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FINAL TECHNICAL REPORT

**Environmentally Responsible Recycling of Thin-Film
Cadmium Telluride Photovoltaic Modules**

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DOE Patent Clearance Granted

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Introduction

Continuing from the third quarter, all technical objectives of this Phase II SBIR work were previously and successfully completed. This report is therefore brief and contains two elements:

1. A comparison of technical objective accomplishments to the stated goals in the original grant proposal
2. A summary of the third key element of this work; a market analysis for the developed recycling technology systems

Technical Objective Summary

Original Phase II SBIR Grant Proposal Objective

1. Design, construct and operate a one megawatt annual throughput PV module recycling plant.

Results Summary

- The goal of one megawatt annual throughput capacity per operating shift (approximately 350 tons annually per shift) has been met.
 - The goal of one-half shift labor requirement per megawatt throughput has been achieved.
 - Total regulated waste discharges under 100 pounds per year per megawatt throughput was not achieved because an economic recovery pathway for cadmium was not identified. However, the target was missed only by a factor of about five and is still very low as a percentage of total weight processed; only about 0.1% by weight of regulated waste discharges are generated even without reclaiming cadmium.
 - Total treatment costs of cents per watt or less excluding transportation and facility costs has been achieved and a cost model actually predicts costs closer to 2 cents per watt at maximum throughput rates.
2. Increase the separation and purity of the recovered metals, particularly the tellurium semi-metal, to increase their value and provide an increased economic offset for the module recycling process.

Results Summary

- As mentioned above, an economically viable recovery pathway for cadmium was not achieved and was consciously abandoned because of the low intrinsic value of cadmium and the low percentage of cadmium in the recycled materials stream. On the other hand, a potentially economic pathway of selectively reclaiming tellurium from the mixed metal sludge resulting from the precipitation of the etched elements was defined. Lacking large quantities of scrap to develop and optimize this process, 50 to 80% yields of metallurgical grade tellurium (>99% pure) were achieved by extracting the mixed metal sludge with concentrated potassium hydroxide then electrowinning. Therefore this objective has been achieved satisfactorily.

3. Do a comprehensive market analysis and product testing to identify and qualify other end-of- products or manufacturing wastes that have potential for recovery using this process.

Results Summary

For the fourth quarter, this was the only active remaining objective. A company called Environmental Business International, Inc. was contracted to do a comprehensive marketing study which included the elements of:

- Verifying contact information.
- Defining the manufacturers' product potentially recyclable by the First Solar recycling processes.
- Establishing current disposal methods, volumes and costs.
- Probe willingness to provide samples to First Solar to evaluate.

This scope of work was completed by Environmental Business International, Inc and their complete results are attached as Addendum I.

In conclusion, there is a small market for recovery of cathode ray tubes and mirror glass using the apparatus and process technology developed by First Solar for recycling CdTe PV modules. However, it the advice of Environmental Business International that perhaps the most cost effective and least distractive way to ensure continued commercial success of the recycling technology is to simply grow it along with the core business of module manufacturing. Said in other words, because the immediate market for First Solar recycling machines is estimated at only 6 to 12 units annually, it is not worth the business risk to develop this market; especially without additional market drivers such as new, more stringent waste disposal regulations on items such as mirror glass and cathode ray tubes. First Solar may be better served to simply replicate the recycling machinery with each new module manufacturing plant. That is the recommendation that First Solar has determined to accept and no plans to independently market , through license agreement or outright sales, recycling equipment outside the Company.

Please see the attached Addendum I for a comprehensive account of the market investigation.

4. Objectives that were achieved, but not listed, in the original Phase II SBIR grant proposal.

Results Summary

In addition to by and large successfully completed all original technical objectives, there were significant technical achievements accomplished that greatly added to the value of this Phase II SBIR work.

These extra achievements have been reported on in previously, but are listed again as a summary for this final report.

- First, an inert gas pyrolysis process for crystalline silicon wafer recovery from laminated crystalline silicon PV modules was developed. For the first time, intact and functioning crystalline silicon wafers have been recovered from laminated modules. A patent for this process has been applied for.
- Next, a novel, computer controlled, inexpensive ultrasonic etching apparatus has been developed to recover non-laminated, in-process, CdTe module substrates, potentially for re-use. This is important because for manufacturing operations, most yield fall-off is before the lamination process. This process and apparatus is an excellent compliment for thin-film PV module manufacturers along with the end-of-life PV module recycling apparatus and process. A patent has been applied for this apparatus as well.
- Last, processing technology was developed and demonstrated to effectively recycle mirror glass scrap and plasma flat panel display scrap.

This concludes the technical reporting requirements for the Phase II SBIR grant, DOE Project Number DE-FG02-95ER82068.

Respectfully submitted,

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DOE Project Number DE-FG02-95ER82068

**Environmentally Responsible Recycling of Thin-Film
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Third Quarter Technical Report

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Introduction

Continuing from the second quarter, significant progress has been made toward the project goal of defining an economical, high-throughput process for environmentally responsible recycling of end-of-life cadmium telluride (CdTe) thin-film modules. Technical achievements in this quarter include:

- Completion of all recycling equipment including automation equipment, material handling equipment and ancillary equipment such as a ventilation and dust control systems.
- Commissioning and optimization of all systems.
- Optimization of a high purity tellurium metal recovery scheme.
- Evaluation of the feasibility of recycling mirror scrap.
- Evaluation of the feasibility of recycling flat panel display scrap
- Preparation of an updated cost model.
- Crystalline silicon (x-Si) wafer recovery
- In-process CdTe module substrate reclamation
- Confirmation of regulatory status of the CdTe module recycling facility (i.e. confirmation of recycling Vs hazardous waste treatment facility status).

Following are technical descriptions for each of these achievements.

A paper titled *Photovoltaics as Hazardous Materials; The Recycling Solution*, presented at the Second World Photovoltaic Conference in Vienna in July 1998, additionally summarizes the project results to date and is attached as Addendum I.

Third Quarter Milestone Descriptions

Equipment Installation, Commissioning and Optimization

All equipment for recycling the end-of-life cadmium telluride PV modules has been received, installed and made operational. See Figure 1 below:

Figure 1 – Module recycling equipment as installed

Skip Hoist, Hammer Mill and Hammer Mill Discharge Trap

Since the last quarter, the hammer mill has crushed several thousand pounds of defective CdTe modules and has demonstrated effective “disassembly” through separation of the substrate and superstrate glass from the ethylenevinylacetate (EVA) interlayer and the polyurethane mounting feet. The skip hoist module delivery conveyor has been optimized to deliver three modules at a time in two minute time intervals. This equates to a throughput rate for this part of the operation of 1,800 pounds of modules per hour or 4.5 KWH_p (kilowatt-hours peak power) of modules per hour.

High Speed Inclined Belt Conveyor and Conical Barrel Finisher

The Cambelt® high speed, high incline conveyor has been installed and is used effectively to deliver the crushed glass solar module cullet from the hammer mill to the rotating conical barrel finishing machine. It indeed has proven to accept the cullet from the hammer mill discharge chute on a “choke feed” basis. It was discovered though, after breaking the transfer belt (which was subsequently repaired by splicing), that routine cleaning of the conveyor at the hammer mill discharge point is required to prevent internal glass spillage from creating excessive drag on the belt.

The neoprene lined barrel finishing machine, which is resistant to both the corrosiveness of the etchant and the abrasiveness of the glass and imparts a high amplitude, low frequency agitation motion to the glass load, has been working

excellently. Adjustments of speed and tilt angle have been made to reduce the etching time at ambient temperature to about 30 minutes.

After the initial etching, a series of surfactant aided water rinses reduce the free cadmium level in the etched, cleaned glass to less than 1 PPM.

Chemical Precipitation Equipment

A system of tanks, pumps, valves, mixers and filters have been installed and made operational to precipitate the cadmium, tellurium and back contact metals put into solution by the etching process. See Addendum I, Figure 2 for a general arrangement drawing of the chemical precipitation system. The sodium carbonate precipitation has effectively reduced effluent cadmium levels to meet the City of Toledo discharge levels of 0.3 mg/L. The resulting mixed metal sludge is pressed effectively by a small filter press.

The end-of-life module recycling system is considered to be "commissioned" as of April, 1998 and has been used on a daily basis since then.

Optimization of a High Purity Tellurium Metal Recovery Scheme

A custom electrowinning cell was designed and made in-house for experimentation of tellurium recovery from a highly alkaline tellurium rich extract of the mixed-metal precipitation sludge.

A report outlining the technical details of this process is attached as Addendum II.

Using the limited quantities of sludge available (the recycling process does not generate much metals for precipitation because the semiconductor films are very thin and only a fraction of the small production output becomes available to the recycling stream), final recovered high purity (>99% pure) tellurium yields of 50 to 80% were achieved. Until more waste is generated, further optimization of the tellurium extraction process, if economically justifiable, will have to wait.

Evaluation of the Feasibility of Recycling Mirror Scrap.

Mirror scrap was identified as a potential market for the First Solar recycling process because potentially hazardous materials are used in mirror construction (silver and lead) and the substrate is glass. Samples of two types of mirror glass, one from Toledo Glass and Mirror, and one from a Connecticut manufacturer seeking a recycling technology were studied.

A complication with recycling mirror scrap is removing the organic paint backing layer of the mirror. This layer is to protect the silver in the mirror from oxidation and sulfation and is typically composed of up to 5% by weight lead to act as a sulfur scavenger. To chemically digest and break through the organic interlayer, it was discovered that a more complex etchant system be used. Specifically, various proportions of HNO_3 (nitric acid) had to be added to the original sulfuric acid and hydrogen peroxide etchant used to solubilize the CdS and CdTe semiconductors from the First Solar PV modules.

It was determined that it would be possible to recycle mirror scrap using the appropriate chemistry with the First Solar end-of-life module recycling apparatus and process. A detailed report showing the etchant chemistry development work that demonstrated this is attached as Addendum III.

Evaluation of the Feasibility of Recycling Flat Panel Display Scrap

As with mirror scrap, plasma flat panel displays are built on a glass substrate but in this case the incentive for recycling is twofold: the displays contain a lead based dielectric material that in fact failed the EPA's TCLP test for lead as toxicity characteristic but also contain a fair amount of gold which is used as the display's interconnection grid. Samples were obtained for analysis from a local flat panel display manufacturer and used to develop possible recycling process based on the First Solar recycling technology.

In this case, there were two complications. First, the lead dielectric coated over the gold interconnection grid must be removed with acetic acid or weak nitric acid. This exposes the gold, which must be removed in concentrated aqua regia (a mixture of nitric and hydrochloric acids). Gold is considered a "noble" metal and is very difficult to oxidize with acids. The aqua regia can then be neutralized and, at the proper pH, sodium borohydride added to reduce the gold back the elemental state.

The conclusion of this work was that lead recovery and gold reclamation is possible using sequential processes and appropriate chemistry in the First Solar recycling apparatus. Additionally, more inert materials of construction for transfer piping, pumps, valves and filtration equipment may be required for adequate chemical resistance to the aqua regia. Last, ventilation control equipment will be required for controlling the aqua regia fumes.

A report detailing the lead and gold etchant chemistry development and removal and recovery processes is attached as Addendum IV.

Preparation of an Updated Cost Model

Updated cost models have been prepared and are presented graphically in Figure 4 of Addendum I. Both in-house and stand-alone cost models were considered. The difference is that an in-house recycling operation would be free from overhead burden such as facility costs. A stand-alone model, including estimated costs incurred from

facility burden and transportation of the defunct modules to the recycling facility is also presented and agrees with a similar estimate prepared by Chris Eberspacher at UNISUN (see Addendum I for reference).

At maximum throughput of 2 MW_p per year, the in-house cost model predicts a cost of just over \$0.02/W_p and the stand-alone cost model predicts a cost of \$0.12/W_p.

Crystalline Silicon (x-Si) Wafer Recovery

One of the ancillary activities undertaken by this grant, in addition to applying the First Solar CdTe module recycling apparatus and process to mirror and plasma flat panel display scrap, is solving the problem of recycling defunct crystalline silicon module materials. This problem was attacked quite successfully. The reader is referred to Addendum V, *Possibility of Recycling Silicon PV Modules*, presented at the 26th IEEE PV Specialists Conference, October, 1997 in Anaheim CA for a detailed technical discussion on this process.

The results of this work is that, for the first time, by using an inert gas pyrolysis process, crystalline silicon wafers can be recovered from laminated modules intact and functioning. A cost effective recycling methodology for recovering crystalline silicon PV module materials has been developed. A cost model shows about \$0.13/W_p to recover functioning crystalline silicon wafers from modules, not including transportation, facility or administrative costs.

A patent has been applied for from this work.

In-Process CdTe Module Substrate Reclamation

A second significant ancillary activity is the development of an inexpensive apparatus and process to recover CdS/CdTe coated substrates that have not reached the lamination phase. As mentioned in the second quarter report, while the thrust of this project has been on recycling end-of-life, presumably broken or otherwise unsalvageable CdTe PV modules, it is quite desirable as a module manufacturer to have the ability of efficiently reclaiming the solar cell substrate, even for possible re-use, since most yield loss in fact occurs before the lamination process.

The automatic, dual ultrasonic polypropylene etchant tank system reported on in the second quarter report has been functioning flawlessly and has a 200 unit (~10 KWp) per one man shift capacity.

It is particularly economic since the etchant is transferred between the two tanks, "parts" are not transferred. Sophisticated and expensive parts loading and unloading equipment is not needed, the tanks are inexpensive to construct, and the submersible resonant tube transducer ultrasonic units provide the required watt density for etching or cleaning. This dual-tank, high throughput concept appeared to be unique according to our investigation of ultrasonic cleaning tank vendors.

Figure 4 – "Whole Plate" module substrate etching apparatus as installed

Confirmation of Recycling Regulatory Status

The Ohio EPA has made an official determination that First Solar's PV module recycling activities are indeed legitimate recycling activities and has issued a letter to that effect. The letter is attached as Addendum VI.

Next Six Month's (Fourth Quarter) Objectives

All key milestones for the third quarter were met successfully. All technical objectives for the Phase II work have been completed successfully. Therefore the fourth quarter and final report will focus on summarizing the technical achievements according to the stated objectives in the Phase II grant proposal and include the results of the marketing work for the First Solar recycling technologies that has recently been subcontracted to Environmental Business International, Inc., of San Diego, CA.

Respectfully submitted,

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ADDENDUMS

Addendum I --- Photovoltaics as Hazardous Materials; The Recycling Solution

Addendum II --- K. Kamm Report on Recycling

Addendum III -- K. Kamm Report on Mirror Scrap Etching and Silver Reclamation

Addendum IV -- I. Anisimov Report on Flat Panel Display (gold and lead) Recovery

Addendum V -- Possibility of Recycling Silicon PV Modules

Addendum VI -- Copy of Ohio EPA;s letter on Regulatory Status of Recycling Operation