spent solution, 1.5 gallons of combined rinse streams, and 47 gallons of initiated bath solution	8170 gallons/shift	Remove organics and cadmium particulate >0.3µm.	100–200 times reduction

gpm = gallons per minute
µm = micrometers

Both vendors will arrange for samples of the influent and the treated effluent to the tested by a laboratory, as directed by BP Solar, to determine the following:

- The total and dissolved cadmium, TOC, pH, and TSS of both the influent and the effluent stream; and
- The percentage waste reduction possible.

Table X. Treatability Test Solution Attributes and Treatment Goals for Cross-Flow Membrane Microfiltration and Chemical Pretreatment and Flocculation

Test Sol'n	Solution Contents	Process Flow Rate	Treatment Goal	Waste Stream Reduction Goal
3	5 gallons of spent solution and 45 gallons of rinse streams	490 gallons/shift	Remove organics.	>50 times reduction
4	50 gallons of initiated bath solution	16 gpm	Remove cadmium particulate larger than 0.3µm.	100–200 times reduction

gpm = gallons per minute
µm = micrometers

5.2.4 Identify Opportunities for Waste Recycle or Reuse

Two opportunities for waste recycle or reuse began to be evaluated during the Phase I program. Because preliminary calculations showed that recycling a spent solution from downstream processes may be economical, as mentioned above, a treatability study is under way to evaluate the technical feasibility of this option. Another option considered was forming a complex of cadmium with an organic compound in the presence of a surrogate metal, which would increase recovery of cadmium in electrowinner. A laboratory feasibility study needs to be conducted to investigate this option further.

Further evaluation of cadmium recovery potential is planned for the next phase of research. Specific areas of this investigation will include:

- Evaluate the economics of cadmium reclamation;
- Determine the potential recovery of cadmium from spent filters;
- Investigate reclamation options for the cadmium recovered from electrowinner; and
- Test the effects of various anodes on the cadmium recovered in electrowinner.

5.3 Summary

BP Solar has focused considerable effort on the optimization treatment system and its improvement to making it ready for released loop. The task of adapting the system so it is suitable for operation in closed loop will require additional equipment, such as high shear membranes.

The study has identified a need to remove other, non-cadmium materials from the effort, such as organic as well as particles in order for the process effluent to be fed back into the DI feed tank. An evaluation of the particle separation technology is under way as this Phase 1 report is being finished. The results will be included in the Phase 2 report.

6. Conclusion

The objective of this Phase 1 subcontract was to establish an efficient production plating system capable of depositing thin film CdTe and CdS on substrates up to 0.55 m^2. This baseline would then be used to build on and extend deposition areas to 0.94 m^2 in the next two phases.
The following achievements have been demonstrated:

- Chemical bath deposition of CdS and electrochemical deposition of CdTe was demonstrated on 0.55 m^2 substrates. The films were characterized using optical and electrical techniques increased the understanding of the materials and aiding in loss analysis.
- A stand alone, scale, prototype CdTe reaction tank was built and commissioned allowing the BP Solar team to perform full scale trials as part of this subcontract.
- BP Solar installed two outdoor systems for reliability and performance testing.
- The 2kW ground mounted system contains 72, 0.43 m^2 Apollo® module interconnects. This system is grid connected.
- Two modules have been supplied to NREL for evaluation on their Performance, and Energy Rating Test bed (PERT) for kWh evaluation.
- BP Solar further characterized the process waste stream with the aim to close loop the system. Currently various pieces of equipment are being investigated for suitability of particle and TOC removal.

7. Future Plans

During the 2nd phase of the Thin Film PV Partnership program BP Solar will focus on the following areas:

- Further semiconductor optimization. BP Solar will continue to work towards improving CdS and CdTe quality and increasing efficiency.
- The BP Solar team will commence a program to plate a 0.94m^2 TCO glass substrate.
- Environmental testing will continue. The 2 kW ground mounted system data will be evaluated.
- A second outdoor array will be designed for the larger, 0.55m^2 modules.
- Pilot line filtration systems will be set up to assess close looping on actual process waste water.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB NO. 0704-0188*

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 1999	3. REPORT TYPE AND DATES COVERED Phase 1 Technical Report, May 1998 – April 1999

4. TITLE AND SUBTITLE Thin-Film Photovoltaic Partnership - Apollo® Thin Film Process Development; Phase 1 Technical Report, May 1998 – April 1999	5. FUNDING NUMBERS C: RAK-7-17619-27 TA: PV905001
6. AUTHOR(S) D.W. Cunningham and D.E. Skinner	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) BP Solar Inc. 2300 North Watney Way Fairfield, CA 94533	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393	10. SPONSORING/MONITORING AGENCY REPORT NUMBER SR-520-26948
11. SUPPLEMENTARY NOTES NREL Technical Monitor: H.S. Ullal	
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161	12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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- Chemical-bath deposition of CdS and electrochemical deposition of CdTe was demonstrated on 0.55 m^2 substrates. The films were characterized using optical and electrical techniques, to increase the understanding of the materials and aid in loss analysis.
- A stand-alone, prototype CdTe reaction tank was built and commissioned, allowing the BP Solar team to perform full-scale trials as part of this subcontract.
- BP Solar installed two outdoor systems for reliability and performance testing.
- The 2-kW, ground-mounted, grid-connected system contains seventy-two 0.43-m^2 Apollo® module interconnects.
- Two modules have been supplied to NREL for evaluation on their Performance and Energy Rating Test bed (PERT) for kWh evaluation.
- BP Solar further characterized the process waste stream with the aim to close-loop the system. Currently, various pieces of equipment are being investigated for suitability of particle and total organic compound removal.

14. SUBJECT TERMS photovoltaics ; Thin-Film Photovoltaic Partnership ; thin films process development ; CdTe ; CdS ; laser processing ; Apollo®	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL