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Photovoltaic Materials

Final Technical Report

October 2012

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Final Technical Report

PHOTOVOLTAIC MATERIALS

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ACRONYMS

AFM	Atomic Force Microscopy
AMO	Advanced Manufacturing Office
AR	Anti-Reflection
ARRA	American Reinvestment and Recovery Act
c-SI	crystalline-Silicon
CAGR	Compound Annual Growth Rate
CATS	Center for Advanced Thin-film Systems
CBD	Chemical Bath Deposition
CCD	Constant Capacitance DLTS
CI	Confidence Index
CIGS	Copper Indium Gallium diSelenide
CNMS	Center for Nanophase Material Science
CRADA	Cooperative Research and Development Agreement
CRO	Collaborative Research Opportunity
CTS	current transient spectroscopy
CVD	Chemical Vapor Deposition
CW	Continious Wave
CZTS	Copper Zinc Tin Sulfide
DI	De-ionized
DOE	Department of Energy
DLTS	Deep Level Transient Spectroscopy
DPI	Dots Per Inch
EBSD	Electron Backscatter Diffraction
ECGM	Electronic, Color and Glass Materials
EDAX	Energy Dispersive X-ray spectroscopy
EDS	Energy-Dispersive X-ray Spectroscopy
EERE	Energy Efficiency and Renewable Energy
EST	Eastern Standard Time
eV	Electron Volt
FCC	Face Centered Cubic
FIB	Focused Ion Beam
FTO-SLG	Fluorine Doped Tin Oxide - Soda Lime Glass
GSE	Global Solar Energy
GW	Gigawatt
HEM	Heat Exchanger Method
HTML	High Temperature Materials Laboratory
HW-CVD	Hot-Wire Chemical Vapor Deposition
Hz	Hertz
ITO	Indium Tin Oxide
ITP	Industrial Technologies Program
Kw	Kilowatt
KWh	Kilowatt Hour
LBIC	Light Beam Induced Current
LCOE	Levelized Cost of Electricity
MCS	Mossy Creek Solar
MLS	Monochromatic Light Source
MPG	Materials Processing Group
NDA	Non-Disclosure Agreement

NIST	National Institute of Standards and Technology
NP	NanoParticle
NREL	National Renewable Energy Laboratory
NSTL	Nanoscale Science & Technology Laboratory
OLED	Organic Light-Emitting Diode
ORNL	Oak Ridge National Laboratory
PITS	Photo-Induced Transient Spectroscopy
PL	Photoluminescence
PLD	Pulsed Laser Deposition
PTP	Pulse Thermal Processing
PV	Photovoltaic
QE	Quantum Efficiency
R&D	Research and Development
RFP	Request for Proposals
SEI	Secondary Electron Image
SEM	Scanning Electron Microscopy
SLG	Soda Lime Glass
STEM	Scanning Transmission Electron Microscopy
STO	Strontium Titanate
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
UV	Ultraviolet
UV-VIS-IR	Ultraviolet-Visible-Infrared
WVTR	Water Vapor Transmission Rate
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

ACKNOWLEDGMENTS

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There is no proprietary data contained within this report.

EXECUTIVE SUMMARY

The goal of the current project was to help make the US solar industry a world leader in the manufacture of thin film photovoltaics. The overall approach was to leverage ORNL's unique characterization and processing technologies to gain a better understanding of the fundamental challenges for solar cell processing and apply that knowledge to targeted projects with industry members. ORNL has the capabilities in place and the expertise required to understand how basic material properties including defects, impurities, and grain boundaries affect the solar cell performance. ORNL also has unique processing capabilities to optimize the manufacturing process for fabrication of high efficiency and low cost solar cells. ORNL recently established the Center for Advanced Thin-film Systems (CATS), which contains a suite of optical and electrical characterization equipment specifically focused on solar cell research. Under this project, ORNL made these facilities available to industrial partners who were interested in pursuing collaborative research toward the improvement of their product or manufacturing process. Four specific projects were pursued with industrial partners:

> Global Solar Energy is a solar industry leader in full scale production manufacturing highly-efficient Copper Indium Gallium diSelenide (CIGS) thin film solar material, cells and products. ORNL worked with GSE to develop a scalable, non-vacuum, solution technique to deposit amorphous or nanocrystalline conducting barrier layers on untextured stainless steel substrates for fabricating high efficiency flexible CIGS PV.
>
> Ferro Corporation's Electronic, Color and Glass Materials ("ECGM") business unit is currently the world's largest supplier of metallic contact materials in the crystalline solar cell marketplace. Ferro's ECGM business unit has been the world's leading supplier of thick film metal pastes to the crystalline silicon PV industry for more than 30 years, and has had operational cells and modules in the field for 25 years. Under this project, Ferro leveraged world leading analytical capabilities at ORNL to characterize the paste-to-silicon interface microstructure and develop high efficiency next generation contact pastes.
>
> Ampulse Corporation is developing a revolutionary crystalline-silicon (c-Si) thin-film solar photovoltaic (PV) technology. Utilizing uniquely-textured substrates and buffer materials from the Oak Ridge National Laboratory (ORNL), and breakthroughs in Hot-Wire Chemical Vapor Deposition (HW-CVD) techniques in epitaxial silicon developed at the National Renewable Energy Laboratory (NREL), Ampulse is creating a solar technology that is tunable in silicon thickness, and hence in efficiency and economics, to meet the specific requirements of multiple solar PV applications. This project focused on the development of a high rate deposition process to deposit Si, Ge, and Si1-xGex films as an alternate to hot-wire CVD.
>
> Mossey Creek Solar is a start-up company with great expertise in the solar field. The primary interest is to create and preserve jobs in the solar sector by developing high-yield, low-cost, high-efficiency solar cells using MSC-patented and -proprietary technologies. The specific goal of this project was to produce large grain formation in thin, net-shape-thickness mc-Si wafers processed with high-purity silicon powder and ORNL's plasma arc lamp melting without introducing impurities that compromise absorption coefficient and carrier lifetime.

As part of this project, ORNL also added specific pieces of equipment to enhance our ability to provide unique insight for the solar industry. These capabilities include a moisture barrier measurement system, a combined physical vapor deposition and sputtering system dedicated to cadmium-containing deposits, a deep level transient spectroscopy system useful for identifying defects, an integrating sphere photoluminescence system, and a high-speed ink jet printing system. These tools were combined with others to study the effect of defects on the performance of crystalline silicon and thin film solar cells, to explore non-vacuum ink-based approaches to solar cell production, as well as large-scale and low-cost deposition and processing of thin film CdTe material.

ABSTRACT

The goal of this project was to help make the US solar industry a world leader in the manufacture of thin film photovoltaics. The overall approach was to leverage ORNL's unique characterization and processing technologies to gain a better understanding of the fundamental challenges for solar cell processing and apply that knowledge to targeted projects with industry members. Four specific projects were pursued with industrial partners: Mossey Creek Solar, for producing low-cost high-quality silicon wafers with significant reductions in waste material and energy consumption; Global Solar Energy, for developing scalable non-vacuum deposition techniques for thin-film copper indium gallium diselenide, a direct-bandgap material for solar cells; Ferro Corp., for developing inks and pastes to be used for highly conductive layers in thin-film solar cell applications; and Ampulse, for developing an efficient roll-to-roll manufacturing process to deposit thin-film silicon. As part of this project, ORNL also added specific technical equipment to enhance the laboratory's ability to provide unique insight for the solar industry and also conducted research that could be applied to the advanced manufacturing of solar cells.

1. INTRODUCTION

The grand challenge for the wide spread use of thin film photovoltaic materials is obtaining a high conversion efficiency over large areas at a reasonable cost. Simultaneous optimization of these three parameters (efficiency, area, and cost) not only demands a fundamental understanding of the material science involved in photovoltaics, but will also require careful characterization and process control to achieve large-scale performance on a flexible substrate. For instance, the lab-scale efficiency of CIGS solar cells is around 20%, but the best commercially available CIGS cells operate at only 5-11% efficiency. The purpose of this project was to apply the vast resources and expertise of Oak Ridge National Laboratory to the challenges facing today's manufacturers of thin film solar cells – bridging the gap between the promise of science and products on the shelf.

The goal of this project was to help make the US solar industry a world leader in the manufacture of thin film photovoltaics. This was accomplished by collaborating with industry in order to apply a fundamental understanding of solar cell materials to the optimization of manufacturing processes. Widespread adoption of thin film photovoltaics will enable significant increases in the production of renewable solar energy throughout the US. This project helped catalyze the efforts of US thin film PV manufacturers creating jobs in both the manufacturing and installation of thin film solar PV arrays.

As one of the nation's leading material research laboratories, ORNL has the capabilities in place and the expertise required to understand how basic material properties including defects, impurities, and grain boundaries affect the solar cell performance. ORNL also has unique processing capabilities to optimize the manufacturing process for fabrication of high efficiency and low cost solar cells. In addition to the unique characterization capabilities at the Center for Nanophase Material Science (CNMS) and High Temperature Materials Laboratory (HTML), ORNL recently established the Center for Advanced Thin-film Systems (CATS), which contains a suite of optical and electrical characterization equipment specifically focused on solar cell research. This facility has been lauded by the solar industry due to its unique and diverse solar characterization capabilities situated in one location. Having such capabilities in close proximity to world-class fabrication and processing facilities makes ORNL a truly unique place for solar research and development by laboratory and industrial researchers.

Under this project, ORNL made these facilities available to competitively selected industrial partners interested in pursuing collaborative research toward the improvement of their products or manufacturing processes. The project also enabled ORNL staff members to pursue a sustained level of research that addresses issues common to several facets of the solar industry.

Accordingly, the PV Materials project had two major tasks. The first task was to establish a mechanism for industry members to leverage the capabilities at ORNL for advancing the manufacturing of photovoltaic technologies. ORNL announced a Collaborative Research Opportunity in the fall of 2010 that would allow selected companies to engage in a Cooperative Research and Development Agreement (CRADA) with ORNL. These projects were initiated in the spring of 2011 and had a duration of one year. The four projects selected were with Mossey Creek Solar, for producing low-cost high-quality silicon wafers with significant reductions in waste material and energy consumption; Global Solar Energy, for developing scalable non-vacuum deposition techniques for thin-film copper indium gallium diselenide, a direct-bandgap material for solar cells; Ferro Corp., for developing inks and pastes to be used for highly conductive layers in thin-film solar cell applications; and Ampulse, for developing an efficient roll-to-roll manufacturing process to deposit thin-film silicon.

The second major task of the project was to conduct fundamental research that would be applied to the manufacture and improved performance of solar cell technologies. As such, ORNL conducted various measurements using light beam induced current (LBIC) and photoluminescence (PL) to investigate the impact of internal defects on solar cell performance. ORNL also looked at non-vacuum, low-cost approaches for the manufacture of CIGS and CdTe solar cells using a novel nanoparticle synthesis route as well as room temperature sputtering of material.

2. BACKGROUND

Photovoltaics (PV) is the field of technology and research related to the conversion of sunlight directly into electricity. Due to the growing need for a renewable and abundant source of energy, the manufacture of solar cells and photovoltaic arrays has expanded dramatically in recent years. The solar energy market is currently valued at \$38.5B with over 13.9 GW of solar panels installed globally.[1] The area is rich with potential investors, with nearly \$12 billion in investments from stock offerings, loans, and venture capital funds in 2007 alone.[2] The market is growing rapidly (5-year Compound Annual Growth Rate (CAGR) of 56% through 2008)[3], but is in need of a low-cost approach to solar cell manufacturing in order to become competitive with traditional energy sources (\$0.07/kWh).

Meeting the world's energy demands is one of the greatest societal challenges currently facing the global community. The reliance on non-renewable, and heavily-polluting, energy sources (i.e., fossil fuels) is simply not sustainable. Technologies that make use of renewable energy sources efficiently are desperately needed. Sunlight provides one of the most abundant renewable energy sources – in fact, the sun provides more energy to the earth's surface in a single hour than the entire world's population consumes each year. However, the cost of generating electricity from solar radiation remains 2-3 times higher than traditional energy sources, such as coal, gas, and oil. Thus, the biggest challenge facing PV technologies is the need for a low-cost, scalable, and reliable manufacturing approach to produce solar cells with efficiencies of 10-20% that are stable for more than five years. In order to dramatically cut the cost/watt delivered by solar cells, new technologies are needed.

Figure 1 chronicles the improvements in laboratory-scale PV device efficiency from 1976 to 2011 for various PV technologies: high efficiency multi-junction cells; crystalline and polycrystalline Si; thin film technologies like CIGS, amorphous Si and CdTe; and "emerging technologies" like dye sensitized solar cells and polymer cells.

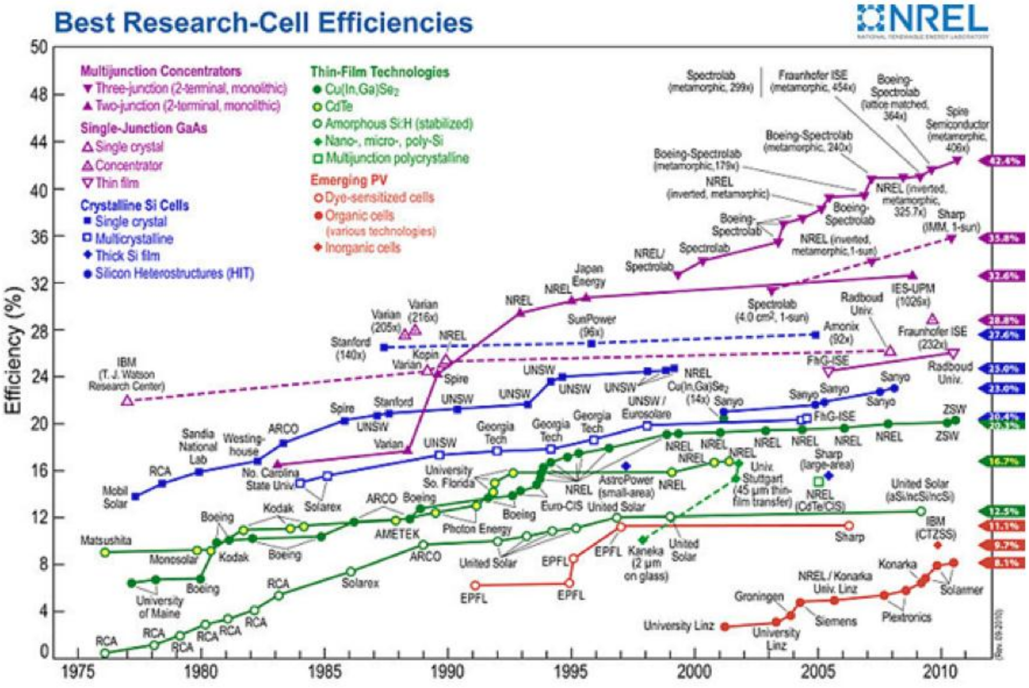


Figure 1. Solar cell efficiency by system from 1976 to 2010.

The highest efficiency solar cells are multi-junction concentrator solar cells. These solar cells can achieve more than 40% power conversion efficiencies on a laboratory scale, but they are extremely expensive to fabricate, requiring expensive ultra-pure materials and slow ultrahigh vacuum deposition processes that are difficult to manage on large area substrates. These types of solar cells are not economical or commercially scalable enough for widespread commercial adoption and were studied here. Crystalline and polycrystalline silicon have been two of the most successful commercial PV technologies. Devices can be manufactured with relatively good stability and efficiencies greater than 20%. Currently more than 80% of photovoltaic devices are made from crystalline silicon. The manufacturing strategies, however, rely heavily on processes from the microelectronics industry, which are not well suited for PV because they are slow and not designed for large-area flexible substrates. Silicon processing is also environmentally harmful and energy intensive, requiring very high temperatures and produces toxic byproducts. Furthermore, current solar cells require relatively large amounts of Si to absorb all of the incident sunlight because it is such a weak light absorber due to its indirect band gap. Unless steps are taken to dramatically reduce the cost and impact of manufacturing crystalline silicon cells, this technology will not be able to achieve grid parity.

The other broad class of PV devices is based on thin films of light absorbing materials. These materials include amorphous silicon, CdTe, Cu(In,Ga)Se_2 (CIGS), dye sensitized nanoporous films, polymers and nanomaterials like nanocrystals and nanowires. Some of these thin film materials have exhibited very promising, high device efficiencies in the lab, such as CIGS devices, which have now demonstrated ~20% efficiency and CdTe devices, which have achieved ~15% efficiencies. Dye-sensitized solar cells have exhibited ~10% efficiency, which could also be suitable for commercialization if the manufacturing costs were sufficiently low and the stability sufficiently robust. Other new materials with potentially very low manufacturing costs, like polymers and organic films, nanocrystals and nanowires, however, have exhibited only modest efficiencies of <5%, even in the best laboratory-scale devices fabricated under carefully monitored and controlled high-purity conditions. At the moment, there is an aggressive effort by industry to develop new PV technologies, either by improving Si processing or adopting new PV device platforms like thin film materials or dye sensitized solar cells. In the case of the Si-alternatives to PVs, several technologies appear to be very promising, including CdTe, CIGS and dye-sensitized solar cells and large companies as well as smaller start-ups are working hard at commercializing these technologies.

3. COLLABORATIVE SOLAR CELL RESEARCH

As one of the nation's leading material research laboratories, ORNL has the capabilities in place and the expertise required to understand how basic material properties including defects, impurities, and grain boundaries affect the solar cell performance. ORNL also has unique processing capabilities to optimize the manufacturing process for fabrication of high efficiency and low cost solar cells. In addition to the unique characterization capabilities at the Center for Nanophase Material Science (CNMS) and High Temperature Materials Laboratory (HTML), ORNL recently established the Center for Advanced Thin-film Systems (CATS), which contains a suite of optical and electrical characterization equipment specifically focused on solar cell research. This facility has been lauded by the solar industry due to its unique and diverse solar characterization capabilities situated in one location. Having such capabilities in close proximity to world-class fabrication and processing facilities makes ORNL a truly unique place for solar research and development by laboratory and industrial researchers.

Under this project, ORNL created a Collaborative Research Opportunity (CRO) to make these facilities available to industrial partners through who were interested in pursuing collaborative research toward the improvement of their product or manufacturing process. The CRO was established to work with manufacturers of thin film solar cells to help them better understand their product, optimize their material processing techniques, reduce the cost of manufacturing, and increase the performance of solar cells. The intention of the CRO was for ORNL staff members to conduct a series of short-term, focused research programs with industry partners selected through an open solicitation and proposal format. The projects of interest would address various concerns of industry focused on either increasing the performance of a solar cell or decreasing the manufacturing costs.

In order to fully leverage the capabilities at ORNL for the CRO, it was necessary to install some complementary pieces of equipment and place appropriate staff members to assist with the work. These tasks are described in further detail below along with descriptions of the four CRO projects.

3.1 EQUIPMENT

Although ORNL had a vast array of fabrication, processing, and characterization equipment, there are a few strategic pieces of equipment that were added under this project to make our facilities much more relevant to industry-focused research programs. The pieces of equipment identified for maximum impact are listed below.

3.1.1 Barrier Coating Measurement System

Advancements in barrier quality of certain materials have pushed the sensitivity limits of commercially available water vapor permeation equipment. In order for products such as organic light-emitting diodes (OLED's) and solar cells, which incorporate these high barrier materials, to be viable, current permeation testing methods, must be enhanced or altered. In designing a more sensitive method, the limitations of the current methods were studied. From there, enhancements and modifications to the traditional comparative or concentration sensor produced an order of magnitude increase in sensitivity (from $5x10^{-3}$ to $5x10^{-4}$ g/(m^2xday.). ORNL identified an instrument that can measure down to 5E-4 g/m2-day given our expectation that barriers with WVTR (Water Vapor Transmission Rate) in the low E-3 g/m2-day.

Under this project, ORNL purchased and installed the Mocon Aquatran barrier coating measurement system (see Figure 2). The Mocon Aquatran has the following features: WinPerm Software (Transient Data provides view of every signal going to the sensor, 96 hour graph of Sensor, Carrier Gas Flow, Temperature activity, complete reporting function, and data exportable to EXCEL); Patented AQUATRACE Coulometric (absolute sensor) that does not require calibration; Provides transmission rates of films or packages (Films - 0.5 to 5000 mg/(m2-day); Packages – 0.0025 to 25 mg/(pkg-day)); NIST Traceable Reference Films provided to verify instrument functionality; Measures duplicates (2 cells); Measures Precise RH (35-90%) (Model MG) or 100%RH (Model MG or MW); Holds a set temperature of 10-40C +/-0.5C (Model MG); Holds a set temperature of 5-50C +/-0.5C (Model MW); Conforms to ISO 15106 Part 3; Developed by MOCON, a company with over 45 years of experience in WVTR technology.

Figure 2. Mocon Aquatron Water Vapor Permeability System

ORNL established the Aquatran Instrument to measure water vapor transfer rates (WVTR) using standard black certified barrier films. Figure 3 shows that by fitting a decaying exponential [y=y0 + a•exp(-t/t0)] to the data, measurement times can be reduced by more than two times. The time to measure water vapor permeability can be significantly reduced by curve fitting WVTR trends.

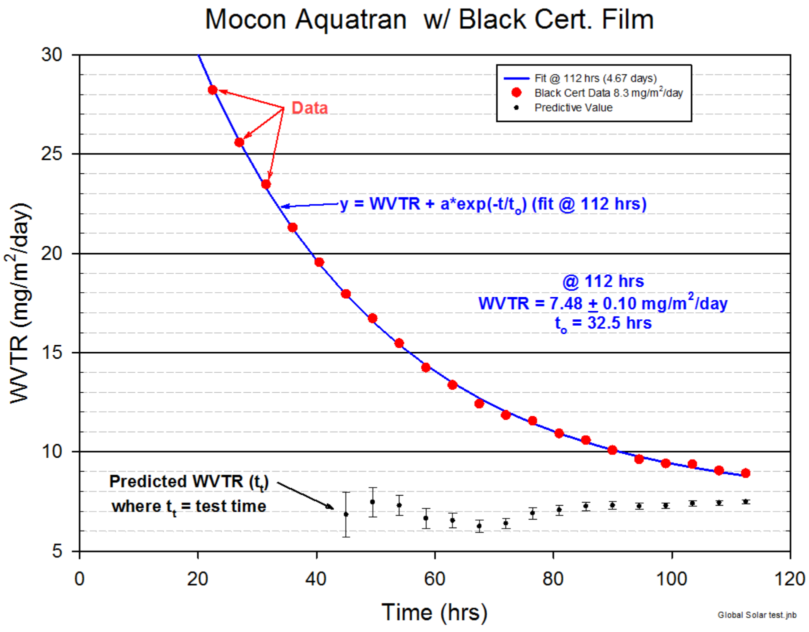


Figure 3. Aquatran measurement of WVTR values for barrier film.

ORNL also demonstrated the use of barrier coating facility to measure Global Solar Energy's barrier film properties. For typical customer barrier films, approximately 48 hrs are required for a good measurement of WVTR. The "settling time" (t_0) affects the time needed to obtain a "good" measurement of WVTR. Factors that affect t_0 include: film thickness, film history, aquatran history, and companion film. Figure 4 below demonstrates this measurement.

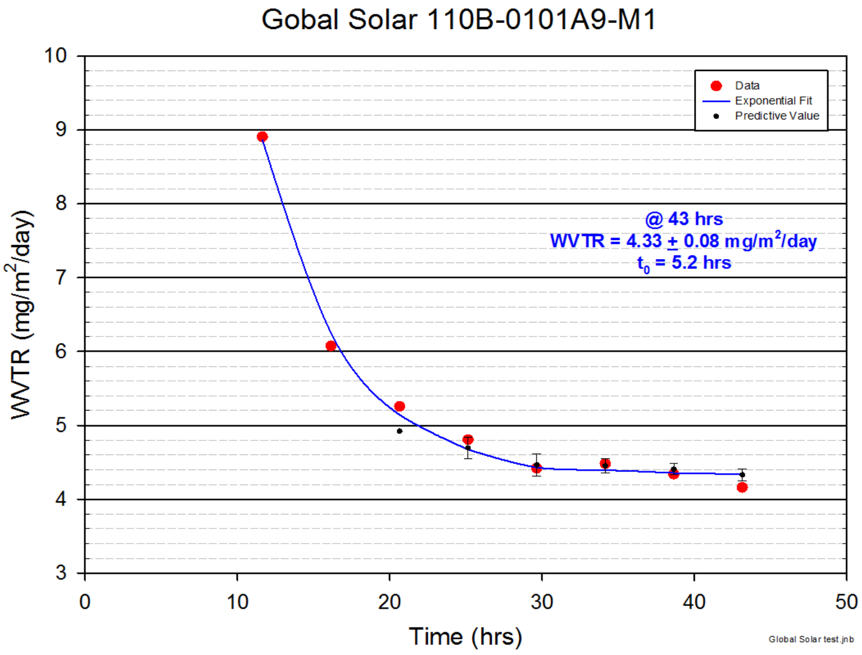


Figure 4. Barrier film properties for Global Solar cells.

3.1.2 Roll-to-Roll Ink Jet Printing System

ORNL worked with NoavaCentrix to develop a high speed roll-to-roll ink jet printing system for thin film electronics and solar cells. Initially, the system is being operated by having a moving table as the transport system. This allows printing of individual samples with the Morpho control system (Figure 5), which are representative of a roll-to-roll system while still allowing the advantages of separate control over drying times, temperatures and thermal processing. At some later date, the same Morpho system could print on either the roll-to-roll or the moving table to allow maximum flexibility. The Morpho X2 is a 210mm wide hybrid digital inkjet press for variable data printing applications. Its design is simple and compact using the world's fastest and highest resolution inkjet print head technology. The Morpho system can be customized to use UV, MICR, or water-based ink for a wide range of industrial printing applications. The Morpho system can be easily installed on any existing web press as a digital add-on module for variable data printing. This inkjet press technology is proven commercially in use at various print factories around the world. The print head used on the Morpho system is a Kyocera KJ4, which is the best value and highest performance available for roll-to-roll printed electronics applications (capable of 600dpi speeds over 150'/min).

Figure 5. **The Morpho Ink Jet Printing System**

The Kyocera/Morpho system was installed at ORNL early 2011 under the supervision of Fred List. During NovaCentrix's installation visit (Figure 6), several attempts were made to print both copper and silver nanoparticle inks using desktop Epson C88+ printers. The copper ink clogged the print head and appeared to be unsuitable for printing. Perhaps the shelf life of the copper ink had been exceeded. Printing of fresh silver nanoparticle ink with the Epson C88+ printer was also explored. Single pass printing resulted in fair quality silver lines. Overprinting with a second pass of silver ink led to substantially better quality (lower resistivity) lines.

Figure 6. **NovaCentrix industrial inkjet printer during installation.**

To understand better the possible causes for line quality variations using the Epson C88+ printer with non-porous substrates, printer traces for a range of printer settings were examined with optical microscopy and profilometry. Figure 7 shows two optical micrographs of single-pass lines for a range of line orientation. The individual printed droplets are elongated in the direction of the print head travel, and, as a consequence, the line continuity, thickness, and width vary with line orientation. Figure 8 shows the results of stylus profilometry for both horizontal and vertical scans. Lines printed horizontally are both narrower (35 vs. 80 μm) and thicker (1.5 vs. 0.75 μm) than lines printed vertically. Clearly better control of ink droplet delivery is required to ensure consistent quality of printed conductive lines.

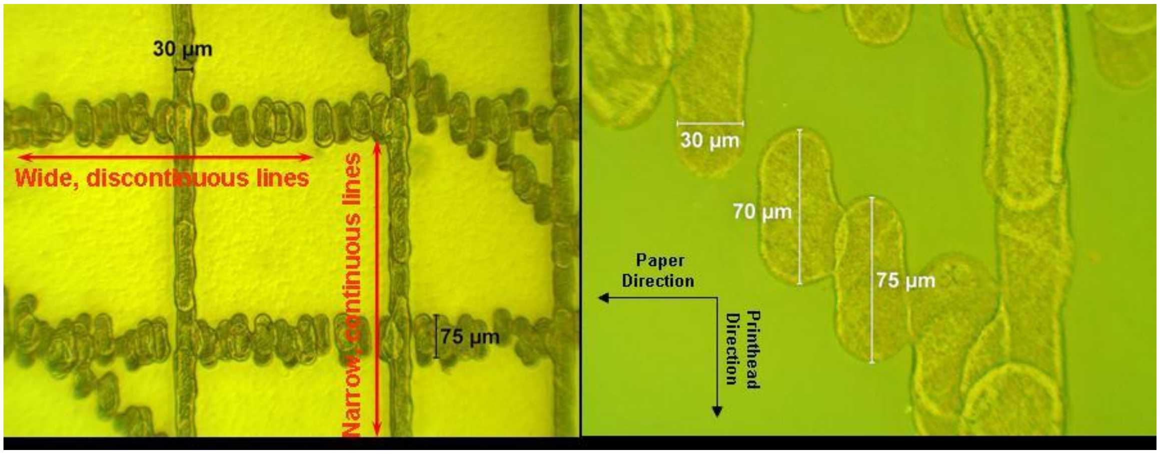


Figure 7. **Optical micrograph of single-pass lines printed for a range of orientations.**

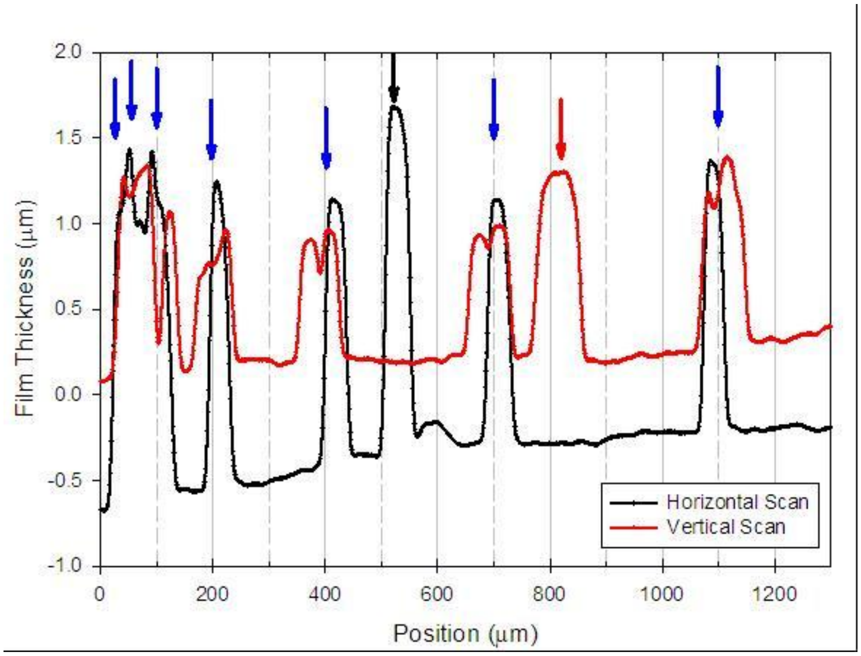


Figure 8. Stylus profilometry for both horizontal and vertical scans.

A Dimatix desktop materials printer (Model 2831) was installed at ORNL to help improve droplet delivery control (Figure 9). This system is useful for developing inks for research-scale manufacturing. Initially, conductive inks containing silver and copper were be printed on temperature sensitive substrates and processed with rapid thermal annealing. The high degree of control of droplet delivery achievable with this system is expected to result in low resistance, conductive lines.

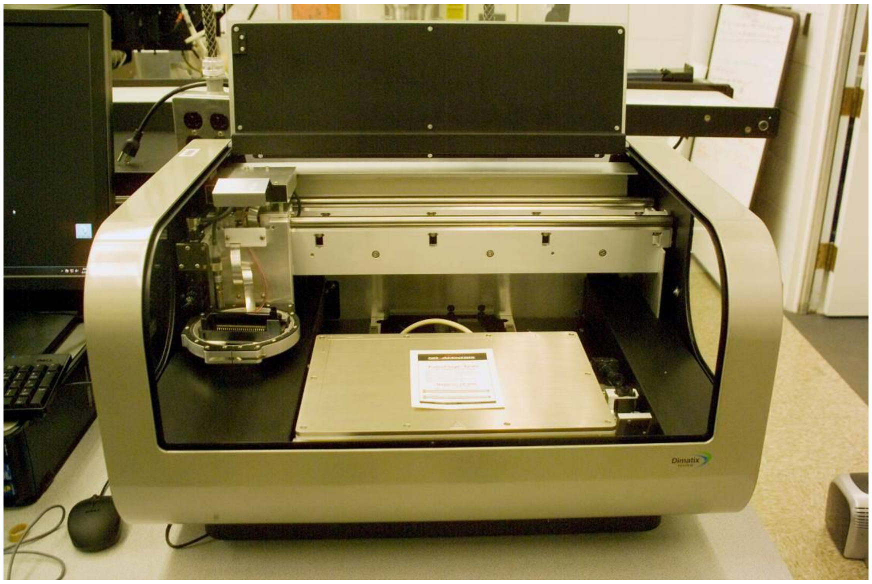


Figure 9. **Desktop inkjet printing system recently acquired at ORNL.**

3.2 STAFF MEMBERS

The Collaborative Research Opportunity was anticipated to require the full time attention of at least one staff member as well as the part time effort of a characterization technician, a fabrication technician, as well as a processing technician. Not all of these resources were originally in place at ORNL, so a few people were needed to provide the required support. Some staff members were re-tasked to focus on the CRO project while others were hired specifically. The names of personnel primarily involved with this project are listed below – new hires are specifically identified.

Chad Duty (Principle Investigator) – Project management, CRO contact, material processing
Jay Jellison – Optical and electrical characterization, solar cell performance
Charlee Bennett (new hire) – Optical and electrical characterization
Joseph Angelini (new hire) – Material processing
Boyd Evans – Thin film material synthesis
Parans Paranthaman – Barrier coating analysis
Chad Parish– structural characterization.

3.3 COLLABORATIVE RESEARCH OPPORTUNITY (CRO) FRAMEWORK

The Collaborative Research Opportunity (CRO) established under this project was intended to provide a framework for initiation of Collaborative Research and Development Agreements (CRADAs) between industrial partners and ORNL. The process of initiating the CRO program at ORNL involved the development of a request for proposals (RFP), the public release of the RFP, peer-reviewed evaluation of the applications, selection and notification of awardees, and establishment of CRADA agreements with each of the awardees.

The request for proposals (RFP) for the CRO program was developed in the fall of 2010. The full RFP is included as Appendix A of this report. The primary description of the RFP was stated as:

> ORNL is requesting from industrial partners R&D proposals to enter Cooperative Research and Development Agreements (CRADAs) that promote and enhance the objectives of the American Recovery and Reinvestment Act (ARRA) of 2009, P.L. 111-5, especially economic recovery in an expeditious manner. Only projects that promote economic recovery, assist those impacted by the recession, or provide general economic benefit will be selected. The selected projects will be conducted under CRADAs between UT-Battelle and the industrial partners.
>
> Selected projects will focus on advanced materials and processing methods for photovoltaic applications and will be conducted over a 6-month period. The industrial partner is required to provide at least 50% cost share, which can be funds-in to ORNL or in-kind contributions (e.g., facilities, services, and staff time). ORNL will not provide any funds to the industrial partner.

The main objective of the RFP was stated as:

> The ORNL objective is to collaborate with manufacturers to investigate, improve, and scale process methodology for the manufacture of high efficiency and low cost solar cells. Creation and preservation of domestic manufacturing jobs is a primary goal of this solicitation. Awards will be granted in one or more of the following categories.

- Crystalline Silicon
- Polycrystalline Silicon
- Thin Film Materials (a-Si, CdTe, CIGS)
- Earth Abundant, Non-Toxic Materials (e.g. CZTS)
- Organic or Nanostructured Materials
- Transparent Conductive Oxides
- Front & Backside Contacts
- Anti-reflective & Barrier Coatings

> A total of $500,000 in matching funds is available to support ORNL services, staff time, and facilities (not including the cost share of the industrial partners). It is anticipated there will be 4-5 partners selected to support industrial-driven solar research at ORNL over the course of a 6-month period. Approximately $100,000 will be allocated for ORNL's effort to support each project.

The CRADA Collaborative Research Opportunity (CRO) was officially released on September 15, 2010. The opportunity was posted on FedBizOps at the following address: https://www.fbo.gov/?s=opportunity&mode=form&id=ce5fea0e79e190c427ffa498a8c23ba1&tab=core&_cview=0 and was advertised extensively by ORNL staff (see the announcement below in Figure 10).

ANNOUNCING

a *collaborative research opportunity* in
photovoltaic material manufacturing

The goal is to decrease the levelized cost of energy (LCOE) of solar energy through increased performance or decreased manufacturing cost.

Oak Ridge National Laboratory (ORNL) will conduct **short-term**, focused research **projects** to address specific needs of the **solar industry**.

FUNDING: ~$100,000 per project (ORNL internal funds)

ANTICIPATED PROJECTS: 4 to 5

DURATION: 6 months

COST SHARE: 50% (funds-in or in-kind)

Projects will be selected based on brief proposal (5 pages)

REVIEW BEGINS: *November 1, 2010*
PROJECT SELECTION: *November 15, 2010*

Submission / Inquiries: indtech@ornl.gov

OAK RIDGE National Laboratory

Industrial Technologies Program

Figure 10. Announcement of Collaborative Research Opportunity

The review of the CRO proposals was initiated on November 1, 2010 by a team of internal ORNL researchers as well as external industry members. The evaluation process for the RFPs included relative ranking criteria and primary categories including: Important of materials or processing problems to be address (25%); Potential of the collaboration to positively impact the U.S. solar industry (15%); Overall economic benefit to U.S. economy (15%); Potential for implementation of industrial energy savings (10%); Technical merit (10%); Level of cost share to be provided by industrial partner (15%); Importance of technology development and testing results to general market acceptance (10%). The applications were independently reviewed and ranked. They were submitted to DOE's Industrial Technologies Program Office for programmatic review and also discussed with DOE's Solar Energy Technologies Program Office. The CRO awardees were announced in December of 2010 and work commenced immediately with ORNL's Technology Transfer office to streamline the process to get CRADAs in place with the various companies in a reasonable time period. Projects were initiated in March of 2011 and officially terminated one year later.

The selected industrial partners were Global Solar Energy, Ferro Corporation, Ampulse Corporation, and Mossey Creek Solar. A description of each project along with primary objectives and outcomes are given the following sub-sections. A press release regarding this collaborative initiative is shown below (see Figure 11) and released publicly at http://newsblaze.com/story/2011040112251100001.wi/topstory.html.

ORNL in the News

A service of ORNL Research Libraries

ORNL, Industry Collaboration Puts Spotlight on Solar

(NewsWise) Four manufacturers of solar energy components are working with the Department of Energy's **Oak Ridge National Laboratory** to address some of their biggest challenges...4/1

$12M contract goes to Lancaster co.

(Buffalo Business First) Harper International has finalized a contract with the United States Department of Energy's **Oak Ridge National Laboratory** for a full pilot scale carbon fiber process line valued at greater than $12 million.

The Trillion Mile-Per-Gallon Engine

(Forbes) On August 20, 1977, the U.S. National Aeronautics and Space Administration launched the Voyager space probe from Cape Canaveral, Florida...**Oliver Delaire**, a scientist at Oak Ridge National Laboratory, is spearheading research with the Massachusetts Institute of Technology using neutron scattering and computer simulations to tweak the structure and dynamics of thermoelectric materials...4/2

Figure 11. Press release showcasing the winners of the CRO effort.

The text of the press release is as follows:

> **ORNL, industry collaboration puts spotlight on solar**
>
> OAK RIDGE, Tenn., April 1, 2011 – Four manufacturers of solar energy components are working with the Department of Energy's Oak Ridge National Laboratory to address some of their biggest challenges.
>
> Through individual cooperative research and development agreements, or CRADAs, the companies hope to advance solar cell materials and processing technologies. The $880,000 effort is funded by the American Recovery and Reinvestment Act through DOE's Office of Energy Efficiency and Renewable Energy.
>
> "By leveraging our expertise in materials science and manufacturing, ORNL will assist these partners with their individual solar manufacturing challenges and address opportunities to produce high-efficiency devices at substantially lower cost," said Craig Blue, director of ORNL's Energy Materials Program.
>
> Solar cell manufacturing encompasses a broad range of disciplines, including crystal growth, continuous thin-film deposition, thermal annealing, barrier coating, joining and scribing techniques and on-line quality control measures.
>
> The CRADAs are with Mossey Creek Solar, for producing low-cost high-quality silicon wafers with significant reductions in waste material and energy consumption; Global Solar Energy, for developing scalable non-vacuum deposition techniques for thin-film copper indium gallium diselenide, a direct-bandgap material for solar cells; Ferro Corp., for developing inks and pastes to be used for highly conductive layers in thin-film solar cell applications; and Ampulse, for developing an efficient roll-to-roll manufacturing process to deposit thin-film silicon. For these projects, the industry cost share exceeds 50 percent of the total cost.
>
> Through DOE's Industrial Technologies Program, ORNL issued a competitive solicitation to industry for proposals addressing key problems centered around solar cell manufacturing. These projects, expected to be completed over the next six months, were selected following a technical and programmatic review process.
>
> "These short-term focused projects are designed to provide proof-of-principle for innovative approaches to reducing the cost of solar cell manufacturing," said Chad Duty, ORNL program manager for Solar Technologies. "This is a unique and timely opportunity for ORNL to work with industry and set the course for a new generation of solar energy technologies."
>
> Mossey Creek Solar is located in Jefferson City; Global Solar Energy, Tucson, Ariz.; Ferro Corp., Independence, Ohio; and Ampulse, Golden, Colo.
>
> UT-Battelle manages ORNL for DOE.

3.4 COLLABORATIVE RESEARCH

Under the Collaborative Research Opportunity (CRO), four projects were selected for work at ORNL. These are described below.

3.4.1 Global Solar Energy

ORNL-Global Solar CRADA

Project Title: Low-cost Substrate Planarization Layer for High Efficiency Flexible CIGS PV

Covering Period: July 1, 2011 to March 23, 2012
Date of Report: March 30, 2012

Corporate Partner(s): Global Solar Energy Inc.

Project Abstract

Photovoltaic (PV) solar electric technology will be a significant contributor to world energy supplies when reliable, efficient PV power products are manufactured in large volumes at low costs. A promising pathway to reduce PV cost is the use of thin-film technologies in which thin layers of photoactive materials are deposited inexpensively on large-area substrates. One of the most promising thin-film PV technologies is based on copper indium gallium selenide (CIGS). The CIGS cells consist of at least 5 layers: (i) stainless substrate; (ii) back contact (Mo); (iii) CIGS absorber, (iv) window layer, CdS emitter; and (v) front contact (ZnO, ITO). Even though the laboratory-scale, thin film CIGS PV solar cells are reaching efficiencies exceeding 20%, the reported large-scale, thin film CIGS devices on flexible substrates are only 12–13% efficient. One of EERE goals described in the Multi-Year Program Plan for the solar energy technology is to reduce the gap between laboratory-scale efficiency and the manufacturing cell efficiency. One reason for the reported lower efficiencies for large-scale devices is a consequence of interlayer diffusion and hence defect formation in the absorber layer. To increase cell efficiency on flexible foil there is a need to reduce substrate roughness and furthermore limit interdiffusion between the substrate and the absorber layer. This will also assure improved process reproducibility by reducing batch to batch variability. This collaboration focuses on improving the properties of Mo-coated stainless steel substrates to fabricate high efficiency flexible CIGS PV. The main goal of this research is to identify the possible candidate materials and methods and co-develop the substrate/back contact templates. In addition, we are also studying the microstructure-property correlations of a high efficiency vs. low efficiency solar cells. This fundamental understanding will lead to reduce the gap between laboratory-scale efficiency and the manufacturing cell efficiency.

Statement of Objectives

The main goal of this CRADA is to identify the possible candidate materials and co-develop the substrate planarization layer for the substrate/back contact templates.

Benefits to the Funding DOE Office's Mission

To advance technology in partnership with industry, government, and the public and to meet America's need for reliable, efficient, alternate renewable energy source. The total market for flexible thin-film solar photovoltaic devices is expected to exceed $ 10 billion per year by 2015 and $ 100 billion in sales by 2020. The technological development and successful commercialization of flexible CIGS thin film solar cells demonstrates the promise and practicality of PV and they offer fascinating new opportunities for cheaper, more efficient, longer-lasting systems. Higher PV efficiency thus directly impacts the overall electricity cost, because higher-efficiency cells will produce more electrical energy per unit of cell area over the cell lifetime. The key for the PV industry is to reduce the production costs to below $ 1/ Watt ($\$1/W_p$) to compete with other technology in power generation. At present, modules based on single crystal and multicrystalline Si cost more than $ 3-4/W because the manufacturing cost is about $2.20/W. Reducing the cost/watt of delivered electricity by a factor 5-10 will make solar cells competitive with fossil and nuclear electricity. The target of < $1/W can be reached using thin-film fabrication technologies developed at Global Solar Energy. This will create interest in residential and commercial building markets, as well as utility scale PV. ORNL and Global Solar have used a cooperative research and development agreement (CRADA) to collaborate on this project.

Technical Discussion of Work Performed by All Parties
Global Solar Energy (GSE) provided ORNL with all the starting stainless steel substrates and CIGS layers for materials testing and evaluation. The following improvements were made in this CRADA.

- Conducted several feasibility studies in the substrate/back contact templates to produce pin-hole free planarization layers by proprietary substrate modification.
- Nanoindentation and substrate surface properties were studied in detail.
- Studied the microstructure-property correlations of a high efficiency vs. low efficiency CIGS solar cells
- Fundamental understanding of the microstructure of CIGS active layers and interfaces has helped GSE to improve their deposition conditions in order to reduce the gap between laboratory-scale efficiency and the manufacturing cell efficiency.

Subject Inventions (As defined in the CRADA)

All the results obtained in the project have been shared with Global Solar.

Commercialization Possibilities

Joint invention disclosures have been submitted.

Plans for Future Collaboration

ORNL will be interested in working with Global Solar to develop planarization layers if proper funding is available.

Conclusions
Close collaboration and interaction between ORNL, and GSE resulted in significant advancement in process understanding and subsequently in the development of a robust deposition process. The collaboration will function through weekly conference calls, coordinated sample exchanges facilitated, joint development and joint materials evaluation and testing.

3.4.2 Ferro Corporation

Ferro Corporation’s Electronic, Color and Glass Materials (“ECGM”) business unit is currently the world’s largest supplier of metallic contact materials in the crystalline solar cell marketplace. Ferro’s ECGM business unit has been the world's leading supplier of thick film metal pastes to the crystalline silicon PV industry for more than 30 years, and has had operational cells and modules in the field for 25 years. Under this project, Ferro attempted to leverage world leading analytical capabilities at ORNL to characterize paste to silicon interface microstructure and develop high efficiency next generation contact pastes. As part of Ferro’s efforts, they developed pastes for high sheet resistivity wafers using leaded and lead-free glass, and processed cells under various firing conditions. Fired cells were characterized for electrical properties at Ferro. Further microstructural characterizations of these pastes were carried out at ORNL using a variety of analytical tools. In addition, Ferro worked to develop silver based inks for highly conductive layers for thin film solar cell applications. DOE funding for this project was $100,000 with an in-kind cost share from Ferro Corporation of $180,000.

Ferro has been investigating new Ag pastes for both high aspect ratio current collection fingers and contact to high sheet resistance emitters. Pieces of selected solar cells (1x1 cm^2) showing both “good” and “bad” solar conversion efficiency were selected and sent to ORNL for additional characterization (STEM, low temperature electrical). Physical and elemental structures of paste-glass-silicon interface regions of different paste processing conditions were examined at high resolution using FIB + STEM/EDS methodologies. It was found that different processing conditions (top vs. bottom) gave different glass/paste interface morphologies, and different size and shape distributions of the silver inclusions in the lead-rich glass. In particular, sub-100 nm silver precipitates are seen, whose analysis requires FIB+STEM/EDS methodology. Spherical vs. mixed acicular morphologies are seen in the two examined conditions (see Figure 12). Further work will focus on determining the performance impact of these morphology variations.

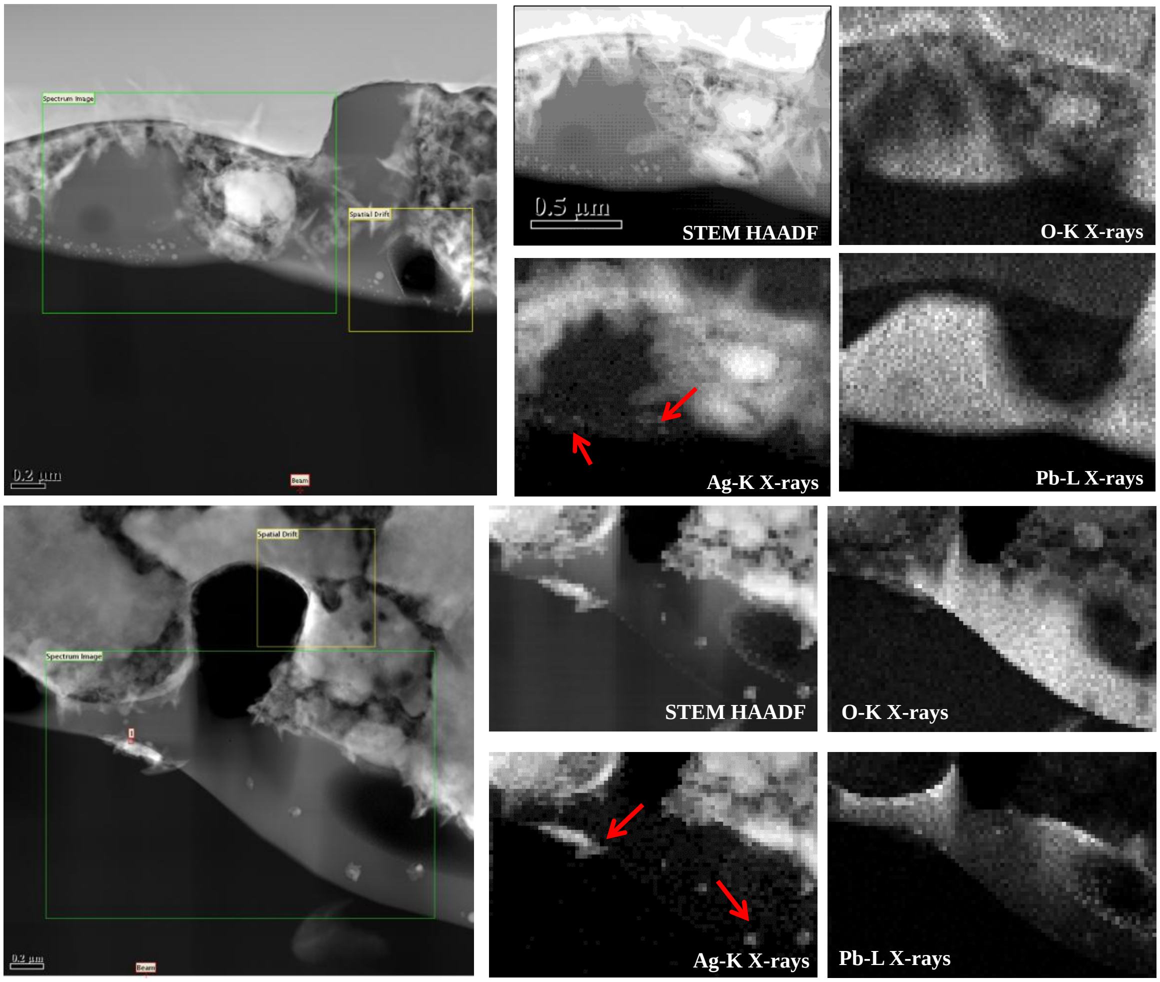


Figure 12. High resolution FIB + STEM/EDS imaging of silver paste / silicon interface.

ORNL also conducted imaging and EBSD analysis of the silver / substrate interface region as well as FIB cross-section preparation for AFM analysis at Ferro. The recently-installed Gatan Ilion argon-ion cross-sectioning tool in the ORNL Microscopy Group was used to prepare high-quality backside-polished cross sections of Ferro Ag lines on Si substrate for high-resolution SEM analysis (QCPMP90-10). The new tool uses argon ions of energy 1-6 keV to polish at a glancing angle, and allows smooth and low-damage cross sections of difficult or heterogeneous materials to be produced quickly.

Shown in Figure 13a is a low-magnification SEM (J6500F, ShaRE user facility) image of the polished specimen. Figure 13b shows secondary electron image (SEI) and X-ray maps for O K, Ag L, and Pb M lines. Ag and Pb-O are seen to vary oppositely in space, and pores seen in SEI imaging are weak in Ag and Pb-O X-rays. Further, Pb-O X-rays are strong along the Ag//Si interface, indicating a preferential agglomeration. Figure 13c-d show Ag islands at the Pb-Si interface.

Electron backscatter diffraction (EBSD) is a microcrystallographic method for evaluating local crystal structure and orientation. Figure 14 shows EBSD data from the silver line. Figure 19a shows a raw EBSD pattern from a single silver crystallite, and Figure 14b the computer assigned indexing of the pattern. Collection of an array of these patterns allows a comprehensive map of the crystallography of the specimen. In Figure 14c, only the silver phase is shown. Colors denote the local crystallographic direction out of the page (unit triangle, inset) and intensity denotes the computer-evaluated confidence index (CI) for the indexing solution at each pixel. White boundaries are high angle (>15°) grain boundaries, gray low angle (2-15°) boundaries, and red FCC twins (Σ3 type 60° <111>). This illustrates that the silver grains are ~1 μm in size and roughly equiaxed, and heavily twinned. Pole figure calculations (not shown) indicate no significant crystallographic texture. Grain boundary character is shown in Figure 15a, indicating the most probable grain boundaries are twins (60°). Grain size is given in Figure 15b, for both the raw data (red) and data ignoring the presence of twins (blue). Most probably grain sizes are ~1 and 2 μm for each calculation.

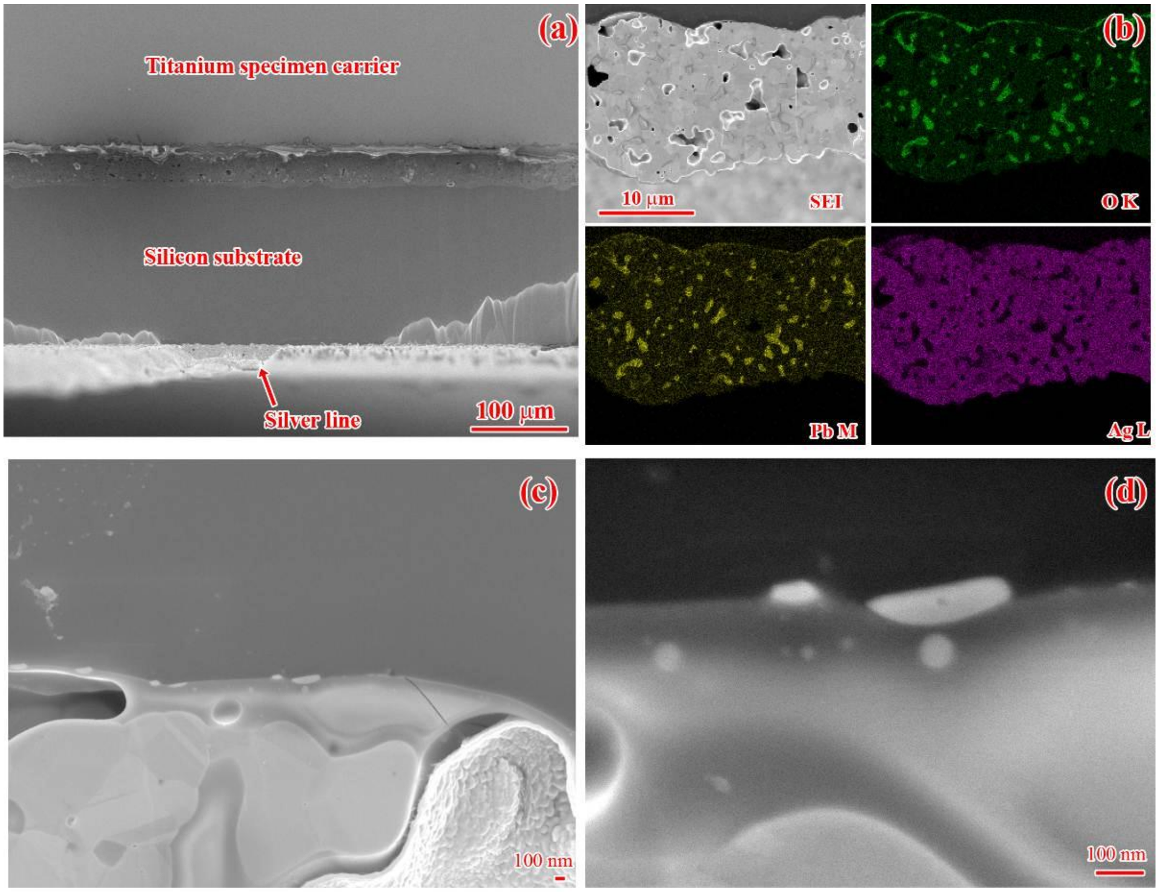


Figure 13. Low magnification imaging and X-ray mapping of polished Ag/Si sample.

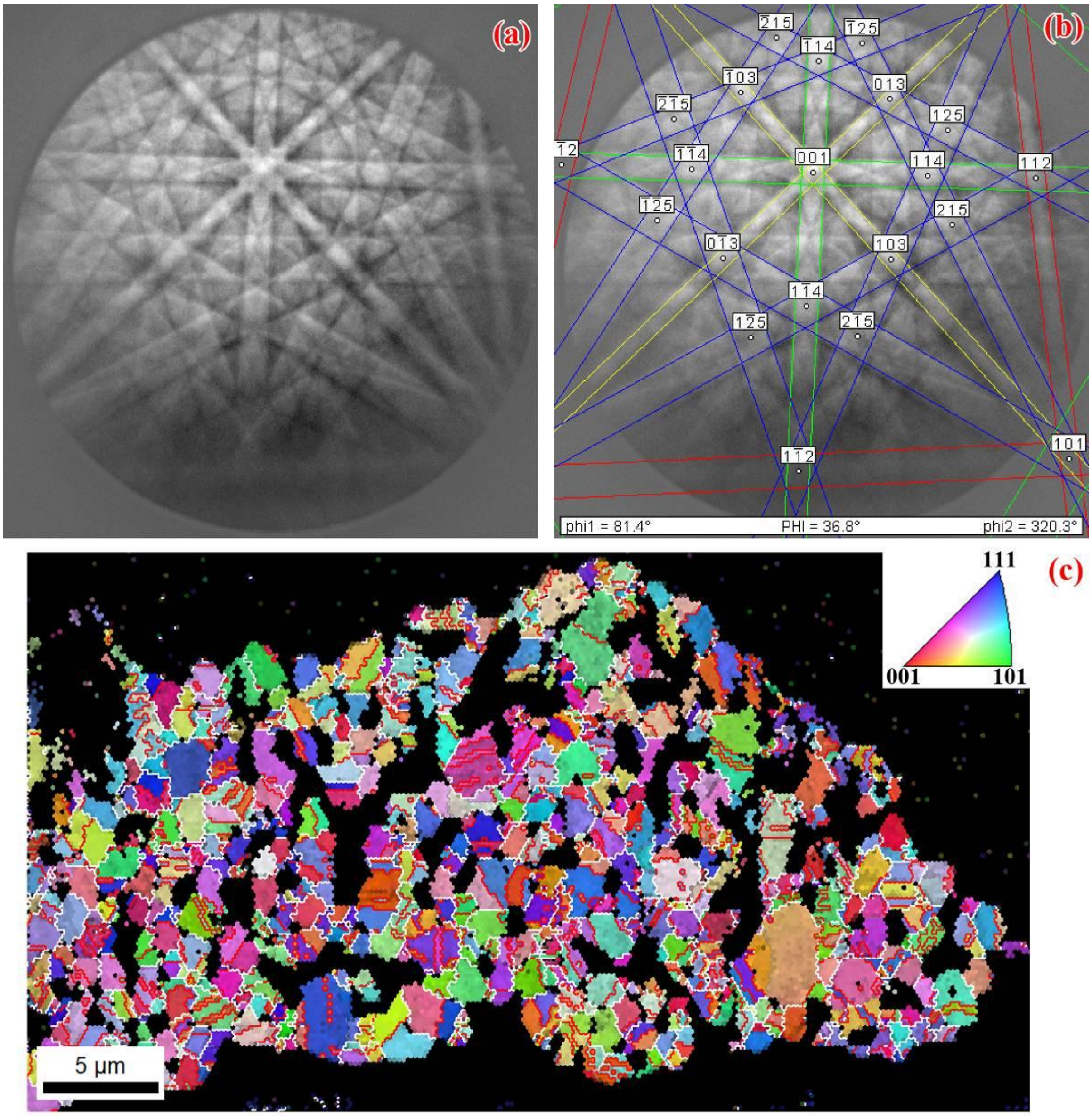


Figure 14. Electron Backscatter diffraction patterns showing local crystalline structure and orientation of Ag line.

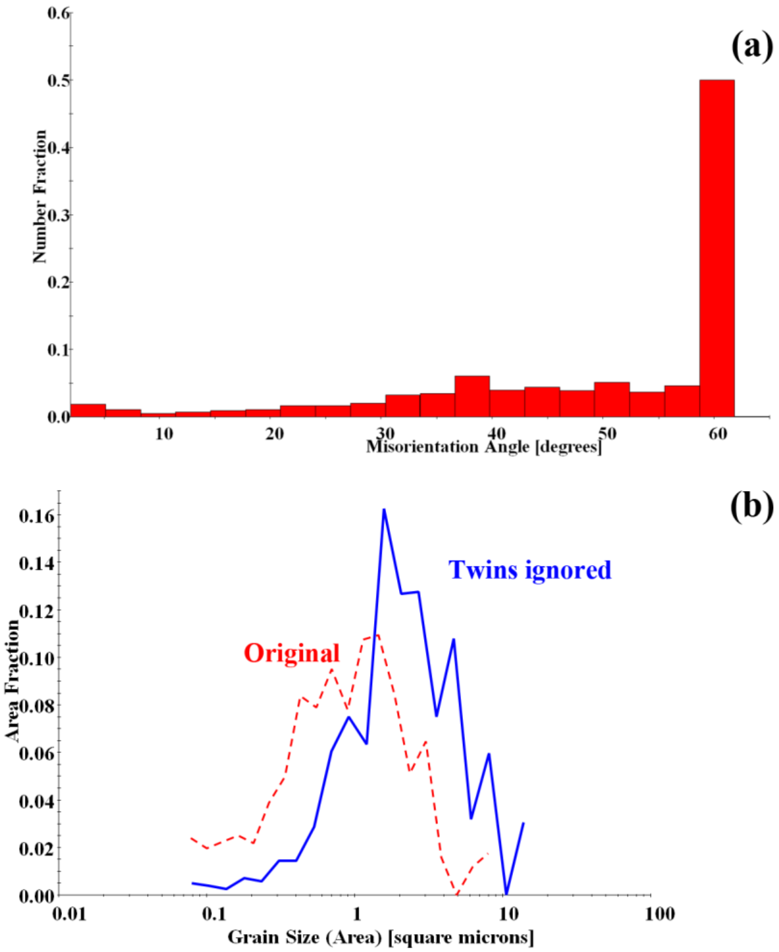


Figure 15. Grain boundary orientation and grain size analysis of silver line.

Focused ion beam (FIB, NB5000 combined FIB-SEM instrument, ORNL-ShaRE) milling was used to prepare lift-out specimens (QCM85120) for conductive atomic force microscopy (cAFM) at Ferro. Figure 16a shows SE imaging of two lift outs attached to a molybdenum specimen carrier in the FIB-SEM instrument. Figure 16b shows a higher resolution SEM image of the lift out on carrier slot "C" in Figure 16a. Silver, interface, and silicon regions can be seen. Figure 16c shows a dark field (DF) STEM-in-SEM image of the specimen. The detailed features of the interface layer are visible (i.e., small silver particles) and small FIB-cut notches are also seen.

Previous proof-of-concept experiments on ORNL FIB-cut specimens examined by cAFM at Ferro have indicated that mapping of electrical conduction may be possible. It is hypothesized that the thin FIB-cut sections, combined with the FIB-notched segments, will reduce electrical cross-talk and allow the explication of the electrical conduction behavior of the silver islands along the interface.

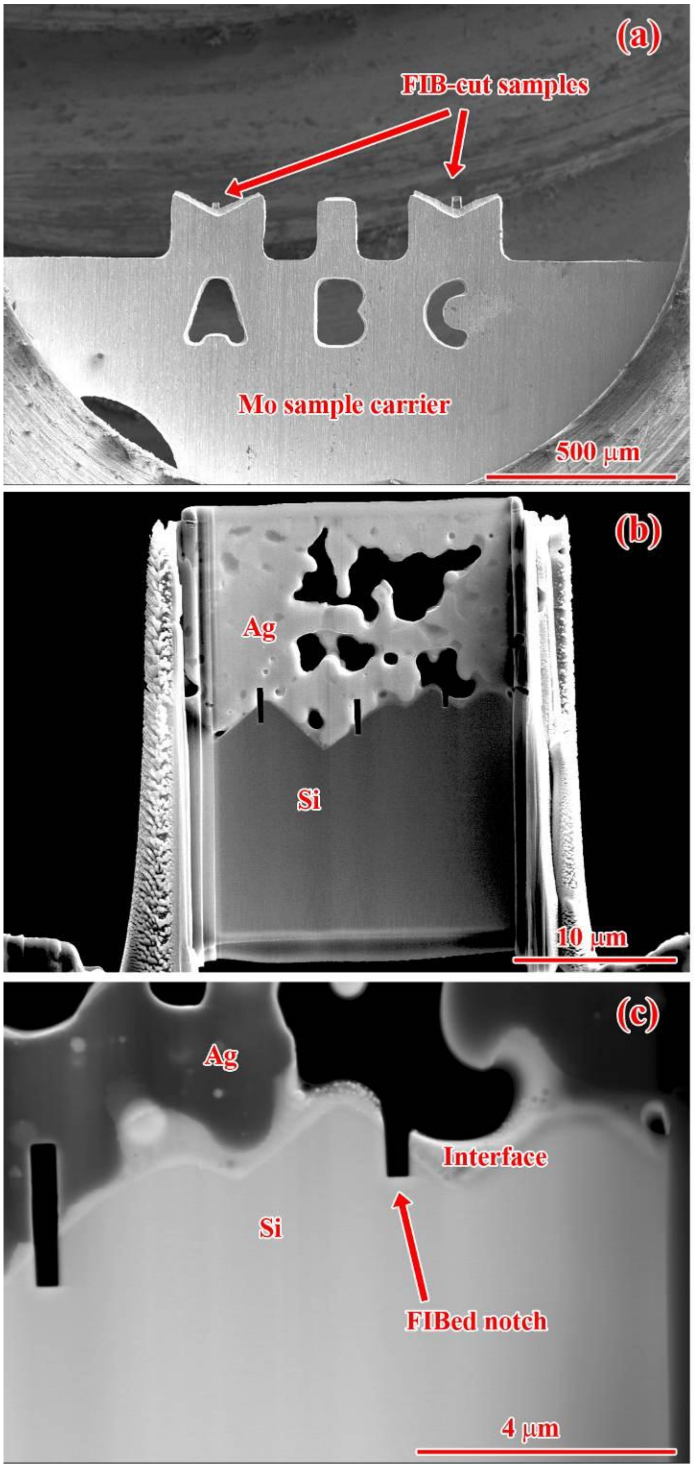


Figure 16. FIB cross sections of Ag line on silicon.

In the formation of contacts on silicon solar cells, one concern is the electrical/doping characteristics of the underlying silicon material. In most silicon solar cells, the emitter (top) of the solar cell is made from very heavily doped silicon, where the dopant is phosphorous, and the back surface is heavily doped with boron or aluminum to make the back surface field. The doping process can incorporate up to 10^{20}-10^{21} atoms in the near-surface region, making the material degenerately doped. Moreover, this concentration of dopant atoms (2-20 parts per thousand) can result in strains in the material, and the Fermi level will be within the conduction/valence band.

In order to examine this possibility, we performed spectroscopic ellipsometry experiments on the front surface of a test silicon solar cell. The solar cell was single-crystal, and was textured and anti-reflection (AR) coated to reduce the reflection losses from the solar cell. In order to perform the ellipsometric measurements, the sample was placed in an ellipsometer from J. A. Woollam, Inc. at Ferro. This device is capable of tilting and rotating the sample so that the incident light is reflected off the 5-10 micron size sides of the pyramids on the sample surface, thus giving a composite flat surface from which one can perform the ellipsometry experiments. The sample surface was known to be AR coated using hydrogenated silicon nitride.

Figure 17 shows the raw ellipsometric data, expressed in the ρ representation ($\rho = \tan \psi \exp(i\Delta)$) at three angles of incidence (45°, 55°, and 65°), along with a fit to the data. In the figure the real part is shown at the top and the imaginary part at the bottom. The model used was a 4 medium model (air / surface roughness / a-SiN / c-Si). The surface roughness was modeled using a Bruggeman effective medium model, with 50% voids and 50% SiN. The a-SiN layer was modeled using a Tauc-Lorentz parameterization. The optical functions of silicon have been obtained from lightly doped single crystal silicon. The final $\chi^2 = 21.5$, which indicates that the fit is close, but there are some significant differences between the model and the data. The fitted parameters are shown in Table 1.

Table 1. Fitted Elipsometry Parameters

Parameter	Value
Surf. Rough Thickness (nm)	1.7±0.2
a-SiN thickness (nm)	88.1±0.1
T-L Eg (eV)	3.68±0.03
T-L Eo (eV)	9.22±0.06
T-L Γ (eV)	7.9±0.7
T-L Amplitude (eV^3)	9064±1235

Upon the examination of the data and fits shown in Figure 17, one can see that the fit is very good, except in the IR region (below ~1.8 eV) and near 3.4 eV. This is very likely caused by the heavy doping of the silicon. If the material is very heavily doped, then the relatively strong feature in the optical functions of silicon at the direct band edge (3.4 eV) will be rounded off compared to the optical functions of lightly doped silicon. Furthermore, the very heavily doped silicon will show Drude-like absorption in the IR, increasing the imaginary part of the refractive index or dielectric function. These effects will be more pronounced in the 65° spectrum, since this angle is closer to Brewster's angle for silicon than the other angles of incidence measured. Thus, the heavy doping of the silicon wafer is likely responsible for the deviations of the model calculation from the experimental results near 3.4 eV and in the IR, resulting in the high χ^2 of the ellipsometric fit.

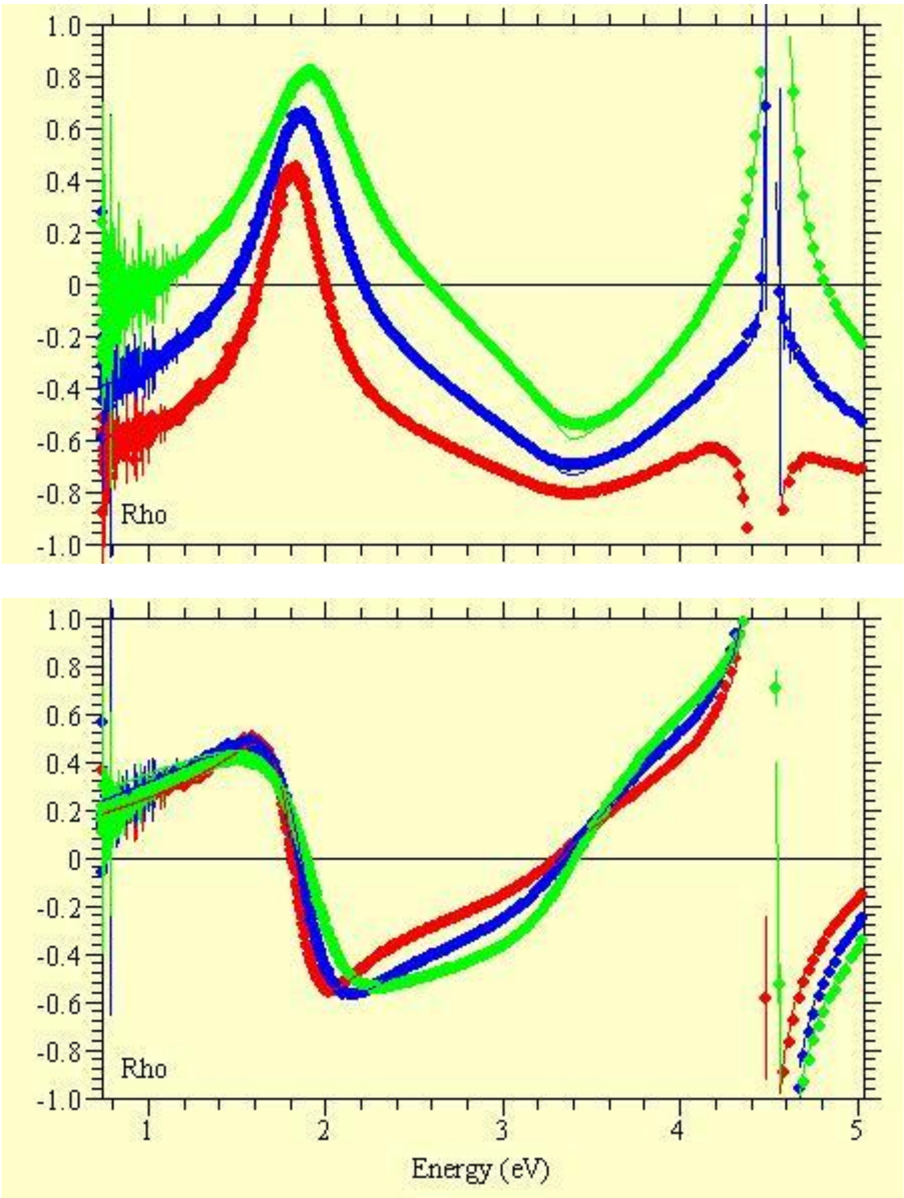


Figure 17. Spectroscopic ellipsometric data expressed in the Rho representation.

In order to improve the efficiencies of silicon solar cells, paste to silicon contact formation mechanisms must be more thoroughly understood as a function of paste chemistry, wafer properties and firing conditions. Ferro Corporation has been involved in paste development for over 30 years and has extensive expertise in glass and paste formulations. This project has focused on the characterization of the interface between the top contact material (silver paste) and the underlying silicon wafer. It is believed that the interface between the front contact silver and the silicon wafer plays a dominant role in the electrical performance of the solar cell. Development of an improved front contact microstructure depends on the paste chemistry, paste interaction with the SiNx, and silicon (“Si”) substrate, silicon sheet resistivity, and the firing profile. Typical front contact ink contains silver metal powders and flakes, glass powder and other inorganic additives suspended in an organic medium of resin and solvent. During fast firing cycles glass melts, wets, corrodes the SiNx layer, and then interacts with underlying Si. Glass chemistry is also a critical factor in the development of an optimum front contact microstructure.

Over the course of this project, several fundamental characteristics of the Ag/Si interface were documented, including a higher-than-expected distribution of voids along the interface, which could significantly impact electrical conductivity. Several techniques were also investigated for the interfacial analysis, including STEM, EDS, FIB, EBSD, and ellipsometry. The primary conclusions from this collaborative project include: (1) Identification of a high density of voids at the interface between the current collection fingers (using the new high aspect ratio paste) and the underlying Si wafer, (2) Schottky-like rectifying nonlinearities were not observed for the control-sample solar cells while electrical resistivity was found to decrease in proportion to the Ag paste mass during TGA, (3) Different processing conditions (top vs. bottom) were found to give different glass/paste interface morphologies, and different size and shape distributions of the silver inclusions in the lead-rich glass, (4) Silver grains near the interface are roughly 1-2 μm in diameter and have no preferred crystallographic texture, (5) FIB cross-sectioning techniques were explored as a means for exploring the electrical conduction behavior of the silver islands along the interface, and (6) Spectroscopic ellipsometry analysis is consistent with heavily doped silicon. A final report detailing the study was also submitted, as referenced below.

> C. Duty, C. Parish, G.E. Jellison, and P. Joshi, "Development of Novel Front Contact Pastes for Crystalline Silicon Solar Cells," CRADA Final Report NFE-11-03418, April 2012.

3.4.3 Ampulse Corporation

ORNL-Ampulse Corporation CRADA

Project Title: High-rate, Low-cost Process for High Efficiency Flexible c-Si PV

Covering Period: July 1, 2011 to March 15, 2012
Date of Report: March 26, 2012

Corporate Partner(s): Ampulse Corporation

Project Abstract

The film c-Si based photovoltaics on RABiTS substrates would be capable of achieving efficiency above 15%, but at costs comparable to thin films. Utilizing a uniquely-textured and flexible metal substrate developed at the superconducting materials program at ORNL, coupled to an NREL breakthrough in hot-wire chemical vapor deposition (HWCVD) processes, silicon heteroepitaxy is for the first time being directly-deposited out of silane gas, into a silicon structure that is less than 5 microns thick, crystallographically-oriented, and large-grained – <u>ideal</u> for solar PV power generation. We have recently overcome the problem of Ni and Cu diffusion into Si forming NiSi/CuSi towers through buffer development. Due to the lattice mismatch between the oxide cap layer and Si, recombination-active threading dislocation defects form in the silicon layer. We can lattice match the buffer with silicon by alloying with germanium, which can subsequently be graded out for the actual device layer. The main goal of this project is to develop a physical vapor deposition process for the growth Silicon, Germanium, or Silicon-Germanium alloy films.

Statement of Objectives

The technical objective of the CRADA is to develop a physical vapor deposition process for the growth of Silicon, Germanium, or Silicon-Germanium alloy films.

Benefits to the Funding DOE Office's Mission

To advance technology in partnership with industry, government, and the public and to meet America's need for reliable, efficient, alternate renewable energy source. Ampulse has proprietary calculations, based on detailed manufacturing cost models and standard calculation techniques that fully-support their target levelized cost of electricity (LCOE) for solar PV of \$0.07 kWh. There are cost reductions not only in eliminating about \$1/W for silicon feedstock, but also from adopting roll-to-roll manufacturing as used in the amorphous silicon PV industry. As in amorphous silicon PV, considerable reductions in balance of systems costs (e.g., transportation and installation) can be obtained by reducing the weight of the PV modules and making them flexible. ORNL and Ampulse have used a cooperative research and development agreement (CRADA) to collaborate on this project.

Technical Discussion of Work Performed by All Parties

The purpose of the CRADA is to develop a high rate physical vapor deposition process for the growth Si or Ge on single crystal substrates. One of the greatest challenges facing the c-Si technology is the formation of recombination-active threading dislocation defects in the silicon layer. The dislocation defects nucleate at the silicon heterointerface with the oxide buffer layers. To reduce the defect densities in the silicon layers, it is necessary to closely match the lattice constants between silicon and the underlying buffers. Our demonstration of silicon epitaxy was done using a γ–Al_2O_3 cap layer with a 1-2% lattice mismatch to silicon. A better match can be obtained through either a different choice of buffer material or by changing the silicon lattice constant through alloying with germanium (which can subsequently be graded out for the actual device layer). Our initial attempts to grow either Si or Ge using PLD or sputtering on γ–Al_2O_3 layers did not work. However, we have identified CeO_2 as a suitable cap layer. ORNL has demonstrated the growth of Ge films on CeO_2 capped STO, r-plane sapphire, and RABiTS templates.

Subject Inventions (As defined in the CRADA)

All the results obtained in the project has been shared with Ampule Corporation.

Commercialization Possibilities

Ampulse Corporation has licensed the RABiTS related template technology for making flexible, high efficiency c-Si PV.

Plans for Future Collaboration

ORNL will be interested in working with Ampulse Corporation to develop conducting buffers if proper funding is available. In addition, ORNL is also working with Ampulse Corporation through a work for others (WFO) agreement to focus on developing buffers on textured Cu substrates.

Conclusions

The CRADA work has provided an improved understanding of the fundamental properties of the buffer layer growth for Ge. The activity was closely coupled to Ampulse Corporation's program. The collaboration functioned through regular conference calls and frequent sample exchanges. Joint publications have resulted from this work. This team has also won the FLC National Award for technology transfer last year.

3.4.4 Mossey Creek Solar

Mossey Creek Solar (MCS) is a start-up company with great expertise in the solar field. The primary interest is to create and preserve jobs in the solar sector by developing high-yield, low-cost, high-efficiency solar cells using MCS-patented and -proprietary technologies. The specific goal of this project was to produce large grain formation in thin, net-shape-thickness mc-Si wafers processed with high-purity silicon powder and ORNL's plasma arc lamp melting without introducing impurities that compromise absorption coefficient and carrier lifetime. If successful, the technology will produce low-cost, high quality silicon wafers with significant reductions in waste material and energy consumption. DOE funding for this project was $100,000 with a matching in-kind cost share by Mossey Creek Solar.

A large portion of the initial effort in the project involved the consideration and optimization of the non-wetting mold coating for the graphite molds. After numerous trials and considerations (e.g., non-wetting, ease of processing, method amenable for mass production, and cost) the use of a controlled silicon nitride coating with a specific additive and heat-treatment steps appears to be the best option. Iterative microstructural (optical and electron microscopy) and phase (x-ray diffraction) exams were used to support the development of the coating.

Numerous melting trials (done with a graphite-lined, resistance-heated furnace) were used to produce melted and solidified billets with a large grain microstructure. Temperature control, environmental management, and starting silicon purity proved to be critical for predictable melting and ultimate electrical and optical properties of the produced wafers. Much attention was also given to optimizing the particle size distribution of the starting silicon powder because it affects the melting response. Various parameters were also investigated to control wafer thickness. Starting particle size distribution, temperature control, and environment affect the produced thickness.

Electrical and optical measurements were made on silicon wafers made by the net shape melting of high purity silicon powders. The electrical resistivity was ~6.5 ohm-cm, with a bulk p-type carrier concentration of 1.8×10^{16} carriers/cm^3. The Hall mobility was low at 54 cm^2/V s. The near band edge absorption coefficient was determined from optical transmission measurements (Figure 18) show that there is no discernable difference between the wafers fabricated from the high purity powders and single crystal silicon. Spectroscopic ellipsometry measurements from 5.6 to 1.5 eV (220 to 850 nm) show that there is no discernable difference between the complex dielectric functions of c-Si and the wafers made from the high purity silicon powders. These results indicate that this material has the potential of being useful as solar grade silicon.

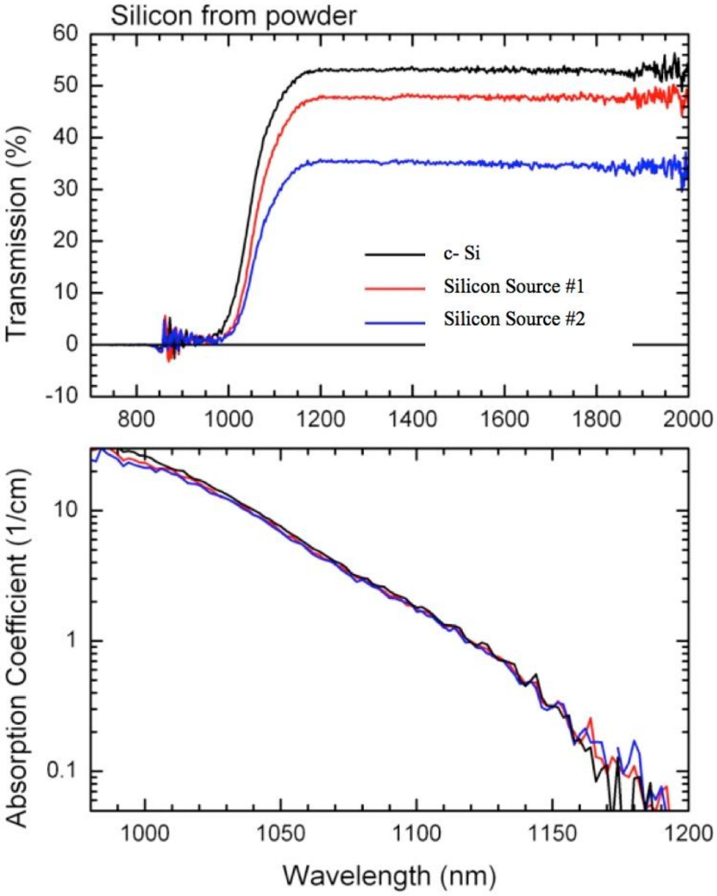


Figure 18. The optical transmission and resulting absorption coefficient determined from the transmission measurements of single crystal silicon (c-Si) and wafers made from two powder sources.

During this project, much attention was also devoted to the chemical and phase characterization of the mold's coating and of the processed silicon coupons because the high-temperature furnace exhibited vacuum control problems, so its maintenance and repair delayed processing progress. An illustration of both characterizations is shown in Figure 19. X-ray diffraction (XRD) showed that the heat-treatment of the coated-graphite (desirably) formed silicon nitride. X-ray photoelectron spectroscopy (XPS) showed that carbon, oxygen, and nitrogen was present in the outer 100 nm of the processed silicon billets and were bonded with the silicon. It is desired to produce silicon billets with minimum surface contamination.

Surface profilometry of the graphite molds was also examined through surface roughness measurement. The rationale is if a thin (e.g., < 250 µm thick) net-shape and mechanically resilient silicon wafer is sought, then the surface roughness of the molds (and coating) may need to be controlled. The average roughness (Ra) was typically on the order of about 6-8 microns; however, the maximum height-to-valley value (Rt) was over 100 microns, so the large Rt value could cause non-uniformities in the net-shape wafers that could lead to stress concentrators and mechanically vulnerable wafers. Future attention to this issue is warranted.

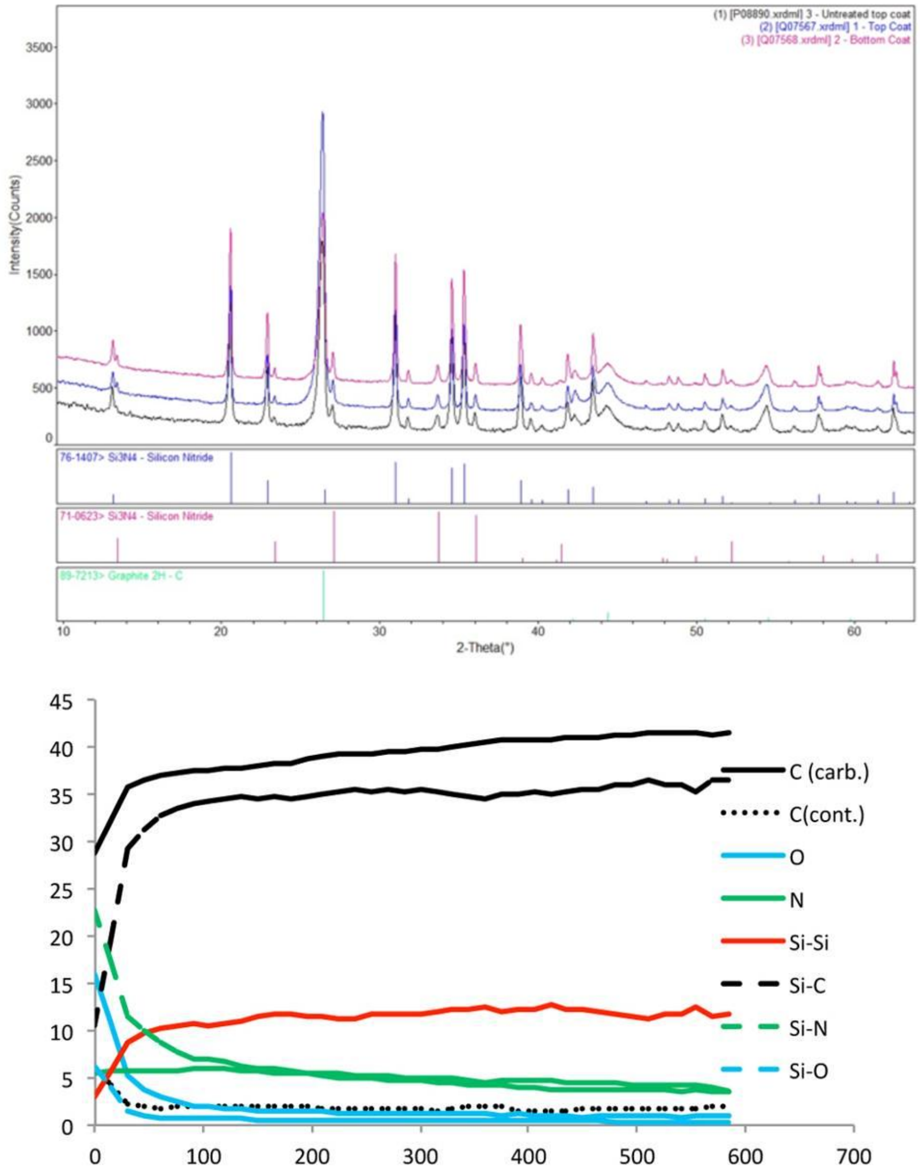


Figure 19. XRD (top) showed that the coating was fully converted to silicon nitride during heat treatment. XPS (bottom) showed that the silicon composition 100 nm in from the surface contained carbon, oxygen, and nitrogen.

Particle size was found to play a dominant role in controlled melting. The high-purity silicon originally provided by MCS possessed a relatively large particle size, - approximately 2-3 mm. When the molds were filled with this silicon, melting resulted in segregation and non-uniformly solidified silicon billets. It was concluded that finer sized silicon is needed for this melting, so MCS provided more silicon that was attrition milled to a finer size.One of the most important characteristics of solar grade silicon is the minority carrier diffusion length. If this parameter is large, then electron-hole pairs that are generated deep in the material have a good probability of contributing to the power of the solar cell. One of the principal contributors to short minority carrier diffusion length is the deep level recombination centers that exist in the material. Depending upon the type of defect, as few as 1 part per billion is sufficient to significantly reduce the minority carrier diffusion length.

Numerous lessons were learned in an attempt to fabricate thin, net-shaped wafers. Although large-areal-sized wafers were not produced within the confines of the project's technical boundary conditions, duration, and funded effort, those lessons serve to guide follow-on or future work that achieves their production. They included the need to: use ultra-high-purity starting silicon and sustain its high purity throughout all stages of powder milling, handling, and silicon wafer processing, employ ultra-rapid heating, measure and control temperature throughout all process heating, choose coating and mold materials that do not introduce impurities into the silicon, mill silicon powder to a small size for efficient and controllable melting flow, appropriately design the mold (and its coating) to promote desirable surface finish of net-shape silicon wafers, and employ capillary flow to promote thinness of net-shape wafers. These results and findings were detailed and summarized in a final report referenced below.

Final Report: A. A. Wereszczak, C. E. Duty, D. J. Vuono, H. -T. Lin, G. E. Jellison, Jr., T. G. Morrissey, J. A. Angelini, and J. J. Carberry, "Promoting Large Grain Formation in Thin Net-Shaped Multicrystalline Silicon Wafers," CRADA Final Report NFE-11-03405, April 2012.

4. FUNDAMENTAL RESEARCH ON PHOTOVOLTAIC MATERIAL

In addition to the short-term research projects that address specific industry concerns from the previous section, staff researchers at ORNL conducted longer-term, more fundamental research on the performance and manufacture of thin film photovoltaics.

4.1 EQUIPMENT

In order to effectively pursue fundamental photovoltaic research, specific pieces of equipment were purchased or brought online specifically for the deposition of CdTe absorber layers and analysis of solar cell materials. Specifically, ORNL installed a dedicated sputtering and PVD system for use with CdTe. The pieces of equipment procured for this project are listed below along with an overview of their capabilities and primary uses.

4.1.1 Combined Sputtering / Physical Vapor Deposition System

In order to conduct basic research on the crystal structure and composition of solar cell materials, it is paramount that ORNL have the capability to synthesize these materials using techniques that offered both flexibility and control over these primary parameters. Initially, a chemical vapor deposition system was identified as the preferred method for investigating the synthesis of crystalline CdTe thin films. However, it was later determined that a physical vapor deposition (PVD) system provided the most flexibility for depositing solar materials with adequate control over various parameters. Not only did a PVD system provide better control over composition and defect density, but PVD offered the potential for lower temperature growth, which would be useful for producing solar cells on temperature-sensitive substrates. The system ordered from Kurt J. Lesker Company also offered an alternate chamber for sputtering of CdTe. The technical requirements of the sputtering system included the following: 3cm ion source and power supply, sample rotation with flip-style shutter and water cooling, glove box extension, and film thickness monitors. The sputtering chamber is separate from the PVD chamber, with a single sample exchange load-lock system joining the two deposition chambers.

The physical vapor deposition system selected was a PVD 75GB Thin Film Deposition System from the Kurt J. Lesker Company. This is a complete system for vacuum depositing coatings on wafers for research regarding materials optimization for solar cells and radiation detectors. The system consists of a vacuum system for evacuating the coating chamber, particulate trapping system to prevent pump contamination, anti-contamination chamber to serve as a buffer area between the vacuum chamber and the laboratory facility, capability to deposit up to four materials simultaneously, and a substrate fixturing and temperature control system. A schematic of the system is shown in Figure 20.

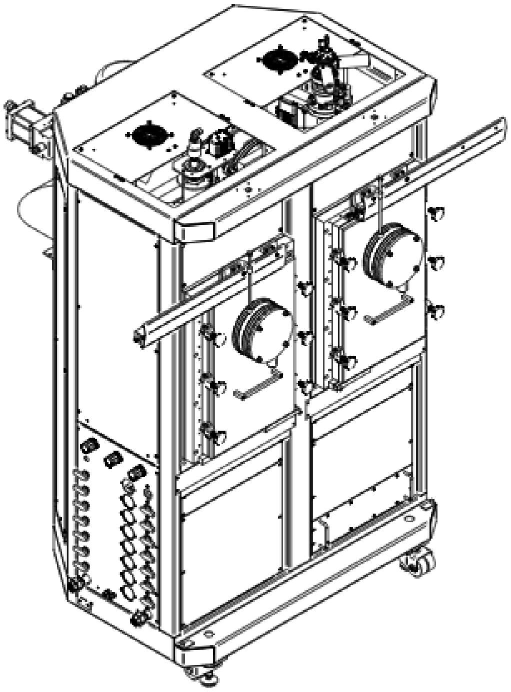


Figure 20. **Combined PVD and Sputtering System Design**

The CdTe coating system was shipped from the Kurt Lesker manufacturing facility in Pittsburgh, PA and arrived on September 29th, 2010. Prior to shipment researchers from ORNL traveled to the Pittsburgh facility for final system evaluation and acceptance testing. Test coating runs were performed on both the sputtering and evaporation chambers, as well as demonstration of the automatic control software. The system was relocated to building 3500 on October 5th. The system was placed in its location in the 3500 clean room facility as shown in Figure 21. Interior pictures of the deposition chambers as well as control screen captures are shown in Figures 22-325 below.

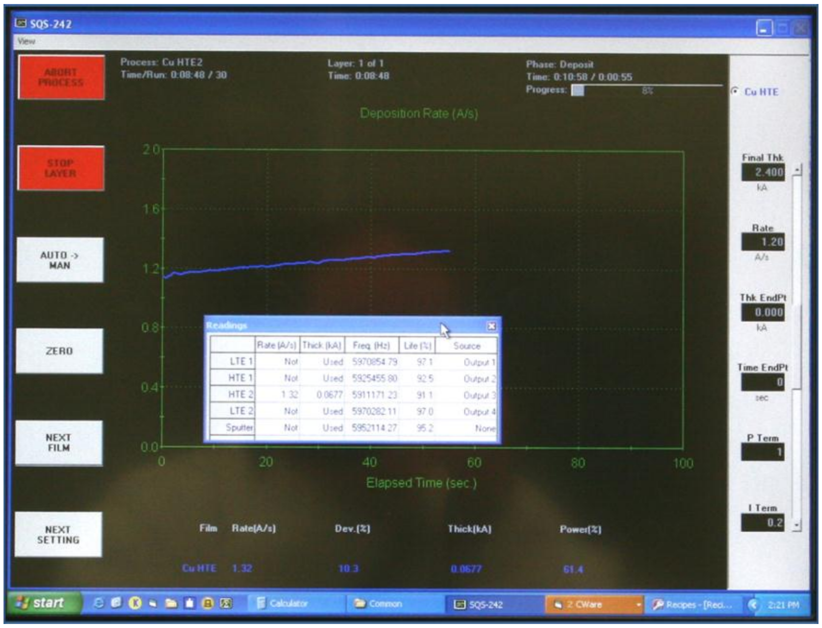
Figure 21. **Dual-chamber (sputtering and thermal evaporation) system for CdTe research shown onsite in the 3500 clean room.**

Figure 22. View inside the coating chambers.

In Figure 22 the left image is of left chamber for high-throughput film research using sputtering or combinatorial sputtering. Theion source for use in polymer processing is shown in the lower left corner of the image. The substrate holder at top of chamber is cooled for flexible/polymer substrate processing. The right image is of thermal evaporation chamber and shows the four sources that can be used for sequential or simultaneous deposition. The upper portion of image illustrates the substrate holder which can control temperature up to 600° C.

Figure 23. CdTe coating system close-up images

In Figure 23 the left image is a close up of the ion source for ion assisted deposition and substrate cleaning or texturing, particularly useful in flexible substrate manufacturing process development. The right image is thermal source during operation.



Process: Cu HTE2
Time/Run: 0:08:48 / 30
Layer: 1 of 1
Time: 0:08:48
Phase: Deposit
Time: 0:10:58 / 0:00:55
Progress: 8%

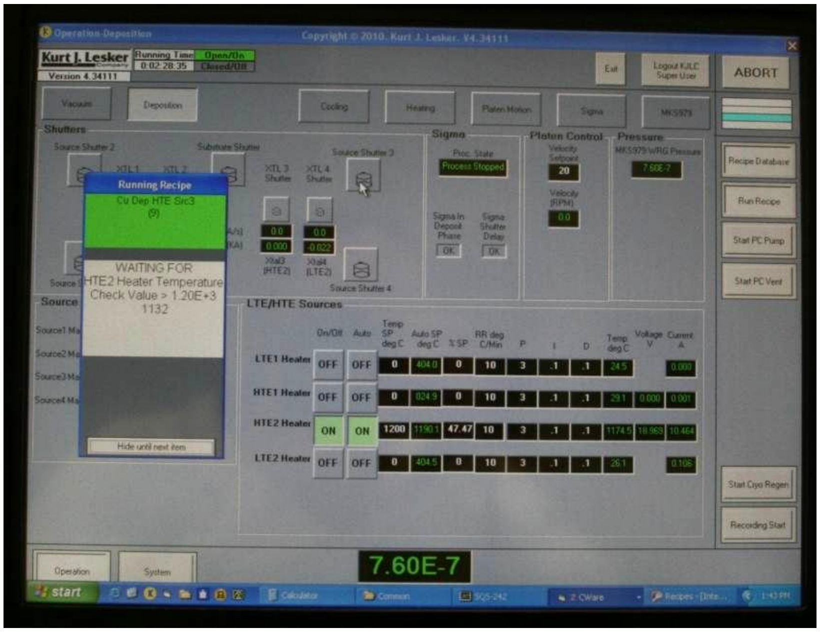
Final Thk 2.400 kA
Rate 1.20 A/s
Thk EndPt 0.000 kA
Time EndPt 0 sec
P Term 1
I Term 0.2

Readings

	Rate (A/s)	Thick (kA)	Freq. (Hz)	Life (%)	Source
LTE 1	Not	Used	5970854.79	97.1	Output 1
HTE 1	Not	Used	5925455.80	92.5	Output 2
HTE 2	1.32	0.0677	5911171.23	91.1	Output 3
LTE 2	Not	Used	5970282.11	97.0	Output 4
Sputter	Not	Used	5952114.27	95.2	None

Film	Rate(A/s)	Dev.(%)	Thick(kA)	Power(%)
Cu HTE	1.32	10.3	0.0677	61.4

Figure 24. **Process monitoring software during thermal deposition showing deposition rate verses time**.



Running Time 0:02:28:35

Running Recipe
Cu Dep HTE Src3
(9)
WAITING FOR
HTE2 Heater Temperature
Check Value > 1.20E+3
1132

Xtal3 (HTE2): 0.0 A/s, 0.000 kA
Xtal4 (LTE2): 0.0 A/s, -0.022 kA

Proc. State: Process Stopped
Sigma In Deposit Phase: OK
Sigma Shutter Delay: OK
Velocity Setpoint: 20
Velocity (RPM): 0.0
MKS979 WRG Pressure: 7.60E-7

LTE/HTE Sources

	On/Off	Auto	Temp SP deg C	Auto SP deg C	% SP	RR deg C/Min	P	I	D	Temp deg C	Voltage V	Current A
LTE1 Heater	OFF	OFF	0	404.0	0	10	3	.1	.1	24.5		0.000
HTE1 Heater	OFF	OFF	0	024.9	0	10	3	.1	.1	29.1	0.000	0.001
HTE2 Heater	ON	ON	1200	1190.1	47.47	10	3	.1	.1	1174.5	18.969	10.464
LTE2 Heater	OFF	OFF	0	404.5	0	10	3	.1	.1	26.1		0.106

7.60E-7

Figure 25. **Process monitoring screen showing system status and status of current process step.**

During initial runs with the Octos PVD coating system, several issues were identified. A company representative was sent from the Kurt J. Lesker Company to Oak Ridge to resolve these issues. During this time a programming error was resolved which was not allowing ramping of the power on the Advanced Energy Pinnacle Plus pulsed DC power supply. This issue had previously caused cracking of one of the targets. Also, the gate valve on the sputtering side of the system was not properly closing to operate in throttle mode and not opening and closing consistently. These issues were properly resolved. As we were preparing to operate the system in glove box mode, we discovered problems with the orientation of the gloves for the box such that the glove placement was not such that critical items in the chamber could be reached, and the gloves occluded the view of the chamber window. The Lesker Company agreed to resolve this by refabricating the front panels on the glove box. These panels were installed and functional near the end of the project, making deposition of CdTe possible.

4.1.2 Hamamatsu Photoluminescence System with Integrating Sphere

The Hamamatsu Photoluminescence (PL) system has the capability of measuring the absolute photoluminescence quantum yield from a variety of powder samples. This measurement is done by illuminating a sample with a light source of known wavelength, and then collecting all the emitted photoluminescence from the sample using an integrating sphere. This measurement is critical for understanding many promising nanomaterials for photovoltaics.

The Hamamatsu C9920-03 system is capable of this measurement (spectral range: 400-1100 nm). It consists of an excitation xenon light source, monochromator, and integrating sphere and multichannel CCD spectrometer for sampling the spectral range simultaneously. Since many of the materials that were studied within this project (CdTe and CIGS for solar applications, etc.) have rather small band gaps, it is important that the spectral range extend as far into the infrared as possible. The Hamamatsu PL system is unique in that it is the only instrument on the market that measures absolute quantum efficiency. Other companies sell Fluorimeters (such as the Fluorolog made by Horiba Jobin Yvon), but these instruments measure relative quantum efficiency and require standards to measure absolute quantum yield. While other systems obtain much higher sensitivity using a photomultiplier tube as a detector, the photomultiplier tube is limited to ~850 nm in the infrared. The system is shown below in Figure 26. The top left corner of Figure 26 shows a Xenon lamp, which produces a radiation spectrum that is continuous over the ultraviolet, visible, and infrared regions. Right of lamp is the monochromatic light source (MLS), where the output of light can be easily adjusted for various samples. On top right is the photonic multi-channel analyzer (PMA-12), which is a spectral measuring system that consists of a compact spectrograph, multi-channel photo-detector, and optical fiber probe and control circuit. This improves the spectral response and wavelength characteristic so that measurements can be carried out simple and accurately. A light guide cable connects from it to the MLS; it freely positions the light output. The MLS also houses a shutter, which can be controlled by the PMA-12.

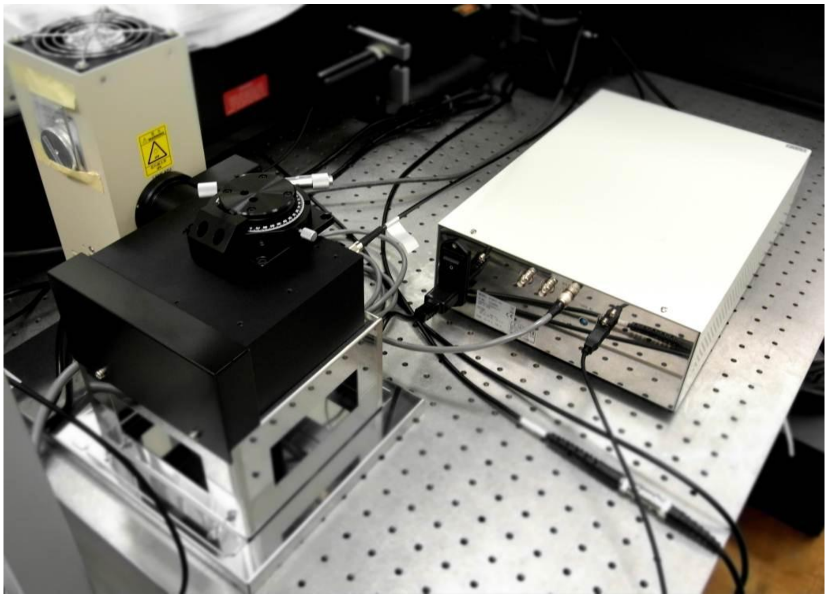


Figure 26. **Hamamatsu Photoluminescence System**

The integrating sphere shown in Figure 27 is a versatile accessory for high precision quantification of the total light radiated in all directions from the lamp. Its hollow cavity is coated for high diffuse reflectivity, and small holes for entrance and exits ports allows for loading of solid samples such as thin films and powders (bottom arm) and liquid samples such as solutions (front arm).

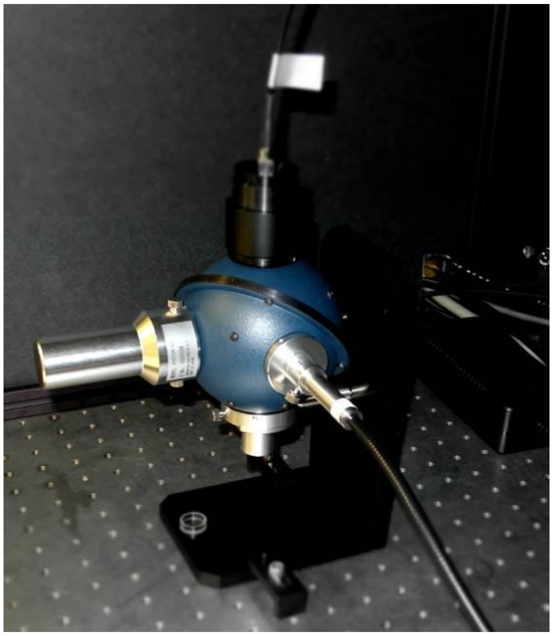


Figure 27. **The integrating sphere for the PL System.**

4.1.3 Deep Level Transient Spectroscopy

Deep Level Transient Spectroscopy (DLTS) is a transient capacitance technique to evaluate defects in semiconductor diodes. The simplest form of DLTS works by first reverse biasing the diode and then superimposing a pulsed voltage onto the reverse biased voltage and observing the transient capacitance of the diode as a function of time. The DLTS spectra are then obtained by recording this data as a function of temperature. From these measurements, it is possible to obtain energy levels, capture cross sections, and concentrations of defects in the material.

While the standard technique works quite will for standard semiconductor materials (Si, GaAs), there are several modifications of the technique that are useful for other non-standard materials. For example, organic diodes (such as solar cells and light emitting diodes) require charge transient spectroscopy (QTS) or current transient spectroscopy (CTS), which are variants of DLTS. Constant capacitance DLTS (CCDLTS) is another example of a DLTS variant that is useful for the study of interface states. Other variations of DLTS include isothermal transient spectroscopy (ITS, useful for samples that cannot tolerate large temperature changes) and photo-induced transient spectroscopy (PITS, where light can be used to create electron-hole pairs for minority carrier injection).

It was determined that it was essential for ORNL to have a proven DLTS instrument with the wide range of capabilities described above in order to understand the fundamental properties of solar cell materials and the impact of defects in the material structure. Therefore, a DLTS system was purchased from SULA Technologies (Ashland, OR). The SULA DLTS instrument has been around for quite a long time, with nearly 200 instruments in the field, but with continuous updates to keep software, etc. compatible with modern computer systems.

The DLTS system was delivered to ORNL on September 20, 2011 and is shown in Figure 28 below.

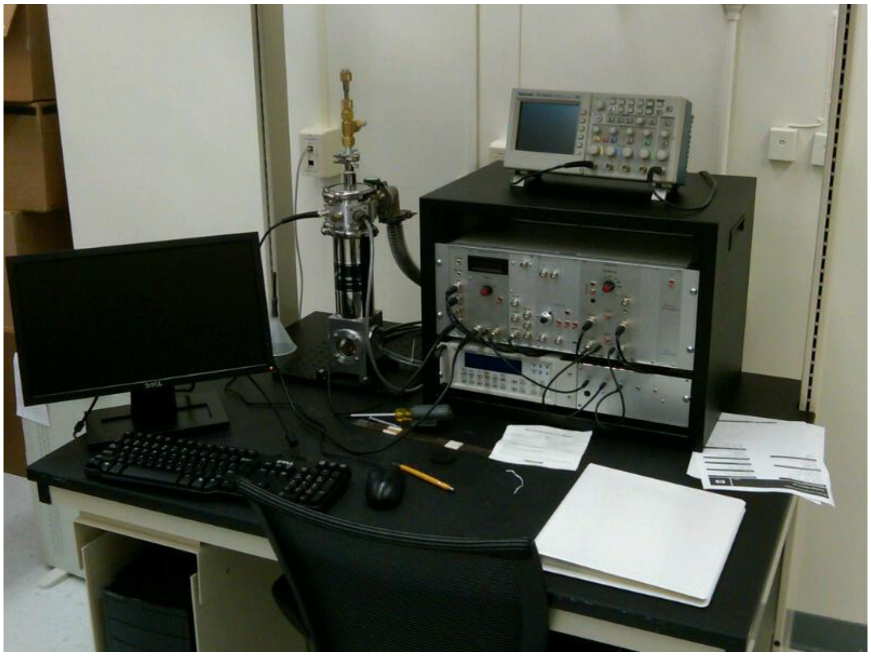


Figure 28. **Deep Level Transient Spectroscopy (DLTS) installed at ORNL**

4.2 FUNDAMENTAL UNDERSTANDING

The foundation for increased performance of thin film solar cells is the fundamental understanding of how these systems work. Currently, this level of knowledge is lacking, especially for the CdTe and CIGS thin film systems. One primary goal of this project was to utilize ORNL's extensive knowledge in material science as well as some of the unique characterization and processing tools at ORNL to address these issues. Several of the fundamental measurements are described below with their potential impact on the solar cell performance.

4.2.1 Light Beam Induced Current Measurements

During this project, ORNL expanded its Light Beam Induced Current (LBIC) system by incorporated two new lasers. This new capability permits LBIC measurements at several wavelengths from 457 nm to 780 nm. Overall, the system utilizes several continuous wave (CW) lasers with different emission lines to be able to illuminate the solar cells with different wavelengths of light. This is particularly important, since different wavelengths of light penetrate different distances into the solar cell, depending primarily on the optical absorption coefficient of the emitter and absorber materials used. The wavelengths available now at ORNL are from an Ar+ laser (6 lines from 457 to 514 nm), a HeNe laser (633 nm) and a diode laser (780 nm).

The laser light is focused onto the sample, and the optical objective determines the resolution. Previous studies have used a short focal length microscope objective, which results in ~2-3 micron resolution. However, this objective is very close to the sample, prohibiting us from examining the sample near the contact point (the objective interferes with the front contact). We have also incorporated a simple lens into the system, which gives us ~10-20 micron resolution, but is sufficiently above the sample that the entire sample can be scanned.

Another issue, particularly for thin film solar cells, is that CW laser light can fill up traps in the solar cell, altering the final resulting quantum efficiency. To address that, we have incorporated a chopper into the light beam so that the light illumination is alternately turned on and off. Of course, this requires phase sensitive detection, so we have incorporated two lock-in amplifiers into the system (one for the sample and one for the reference diode). This has at least two advantages: 1) Lock-in detection is inherently less noise-sensitive than is CW detection. 2) We can now vary the chopping frequency during the LBIC experiment.

ORNL obtained some test polycrystalline silicon solar cells from Ajeet Rohatgi at Georgia Tech to test out the new LBIC system. We also collaborated with John Budai of ORNL to perform microbeam x-ray measurements on the same samples that were used for the LBIC measurements. In this study, high-resolution x-ray Laue patterns and high-resolution light beam induced current (LBIC) measurements are combined to study two multicrystalline solar cells made from the Heat Exchanger Method (HEM) and the ribbon technology. The LBIC measurements were made at 4 different wavelengths (488, 633, 780, and 980 nm), resulting in penetration depths ranging from <1 mm to >100 mm. There is a strong correlation between the x-ray and LBIC measurements (Figure 29), showing that some twins and grain boundaries are effective in the reduction of local quantum efficiency, while others are benign. These measurements were reported on a poster presented at the 35th photovoltaics specialists conference (PVSC 35) [Ref: G. E. Jellison, J. D. Budai, C. J. C. Bennett, J. Z. Tischler, C. E. Duty, V. Yelundur and A. Rohatgi, "High-Resolution X-Ray And Light Beam Induced Current (LBIC) Measurements Of Multicrystalline Silicon Solar Cells," 35th Photovoltaics Specialist Conference, Honolulu, Hawaii (June 2010)].

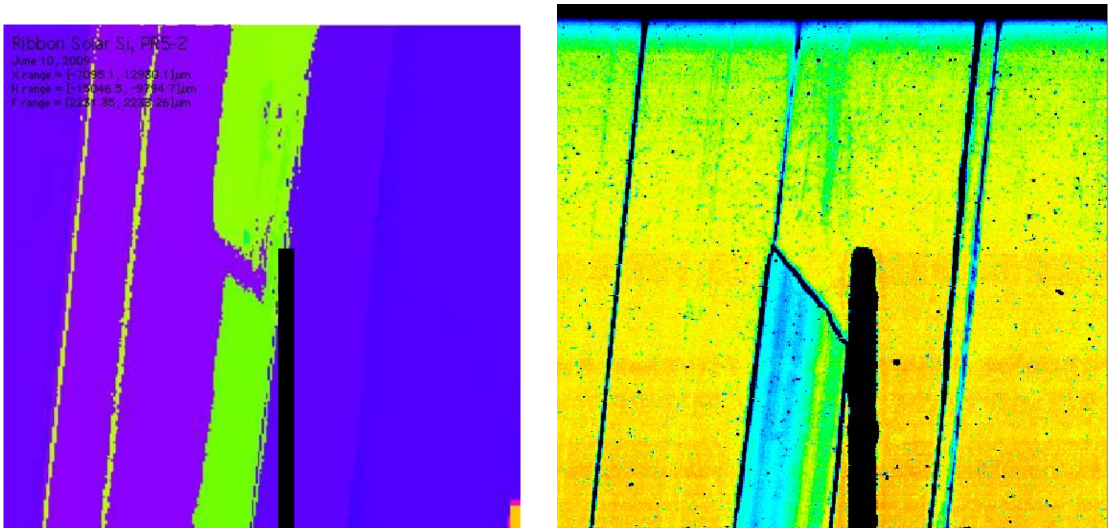
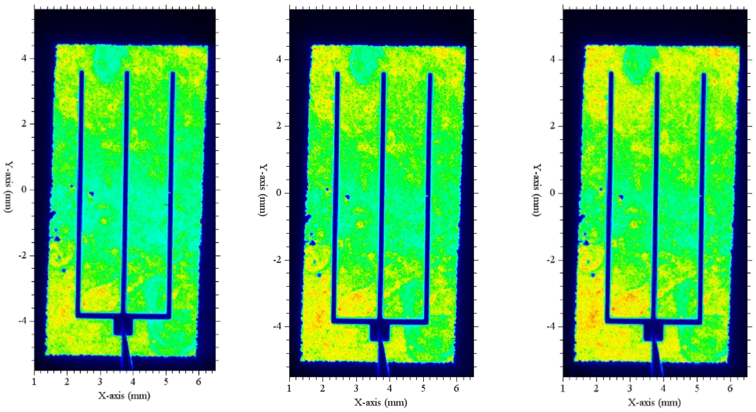


Figure 29. **X-ray (left) and 633 nm LBIC (right) measurements taken on a 2X2 mm area. The x-ray measurements were taken with a 8 mm step, while the LBIC used a 5 mm step.**

Another application of this high-resolution LBIC system ORNL explored was to examine thin film solar cells with a CdS emitter. CdS is a wider band gap material than either CdTe or CIGS (copper indium gallium selenide). For these measurements, we used CIGS cells obtained from Prof. T. Anderson at the University of Florida.

Spectral quantum efficiency (QE) measurements (not shown) show that there is a dramatic difference between the observed quantum efficiency at 457 nm (~0.25) and 633 nm (~0.65) for these CIGS solar cells. The 457 nm light (=2.71 nm) is above the band gap of CdS, while the 633 nm light (=1.96 eV) is below the band gap of CdS. Consequently, the 457 nm light is mostly absorbed in the CdS layer, while the 633 nm light is absorbed mostly in the absorber layer (CIGS).

Several LBIC scans are shown in Figure 30 using 633 nm illumination, taken using different chopping frequencies. There appears to be some variation in the observed quantum efficiency maps, with faster chopping frequencies giving slightly higher quantum efficiencies than slower chopping frequencies. Figure 31 shows similar data taken using 457 nm illumination. While the general LBIC maps appear to be similar to the maps taken at 633, the features are sharper. Furthermore, there is considerably more variation with chopping frequency.



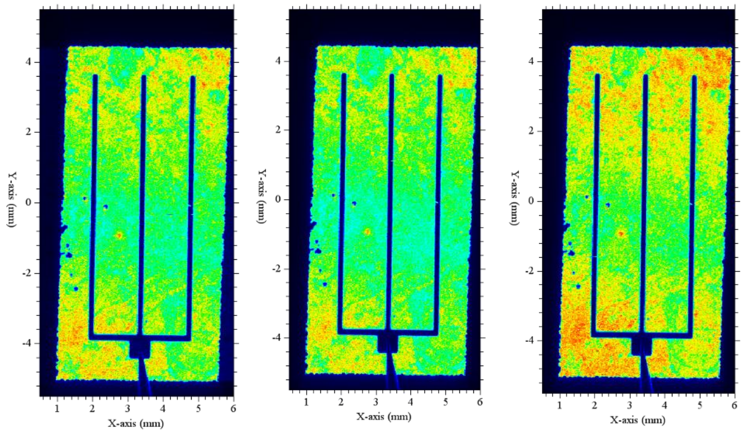
314 Hz

739 Hz

1506 Hz

Illumination wavelength: 633 nm
Pixel Size: 20 microns

Figure 30. **LBIC measurements of CdS/CIGS solar cell illuminated with 633 nm light**. Data taken using different chopping frequencies, given below the individual plots. The quantum efficiency scale is 0.80 (red) to 0.00 (black).



323 Hz

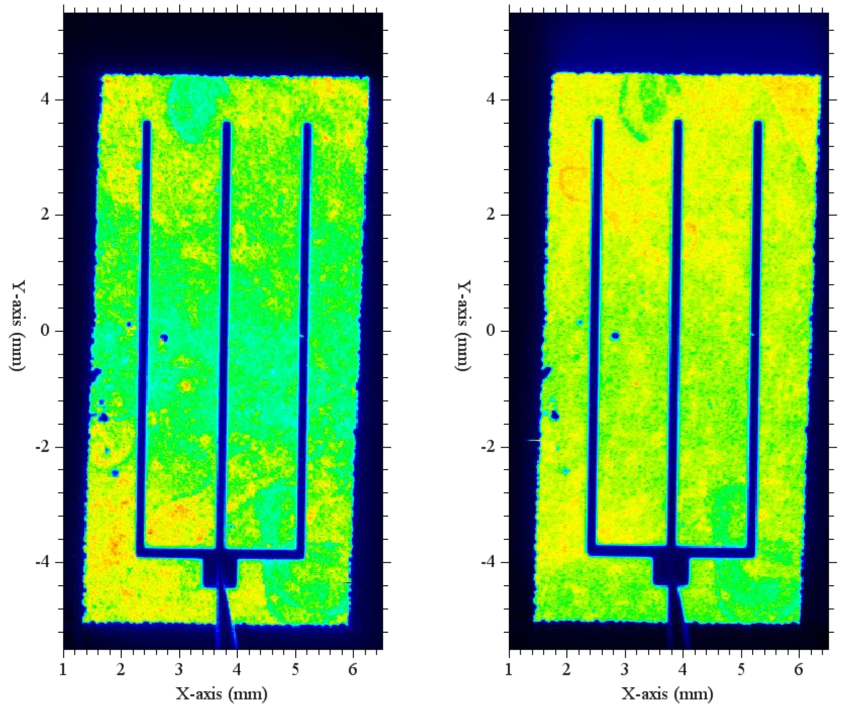
729 Hz

1987 Hz

Illumination wavelength: 457 nm
Pixel size: 20 microns

Figure 31. LBIC measurements of CdS/CIGS solar cell illuminated with 457 nm light. Data taken using different chopping frequencies, given below the individual plots. The quantum efficiency scale is 0.40 (red) to 0.00 (black).

One possibility is that the illumination with 457 light is altering the quantum efficiency of the cell. Figure 32 shows LBIC maps taken before and after the 457 nm LBIC experiments. After the 457 nm experiments, the LBIC map is much more uniform, where many of the lower QE regions have increased their QE significantly.



First

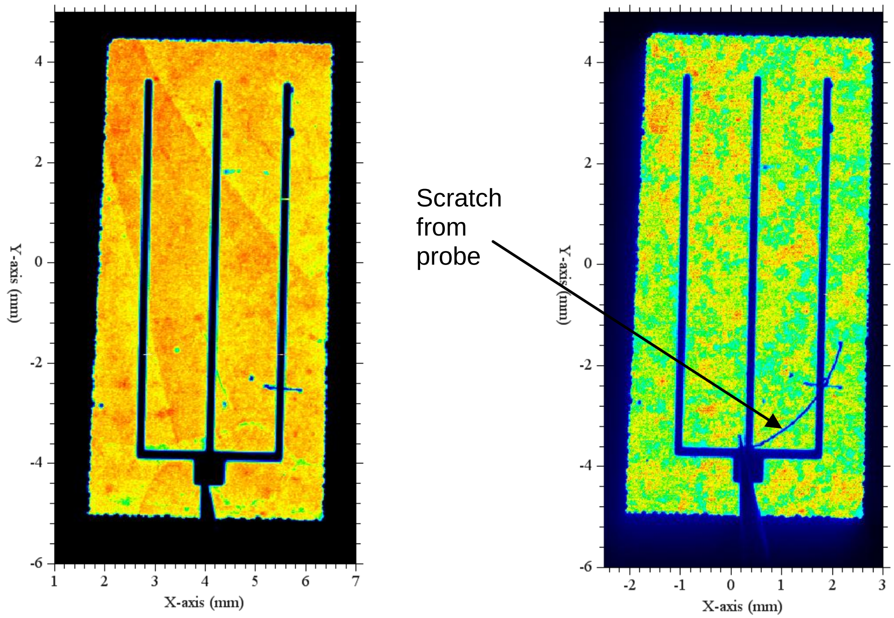
Second 3/15/2011

Illumination wavelength: 633 nm

Chopping frequency: ~750 Hz
Pixel size: 20 microns

Figure 32. LBIC measurements from the same cell as in Figs 40 and 41, but taken at different times. The 457 measurements had been taken between the two measurements shown, so the sample has been illuminated significantly with 457 light.

Figures 33 and 34 show similar data, but on another cell. In particular, Figure 34 shows higher resolution scans (5 micron/pixel) for both 633 nm light and 457 nm light. Clearly, there is considerably more variation in QE for the 457 nm experiment than for the 633 nm experiment. In particular, the 457 nm experiment shows several light blue regions indicating a QE~0.20 (the red regions indicate a QE of greater than 0.32). This suggests that the emitter in the light blue regions contribute little if any current to the device at this wavelength, and all the current comes from light that penetrates to the absorber region.

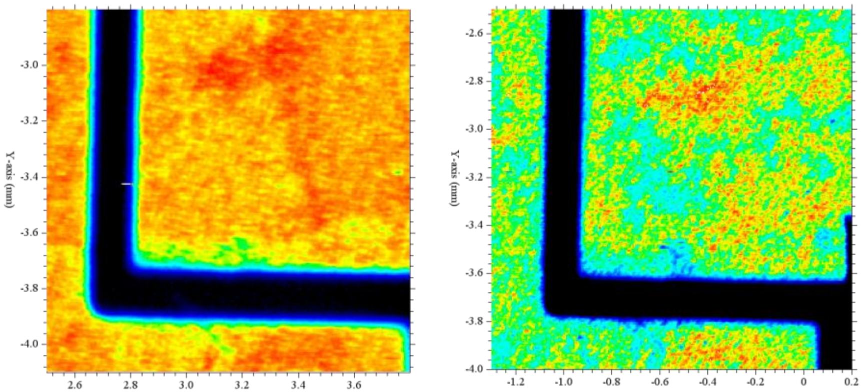


633 nm QE = 0.05-0.90
Ave QE = 0.65

457 nm QE = 0.00-0.40
Ave QE = 0.25

Pixel size: 20 micron
Chop frequency: 800 Hz.

Figure 33. **Comparison of 633 nm LBIC and 457 LBIC of a CdS/CIGS solar cell (a different cell from the one used in Figs 40-41).** The scratch indicated in the figure was inadvertently done after the 633 measurement but before the 457 measurement.



633 nm QE = 0.05-0.90
(ave QE = 0.65)

457 nm QE = 0.05-0.40

(ave QE = 0.25)

Pixel Size: 5 micron
Chop frequency: 800 Hz.

Figure 34. **Higher resolution LBIC measurements taken at 633 and 457 nm using the CdS/CIGS cell used in Figure 33.**

Clearly, these results are quite preliminary, and it suggests that much more work needs to be done. In particular, future research efforts may explore the possibility that illumination with UV light actually improves the collected current from solar cells. Another important issue concerns the current collecting capabilities of the emitter region of the solar cell. The 457 nm LBIC gives us an emitter-specific technique so that we can identify regions where the emitter is contributing to the cell current and regions where it is not. It is anticipated that this tool will help us improve emitters in thin film solar cells.

4.2.2 Photoluminescence System

The photoluminescence system uses a pulsed nitrogen laser (337 nm) to excite the photoluminescence and the emitted light is collected into a monochromator and detected using a photomultiplier tube with a detectivity ranging from 200-850 nm (6.2-1.46 eV). While this system works very well with materials that have a band gap of 2-3 eV, it is not useful for smaller band gap materials. As a result, we have incorporated a HeNe (633 nm) illumination source and an infrared thermoelectrically cooled Ge detector (800-1700 nm, or 1.55-0.73 eV). To improve signal-to noise, we have chopped the incoming laser beam and used lock-in detection. We also calibrated the photoluminescence system using a NIST-traceable light source. While we still cannot measure the absolute quantum efficiency with this system (which would require an integrating sphere), we can compare the quantum efficiencies at different wavelengths. This capability will be useful in characterizing materials utilized for solid-state lighting applications, as well as many other applications, such as photovoltaics.

4.2.3 Plasma Arc Lamp Characterization

One of the unique processing capabilities for thin film solar cells at ORNL is the Pulse Thermal Processing (PTP) facility which uses two high intensity plasma arc lamps. These lamps emit a broad spectrum of radiant energy from a standing DC electric arc in a contained argon plasma. The radiant energy is reflected and directed toward a thin film material. The PTP system can achieve intensities of up to 20 kW/cm^2 over areas of several hundred square centimeters, raising the temperature of thin films at a rate of up to 600,000°C/s.

The spectrum of the radiant energy is considered to extend from about 200 nm to roughly 1.4 μm with strong argon lines in the infrared region. The spectrum of the lamp shown below was provided by the lamp manufacturer (Figure 35). The spectrums of ORNL's lamps have not been previously measured and it is anticipated that the spectrum will shift as a function of power intensity as well as processing time. The wavelength-dependent distribution of radiant energy from the argon lamp will have a strong impact on the thermal distribution of the thin film material being processed.

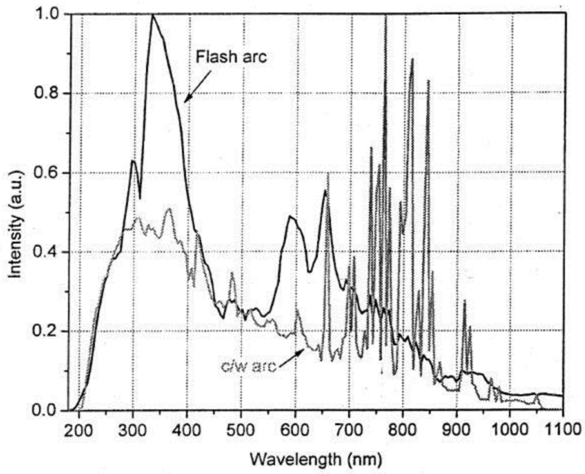


Figure 35. Spectral distribution of plasma arc lamp (provided by manufacturer).

Since the intensity of the plasma arc lamp is so high, it is difficult to directly measure the spectrum of the radiant energy without damaging the sensor. Therefore, an apparatus was needed to greatly reduce the lamp output intensity to below the damage threshold level of the visible range and near-infrared spectrophotometers involved without altering the source spectrum itself. A prototype was developed, tested, and refined for this purpose. It incorporates a series of reflections from quartz materials (each reflect only ~2% of the radiant energy) to provide constant-spectrum intensity reduction together with aperture controls to achieve this unique purpose (Figure 36). Sets of trial spectrum measurements were taken using several different optical fibers and across a range of lamp amperages. These data sets yielded slightly different results and the optimum fiber was identified. The infrared spectrophotometer reading levels were found to be negligible, so wavelengths above 900 nanometers can be neglected. Spectrum measurements were taken with a manual trigger operated during a 2 to 3 second pulse. Figure 37 shows the 700 kW plasma arc lamp spectrum at 600 amps.

Figure 36. **Intensity reduction apparatus for measuring spectrum of the plasma arc lamp.**

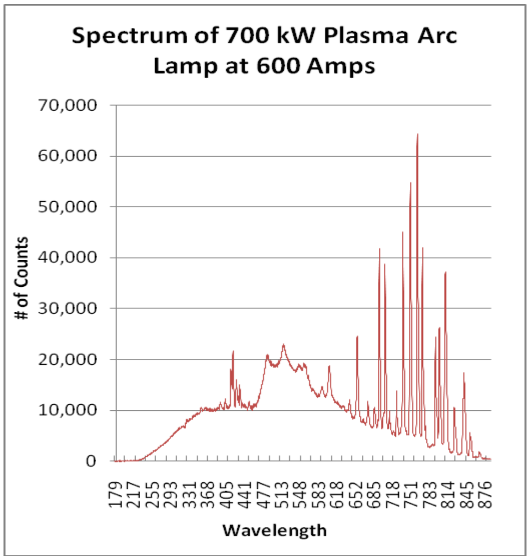


Figure 37. **Measured spectrum of 700 kW plasma arc lamp at 600 amps.**

Intensity measurements were also made on the 700 kW plasma arc lamp using two types of thermopiles and data acquisition systems. Using the available data, the comparative chart in Figure 38 was created to better correlate amperages on the Vortek lamps, which yield the same heat flux.

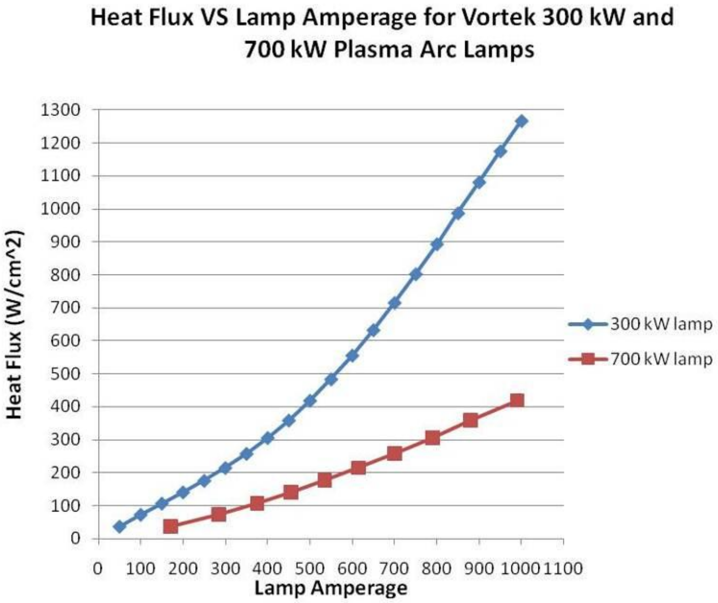


Figure 38. **Heat flux measurements versus amperage for ORNL's two plasma arc lamps.**

To enable better design of experiments, an analysis was performed on the PulseForge 3300 to further reveal its processing space capabilities of relative radiant exposure and relative peak power (or relative heat flux) as a function of processing time and the corresponding maximum voltage. The system was analyzed given the use of 16mm diameter lamp tubes, the original software that came with the control computer, and parameters of 1 pulse, repeat frequency of 1 Hz, micropulse setting of 1, and a duty cycle of 1. The voltage was scanned manually in increments of 10. The maximum voltage was determined to be 10 volts below which the software voltage setting yields the caution yellow color for that time increment. Note that relative radiant exposure and relative peak power vary with sample emissivity, offset distance, and other factors and are provided for relative reference only. The default sample emissivity of the original software used in this analysis is 0.9. These charts are shown in figures 39 and 40 below.

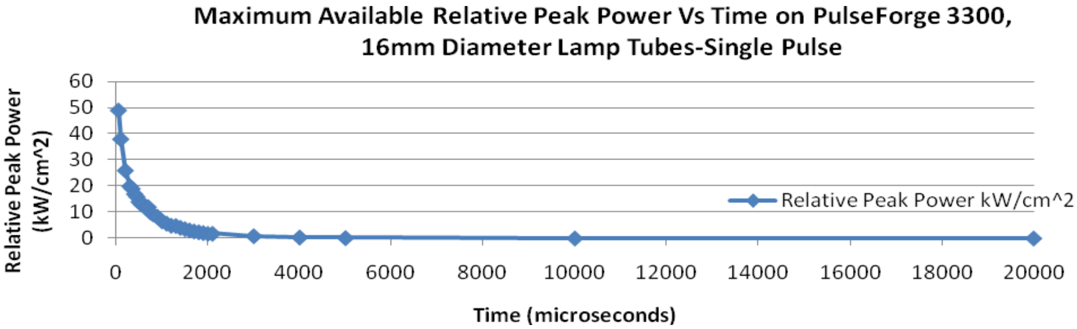


Figure 39. **Maximum peak power versus time on PulseForge 3300.**

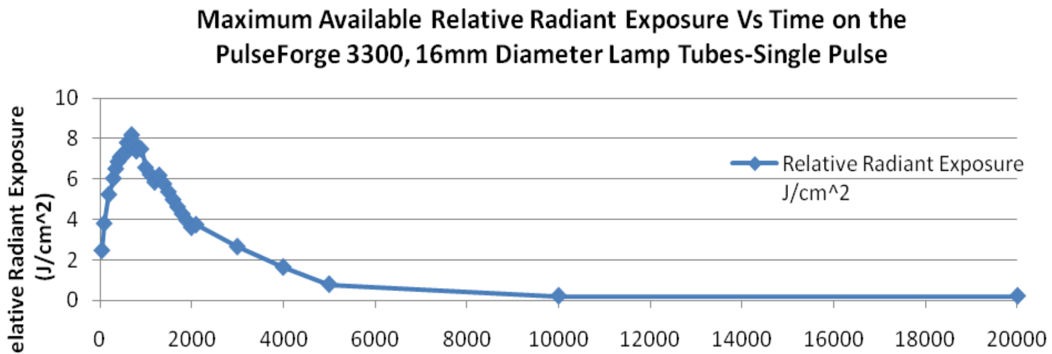


Figure 40. Maximum radiant exposure versus time on the PulseForge 3300.

4.3 MANUFACTURING TECHNIQUES

One of the goals of this project was to apply the fundamental knowledge of solar cell technology toward the manufacture of thin film solar cells with improved performance and reduced costs. Investigations focused on achieving high performance while using large-scale manufacturing techniques such as screen printing, roll-to-roll fabrication, etc.

4.3.1 CIGS Nanoparticles

During the past year, ORNL has explored the use of bacterially-synthesized nanoparticles, called NanoFermentation, in the synthesis of CIGS nanoparticles for solar applications. In this project, nanoparticles were made via a bio-chemical synthesis route and we have demonstrated control of stoichiometry at the particle level. This project involved a closer look at CIGS nanoparticles via Energy-Dispersive X-ray Spectroscopy (EDS) shows elemental mapping of the constituents, consistent with CIGS thin film. This is the first time to our knowledge that a CIGS nanoparticle system has achieved the same stoichiometry as the final thin film system. Scanning Tunneling Electron Microscopy (STEM) shows a porous network with agglomeration of various particles (Figure 41).

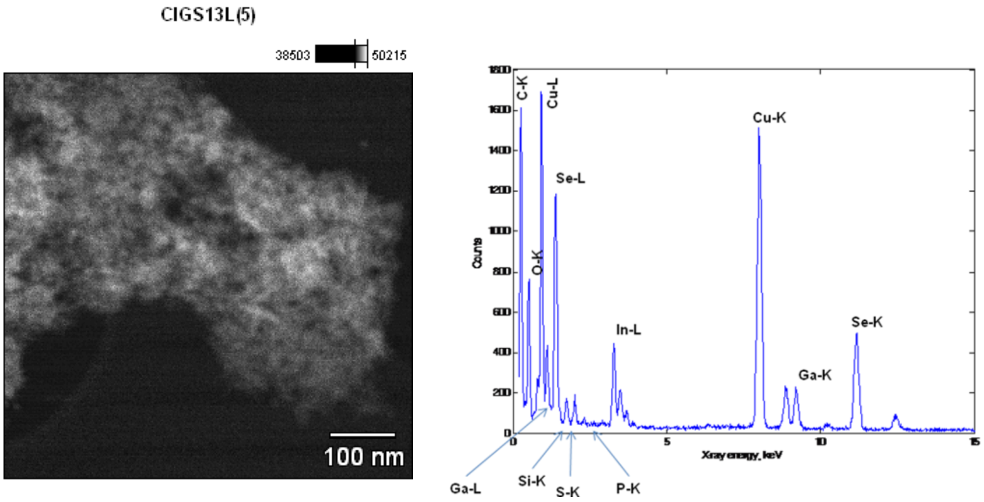
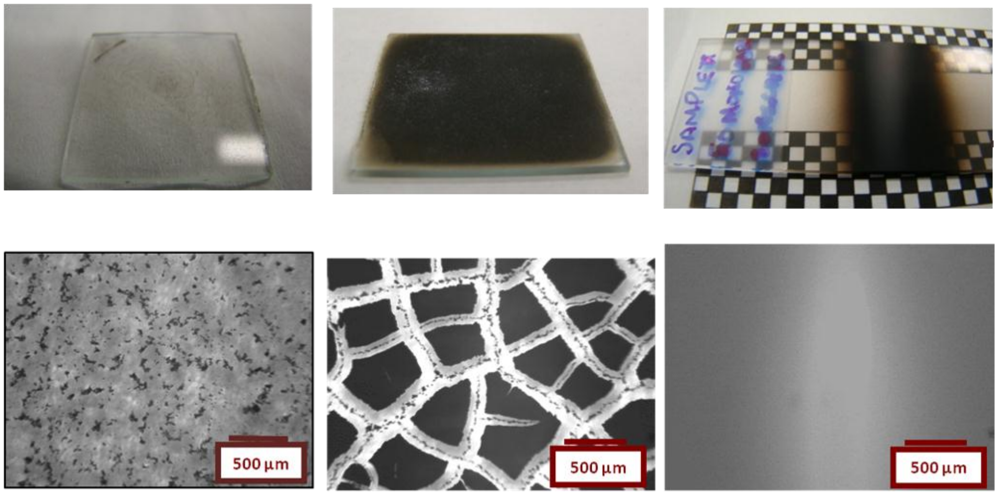


Figure 41. STEM image (left) and EDS map (right) of CIGS nanoparticles.

ORNL also investigated functionalization of the CIGS nanoparticles. Suspension and surface passivation efforts attempted to de-aggregate the CIGS solutions for suitable deposition. Shown in Figure 42 are particle suspension experiments of solution mixtures: CIGS/Isopropanol/Hexane Toluene (1), CIGS/ Thioglycolic Acid (2), and CIGS/Isopropanol/Pyridine (3). In addition, the concentrations of the nanoparticle were increased for purposes of increasing the density of deposited films.

Figure 42. **Solution mixtures of CIGS nanoparticles for improved suspension.**

Also, different deposition techniques were pursued for deposition of CIGS nanoparticles, in particular: sono-spray deposition, spin coating, doctor blade method, and drop cast method. We investigated effective non-vacuum deposition techniques for CIGS nanoparticles that are dispersed in organic solvents and vary from 10-20nm in diameter. The particles were deposited via drop casting, spin coating, and sono-spray deposition methods onto various substrates including Moly/SLG, fluorine doped tin oxide - soda lime glass (FTO/SLG, and Moly/Quartz (see Figure 54). The thickness of the thin films ranges from 0.5 to 1 micron. The top row in Figure 43 shows digital images of CIGS nanoparticles deposited via different deposition techniques. Upon closer examination of the corresponding optical microscope images (bottom row of Figure 54), the general morphology of the films deposited via spin coating and drop casting show discontinuous film platelets (black) with many areas of exposed substrate (gray and white areas) on a sub-millimeter scale. Part of this discontinuity is due to aggregation of the nanoparticles on a macro scale. With sono-spray deposition, the film looks very continuous and mostly uniform on a sub-millimeter scale. In the top right corner image, the lighter area in the middle of the film is from reflection of the organic solvent, which is consistent with the digital image below it. Through sono-spray deposition technique, further work is being done to look into micron level aggregation in these films.



Spin Coating **Drop Casting** **Sono-Deposition**

Figure 43. **Top row: digital images of CIGS films acquired via different deposition techniques: spin coating, drop casting, and sono-spray deposition.** Bottom row: microscope images showing the morphology of the films over a 2.5mm square area.

4.3.2 CdS Nanoparticles

In addition to the work with CIGS nanoparticles, ORNL also explored the use of CdS nanoparticles made by NanoFermentation for use in the emitter layer. Many different thin film deposition techniques were attempted for CdS deposition, as listed in Table 2, using aqueous solutions containing CdS nanoparticles . The spin coating and dip coating methods did not result in any coating on glass or silicon substrates. The drop casting was tried on top of a hot plate at ~75°C. The drop casting technique was effective in depositing a thin film with good adhesion characteristics. However, the film density still needs to be significantly improved for device applications. The spray coating and the chemical bath deposition techniques provided the best coating among the various approaches used in the present study.

Table 2. Various Thin Film Techniques Investigated for CdS Deposition.

Coating Method	Coating Quality	Comments
Spin coating	Poor adhesion	Current aqueous chemistry requires modification
Dip coating	Poor adhesion	
Drop casting	Improved coating but still not dense	
Spray coating	Significantly improved film quality	Film density needs to be improved for reliable device development
Chemical Bath Deposition (Reference sample)	Standard process for CdS deposition for PV applications	

The CdS films were spray-coated on to various substrates by Sono-Tek Exacta-Coat ultrasonic spraying system at the Center for Nanophase Material Science (CNMS). Figure 44 shows a schematic of the spray-coating system. Prior to deposition, all substrates were sonicated in acetone, methanol, and ethanol for 30s each. Initially, the sono-spray was attempted on microscope slides and the effects of temperature, speed, and number of passes on the film growth were investigated. The films were deposited at a speed of 20 mm/s and a nozzle height of 43 mm. The stage temperature was maintained at 70 °C. The deposited films had a rough surface of varying thickness. The four passes across the substrate resulted in a film thickness of about 90 nm.

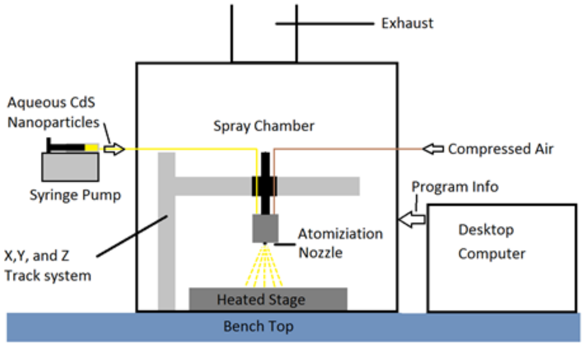


Figure 44. **A schematic of the ultrasonic spraying system.**

Thin film CdS was also deposited by Chemical Bath Deposition (CBD). The CBD of the films was carried out in a solution containing 436mL of de-ionized (DI) water, 60 mL of 0.44 g $CdCl_2$ dissolved in DI water, 20 mL of 1.28 g NH_4Cl dissolved in DI water, 60 mL of 1.86 g Thiourea dissolved in DI water, and 24mL of 30 wt. % NH_4OH. A schematic of the apparatus is shown in Figure 45. Substrates were taped to microscope slides to make them easier to get in and out of the bath. After deposition, samples were removed from slides and cleaned with DI water and then wiped with cotton swab to remove loose particles. It was possible to achieve a thickness of about 90 nm after a deposition time of 4 minutes.

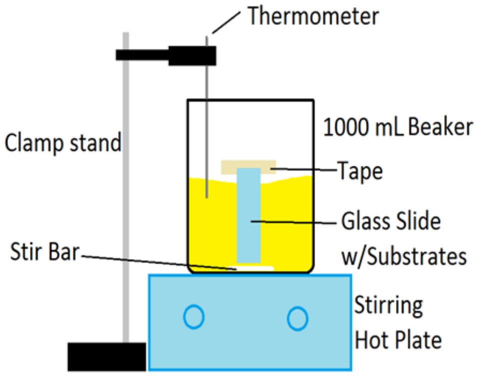


Figure 45. A schematic of the CBD setup.

CdS thin films of both deposition techniques were characterized in terms of the structural, optical, and electrical conductivity characteristics. The structure of the films was analyzed by x-ray diffraction, Raman, and SEM measurements. The optical properties were analyzed from UV-VIS-IR transmission and spectroscopic ellipsometry data. The electrical measurements were conducted on films deposited on FTO coated glass slides. The top Al contacts were deposited by sputtering technique to form metal-film-metal capacitors.

Figure 46 shows the XRD patterns of the CdS thin films deposited by CBD and ultrasonic spray techniques. The films exhibited a well-defined crystalline phase. The XRD pattern indicated the formation of a cubic CdS phase.

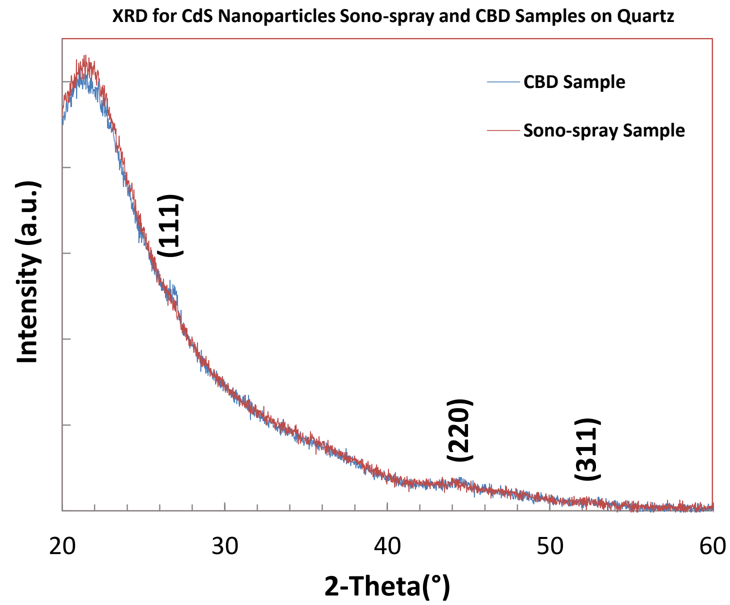
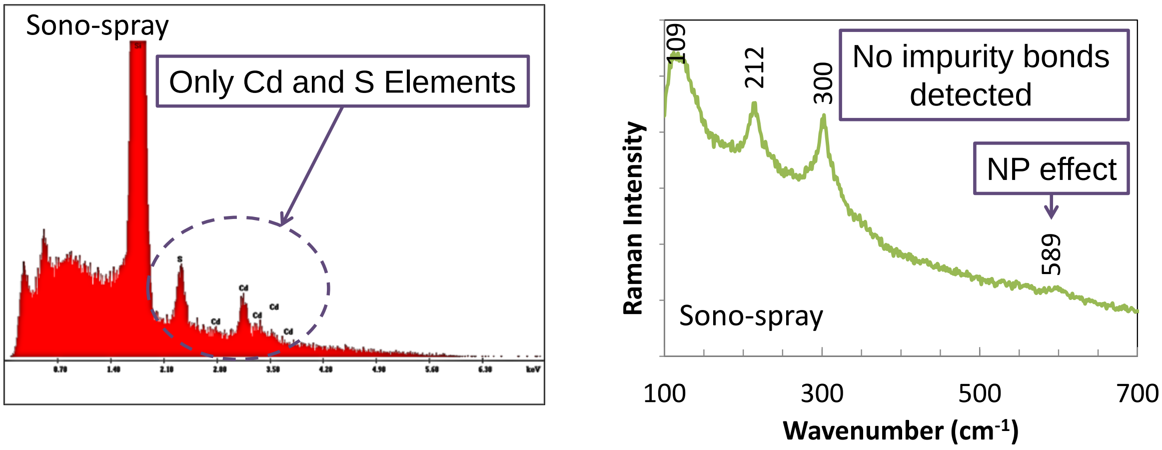


Figure 46. X-ray diffraction patterns of CdS thin films deposited by CBD and ultrasonic spray-coating techniques.

The composition of the films and the bond-structure were analyzed by energy dispersive x-ray spectroscopy (EDAX) and Raman spectroscopy techniques as shown in Figure 47. The EDAX spectra did not show any impurity elements in the films. The Raman spectra also did not show any impurity related bonds in the films. A small signal at around 589 cm^{-1} was observed in the Raman spectra; which clearly indicates the nano-particle effect on the film microstructure.



(a) (b)

Figure 47. The composition of CdS thin films as analyzed by (1) EDAX and (b) Raman spectroscopy techniques.

Figure 48 shows the SEM micrographs of CdS thin films deposited by CBD and ultrasonic spray techniques. The CBD deposited films had a smooth surface morphology. The spray-coated films indicated film growth by particle condensation.

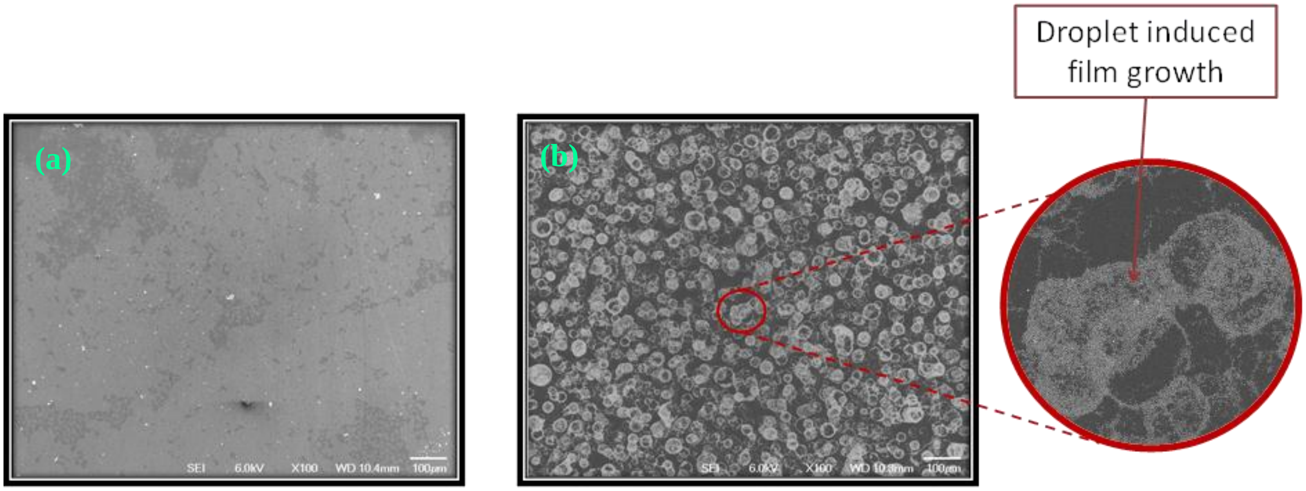


Figure 48. SEM micrographs of CdS thin films deposited by (a) CBD and (b) ultrasonic spray techniques.

The optical bandgap control is critical for PV applications. The optical transmission measurements were conducted to evaluate the optical bandgap of CdS thin films. The value of absorption coefficient αhν as a function of photon energy hν was calculated from the optical transmission characteristics. Then a $(\alpha h\nu)^2$ vs. hν plot was used to calculate the optical bandgap as shown in Figure 49. The ultrasonic spray deposited CdS films showed a wider optical bandgap of about 2.36 eV as compared to a value of 2.28 eV measured for the reference CBD thin films; which is promising for PV applications as a wider optical bandgap of the window layer would enable an increased absorption in the absorber layer.

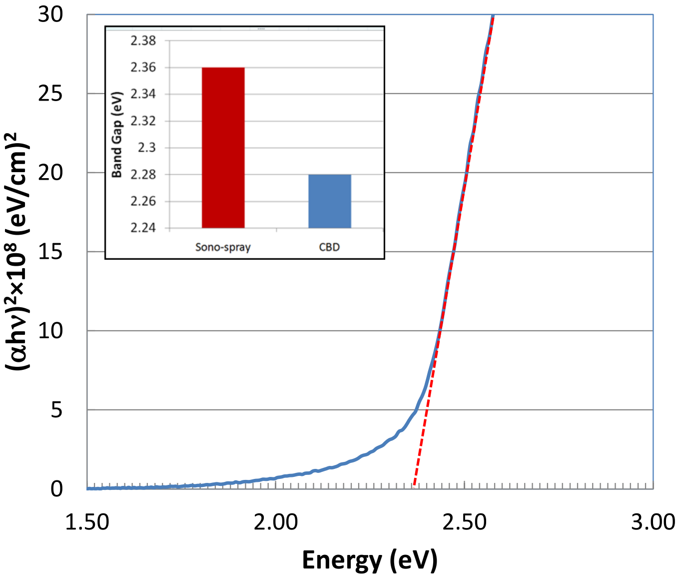


Figure 49. A $(\alpha h\nu)^2$ vs. hν plot to estimate the optical bandgap of CdS thin films. The inset shows the optical bandgap dependence on the deposition method.

The electrical conductivity of CdS thin films is plotted in Figure 50. The electrical measurements were conducted on films in metal-film-metal capacitor configuration. The electrical conductivity was calculated from the I-V characteristics. Both the CBD and ultrasonic spray deposited films showed similar conductivity of the order of 10^{-5} S/cm. The observed conductivity values match well with the peak values reported in literature.[∗]

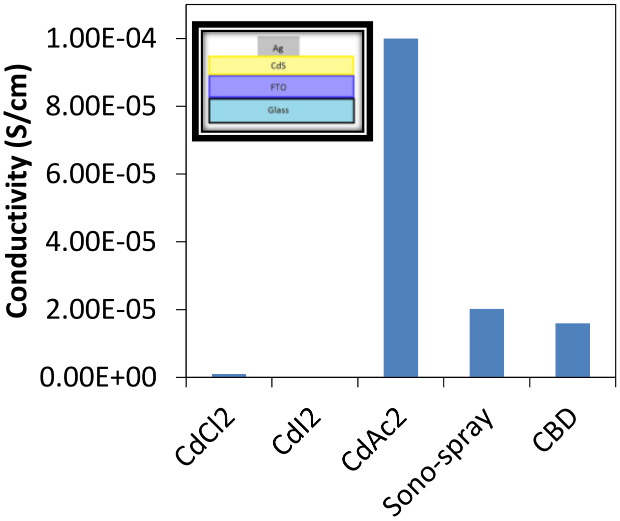


Figure 50. **The electrical conductivity of CdS thin films deposited by various methods.**

4.3.3 CdTe Solar Cell Fabrication

Deposition of thin film CdTe solar cells were explored under this project in collaboration with General Atomics and Strategic Analysis. Devices were successfully deposited onto six 4 inch Kapton discs (see Figure 51 below). Five of the discs were completed with back contacts. The I-V responses of the devices were measured at General Atomics, resulting in the best results to date prior to Pulse Thermal Processing treatment. Short circuit current (I_{SC}) exceeded 20 mA/cm^2 for the devices while open circuit voltage was as high as 200 mV (Figure 52). Furthermore, the devices demonstrated a diode response as opposed to a simple resistor – indicating the usefulness of the material for photovoltaic applications. Two of the discs were taken to NREL for back contact deposition using ZnTe doped with 2% or 5% Cu and Ti. All devices exhibited I-V curves, meaning that none of the devices were shorted (due to pin-hole defects).

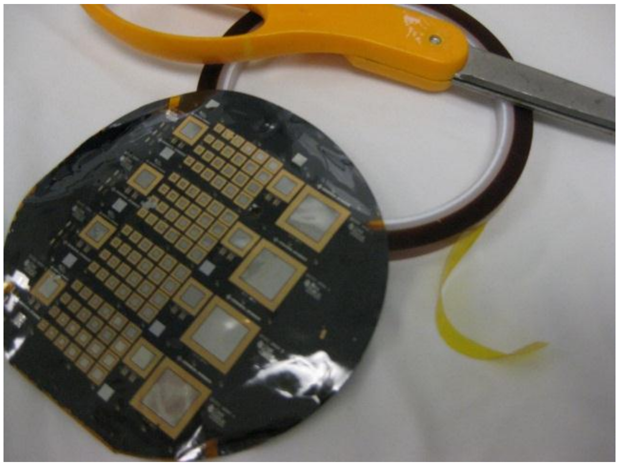


Figure 51. **CdTe thin film solar device array on Kapton disc.**

[∗] H. Khallaf *et al*., “Characterization of CdS thin films grown by chemical bath deposition using four different cadmium sources,” Thin Solid Films 516, 7306 (2008).

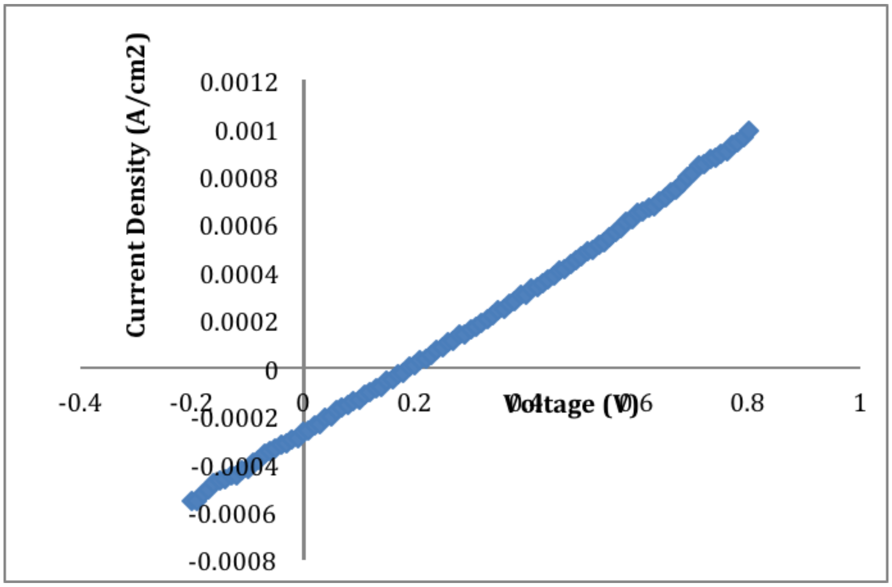
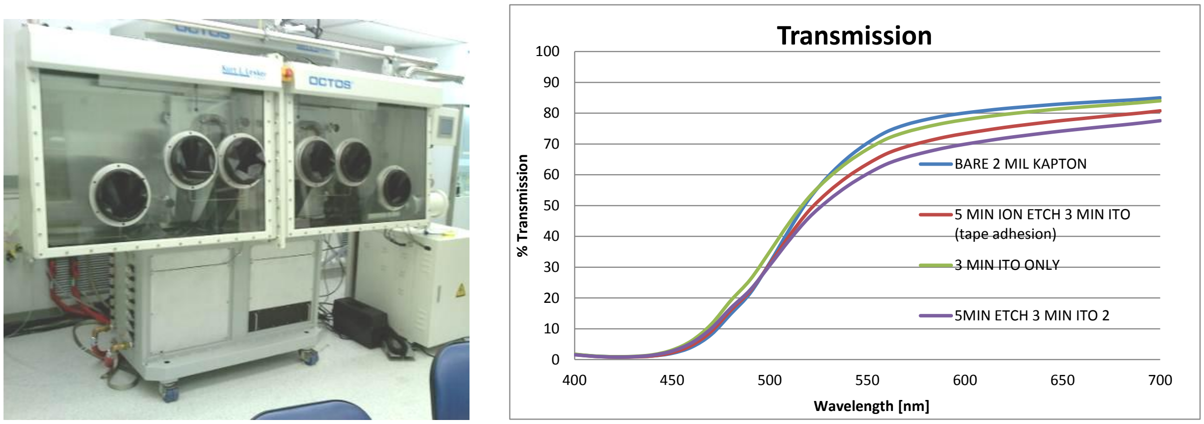


Figure 52. I-V curve trace of as-deposited CdTe thin film solar device (prior to PTP).

The deposition process was optimized for depositing the transparent conducting electrode on the polymer surface. Deposition on polymers is quite challenging due to adhesion and delamination issues. To provide proper adhesion Kapton films were sputter cleaned and textured using the 3 cm ion source prior to ITO deposition. Argon gas flow and pressure (4 x 10^{-4} Torr) for proper texturing were optimized and a computer controlled procedure was developed for this critical step. Samples passed the tape adhesion testing and transmission results are shown in Figure 53 below. ITO process conditions that resulted in a minimum resistivity (340 Ohm/square) and transmission loss of 10% compared to bare Kapton for a 150 nm thick ITO film as shown in Figure 53b, was a chamber pressure of 5 mTorr, Ar flow of 20 sccm, O_2 flow of 0.8 sccm, a deposition power of 150W, operating in pulsed DC mode (0.9µsec, 150Hz) for a deposition time of 1900 seconds.



(a) (b)

Figure 53. (a) Image of glove box system with reconfigured front panels for improved access to chamber internal components and view of chamber windows. (b) Transmission curves for bare Kapton film, 5 min ion etched Kapton followed by 3 min ITO deposition, and ITO deposition without ion etch process.

5. BENEFITS ASSESSMENT

Several of the sub-tasks pursued under this project have the potential to reap significant economic, environmental, and technical benefits. Specifically, the four industrial projects are the nearest to commercialization and leverage the fundamental research conducted elsewhere in this project. A brief account of the benefits expected from each of the industrial projects is summarized below:

5.1 GLOBAL SOLAR ENERGY

The total market for flexible thin-film solar photovoltaic devices is expected to exceed $ 10 billion per year by 2015 and $ 100 billion in sales by 2020. The technological development and successful commercialization of flexible CIGS thin film solar cells demonstrates the promise and practicality of PV and they offer fascinating new opportunities for cheaper, more efficient, longer-lasting systems. Higher PV efficiency thus directly impacts the overall electricity cost, because higher-efficiency cells will produce more electrical energy per unit of cell area over the cell lifetime. The key for the PV industry is to reduce the production costs to below $ 1/ Watt ($1/Wp) to compete with other technologies in power generation. At present, modules based on single crystal and multicrystalline Si cost more than $ 3-4/W because the manufacturing cost is about $2.20/W. Reducing the cost/watt of delivered electricity by a factor 5-10 will make solar cells competitive with fossil and nuclear electricity. This project potentially benefits the average consumer or the public in various ways including job creation in the private sector, energy savings, reduce concerns about global warming, increasing American company's competitive edge in producing clean renewable energy, and environmental benefits. The target of < $1/W can be reached using thin-film fabrication technologies developed at ORNL/Global Solar Energy. This will create interest in residential and commercial building markets, as well as utility scale PV.

5.2 FERRO CORPORATION

The growth of the solar cell industry has been driven by crystalline silicon based solar cell modules. These modules have a proven track record of reliability and energy efficiency management performance for over two decades. As solar energy continues to be an attractive global energy source, intense technological innovation continues in the crystalline silicon segment with a clear focus on achieving grid parity. Ferro has been instrumental in enabling efficiency gains over the past 30 years. Ferro is the industry leader in reliable metallization through innovative front and back contact technology to the highly demanding, dynamic crystalline segment. With over two decades of industry leadership with metal contacts, Ferro addresses the current and future needs of the technology road map being driven by the industry to achieve rapid grid parity. While the thin film segment is touted to be the front runner in the coming years and into the next decade, the crystalline segment continues to have an entrenched position when it comes to large solar farms and grid supply. It is widely believed the crystalline segment will be the majority player for large gigawatt scale installations. To ensure the industry can sustain this challenge when it comes to delivering reliable electrical connectivity, Ferro is pursuing novel and innovative contact solutions.

Ferro believes the expedited proof of concept demonstration of this project could lead to a sustainable competitive advantage to the crystalline silicon solar segment and will potentially impact the metallization of thin film non crystalline cell structures. Furthermore, the project bolsters the United States crystalline silicon solar cell supply chain and will help create a sustainable competitive advantage for U.S. crystalline silicon solar cell manufacturers.

This project has focused on crystalline silicon based solar cell modules that can create high quality, sustainable jobs and revenue benefits in the United States. Ferro estimates the thick film paste segment to grow from $329 million in 2010 to about $450 million by 2015. The Ferro share of the market is projected to grow from about $120 million to a robust $200 million in 2015, with timely introductions of novel metallization solutions to the market place. To sustain this nearly 66 percent growth over the forecasted period, Ferro anticipates making appropriate investments in material assets and human resources. Ferro invested in 20 new jobs in 2010, with plans to add an additional 110 R&D and applied technology professionals along with a field sales, marketing and administrative support of 60 new positions during the forecasted period to help facilitate the business growth in tandem with the industry growth.

5.3 AMPULSE CORPORATION

Ampulse Corporation's technology has the potential to offer manufacturers a foundational material from which solar modules can be built at a cost of $.50/watt, half the cost of the targets supporting the Solar America Initiative's 2015 objective for a levelized cost of electricity (LCOE) for PV at $.10/kWh, and accelerating the achievement of that objective by several years. Ampulse has a management team experienced in technology commercialization, which includes experts in integrated-circuit and laser mass-production.

Ampulse has proprietary calculations, based on detailed manufacturing cost models and standard calculation techniques that fully-support their target LCOE for solar PV of $0.07 kWh. There are cost reductions not only in eliminating about $1/W for silicon feedstock, but also from adopting roll-to-roll manufacturing as used in the amorphous silicon PV industry. As in amorphous silicon PV, considerable reductions in balance of systems costs (e.g., transportation and installation) can be obtained by reducing the weight of the PV modules and making them flexible. However, with efficiencies above 15% area-proportional balance of systems costs is reduced compared with lower-efficiency technologies. All these balance-of-systems cost reduction contribute to the low LCOE.

5.4 MOSSEY CREEK SOLAR

Mossey Creek Solar (MCS) recognizes that the solar demand market is expected by DOE forecasts to be 65 GW in 2012 and 125 GW in 2015 and that about 90% of that is crystalline silicon. MSC believes they can win a substantial, if not all of this, market with their technology, especially since their business plan involves licensing. However, MCS expects the dynamics and metrics of the market to change dramatically once the cost of solar power energy is competitive or less expensive than conventional peak power. MSC expects that the cost of peak power in most markets will be equal to or greater than 0.12 kWh by 2015 and that their cost of generating solar power will be substantially lower than this at that time.

MCS understands the motivations of utility operators are to run a plant to fill base power and to be able to generate peak power when it is required. They also understand that about 650 GW of capacity will be built each year for the next decade or so. Most peak power in most parts of the world is during the daylight hours so MCS believes that at least 7% of new production brought on line each year would be solar in such a case, or about 40 GW of capacity in new PV solar enabled by their technology. In this case MCS is suggesting that the total addressable market from DOE forecasts could exceed 125 GW.

APPENDIX A COLLABORATIVE RESEARCH OPPORTUNITY REQUEST FOR PROPOSALS

Collaborative Research Opportunity Request for Proposals

Collaborative Research and Development Initiative for US Manufacturers of Photovoltaic Materials

In order to advance solar energy technology, Oak Ridge National Laboratory (ORNL) will conduct short-term, focused research projects to address specific needs of the solar industry. This Collaborative Research Opportunity is intended to identify appropriate projects and industrial partners within the solar value chain that will lead to increased performance and decreased cost of materials for solar energy. This opportunity will provide selected industrial partners with limited access to ORNL's experienced staff and unique capabilities in order to demonstrate proof-of-principle for specific solar-related technologies. Creation and preservation of domestic jobs is a primary goal of this program.

Description

UT-Battelle, LLC, acting under its Prime Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy (DOE) for the management and operation of the Oak Ridge National Laboratory (ORNL), conducts research and development (R&D) in support of the DOE Office of Industrial Technologies Program (ITP). ITP's mission is to lead the national drive to reduce energy intensity and carbon emissions by changing the way industry uses energy. ORNL is requesting from industrial partners R&D proposals to enter Cooperative Research and Development Agreements (CRADAs) that promote and enhance the objectives of the American Recovery and Reinvestment Act (ARRA) of 2009, P.L. 111-5, especially economic recovery in an expeditious manner. Only projects that promote economic recovery, assist those impacted by the recession, or provide general economic benefit will be selected. The selected projects will be conducted under CRADAs between UT-Battelle and the industrial partners.

Selected projects will focus on advanced materials and processing methods for photovoltaic applications and will be conducted over a 6-month period. The industrial partner is required to provide at least 50% cost share, which can be funds-in to ORNL or in-kind contributions (e.g., facilities, services, and staff time). ORNL will not provide any funds to the industrial partner. **Note: THIS IS NOT A PROCUREMENT.**

Eligibility

Eligibility is limited to U.S. industries that currently manufacture or process solar materials for commercial applications or that will be able to do so as a direct result of these collaborative efforts. There is no restriction based on a particular material system or generation of solar cell technology.

Background

The efficient conversion of sunlight to electricity represents both a grand technical challenge as well as a tremendous opportunity for clean, abundant energy. The sun delivers more energy to the earth in an hour than the population of the world uses in an entire year, but it accounts for less than 1% of the renewable energy produced in the U.S.

In order for solar energy to gain widespread acceptance, it must be cost competitive with other forms of electricity currently on the market. The Levelized Cost of Electricity (LCOE) for solar technology is currently on the order of $0.20/kWh. In order for solar energy to achieve grid parity with other forms of electricity, the LCOE must be reduced by a factor of 3-4, to roughly $0.07/kWh. The primary metrics impacting LCOE at the solar cell level are performance (efficiency) and manufacturing cost, which are generally tightly coupled together.

The solar energy sector has been growing rapidly over the past several years. In the past 7 years, the solar sector has enjoyed annual growth rates in excess of 30% -- actually exceeding 50% in the past 2 years. Unfortunately, in the midst of such progress, the U. S. has lost market share internationally. Although the US led the world in manufacturing of solar systems in 1997, the US market share has fallen below 10% in recent years. However, the US currently leads the world in thin film PV production (~66% market share), which is an area that can be exploited to increase the overall market share in the future.

Objective

The ORNL objective is to collaborate with manufacturers to investigate, improve, and scale process methodology for the manufacture of high efficiency and low cost solar cells. Creation and preservation of domestic manufacturing jobs is a primary goal of this solicitation. Awards will be granted in one or more of the following categories.

- Crystalline Silicon
- Polycrystalline Silicon
- Thin Film Materials (a-Si, CdTe, CIGS)
- Earth Abundant, Non-Toxic Materials (e.g. CZTS)
- Organic or Nanostructured Materials
- Transparent Conductive Oxides
- Front & Backside Contacts
- Anti-reflective & Barrier Coatings

A total of $500,000 in matching funds is available to support ORNL services, staff time, and facilities (not including the cost share of the industrial partners). It is anticipated there will be 4-5 partners selected to support industrial-driven solar research at ORNL over the course of a 6-month period. Approximately $100,000 will be allocated for ORNL's effort to support each project.

ORNL's expertise in material synthesis, characterization, and process technology will assist various industries in developing new fabrication methods and/or improving existing methods. Research areas could include, but are not limited to:

- Low-Cost Fabrication Techniques
- Non-vacuum Deposition Techniques
- High Temperature Processing
- Roll-to-Roll Manufacturing
- Rapid Thermal Annealing
- Joining and Scribing Techniques
- Microstructure or Defect Characterization
- Computational Science
- In-line Quality Control Measures
- Process Optimization

The materials and processing technologies developed should be deployed in a new or existing manufacturing facility along with demonstration of any energy savings and economic impact.

Laboratory Support

ORNL will provide industrial CRADA partners with appropriate infrastructure, testing, operations, characterization, and analysis. It is anticipated that industrial collaborators will work collaboratively with laboratory staff to conduct research across the various centers of expertise at ORNL. Some of the facilities of interest include:

Nanoscale Science & Technology Lab: (NSTL) Capabilities to design, synthesize, and deposit various amorphous, crystalline, polycrystalline, and nanophase materials on numerous substrates. www.ornl.gov/sci/nstl

Center for Advanced Thin-film Systems: (CATS) User facility dedicated to the optical and electrical characterization of thin film systems and to the evaluation of device performance. In addition to standard IV curve trace and quantum efficiency measurements, capabilities include high resolution light beam induced current (LBIC), generalized ellipsometry, deep level transient spectroscopy (DLTS), electro-paramagnetic resonance (EPR) and photoluminescence. http://www.ornl.gov/sci/eere/research_solar.shtml

Materials Processing Group (MPG): Unique processing and modeling capabilities for the manufacture of structural and functional materials. In addition to extensive conventional processes, unique capabilities include Pulse Thermal Processing, PulseForge annealing, and laser surface modification.www.ms.ornl.gov/mpg/index.shtml

Oak Ridge Science & Technology Park: The Science & Technology Park is the only private research park in America located directly on the campus of a national laboratory. Using a unique development model, the park allows private companies the opportunity to lease office/lab space to work side by side with ORNL research staff to address key commercialization challenges.

Intellectual Property and Proprietary Data

DOE and ORNL respect the importance of industry's intellectual property and data security while balancing the need to document the benefits of public expenditures. Provisions relating to proprietary information and intellectual property are set forth in the CRADA, and the process can include putting in place non-disclosure agreements (NDAs after proposal selections, if necessary. In addition, if company proprietary information is included in the proposal, the specific information should be marked as such, and UT-Battelle will treat that information as confidential. To the extent possible, it is preferred that proprietary information NOT be included in these proposals.

Proposal Preparation

Selection of proposals will start at midnight (EST) on November 1, 2010. Proposals submitted thereafter will be considered as funding allows. Proposal and technical inquiries should be directed to:

Oak Ridge National Laboratory Industrial Technologies Program, indtech@ornl.gov

Final proposals should be submitted via email to the above address. Once a proposal is received, a confirmation email will be sent within one week stating the date and time of receipt.

Proposals should be no more than 5 single spaced pages using 12 point font (Times New Roman preferred), should be in pdf file format, and must include the following components under headings corresponding to the bullets below:

- Title Page (not included in page limit) with proposal title, principal investigator(s), contact information (name, nationality, address, phone number, fax number, and email address of the primary contact for contract issues and for scientific issues), as well as a brief company description.
- Project Abstract: Non-proprietary summary of technical objectives and potential impacts of research. (200 words)
- Background: Present technical challenge to be addressed. Identify materials and processing techniques currently used and motivation for collaborative research. (1 page)
- Project Plan and Objectives: Provide a brief plan of action for research and expected utilization of DOE/ORNL resources. List clear technical objectives with associated metrics. (1-2 pages)
- Impact: Predict the scientific and economic impact of the described research if successful. Also describe associated energy savings and benefit to the economy. (1-2 page)
- Cost Share: Estimate and justification of in-kind cost-sharing. Paragraph or tabular form is acceptable.
- Single page resumes of key project participants should be included (not included in page limit).

Proposal Evaluation

Selection of winning proposals will be at the discretion of DOE ITP and ORNL in cooperation with the DOE Solar Technologies Program. ORNL reserves the right to select all, a portion of, or none of the submitted proposals. The primary categories and relative ranking criteria used to evaluate submissions will be:

Technical
- Importance of materials and/or processing problem(s) to be addressed (25%).
- Potential of the collaboration to positively impact the U.S. solar industry (15%).
- Overall economic benefit to U.S. economy (15%).
- Potential for implementation of industrial energy savings (10%).
- Technical merit (10%).

Programmatic
- Level of cost share to be provided by industrial partner (15%).
- Importance of technology development and testing results to general market acceptance (10%).

Anticipated Schedule

November 1, 2010: Begin reviewing proposals.
November 15, 2010: Selection of partners.
February 15, 2011: CRADA must be fully negotiated (including the SOW) and ready for submission to DOE for approval, or project will be abandoned.

CRADA Information

Partners will be required to enter into a CRADA with UT-Battelle. Information on the CRADA process as well associated terms and conditions are summarized in attachment.

General Information: CRADAs enable industry, academia, and non-profit entities to collaborate with ORNL for the purpose of joint research and development (R&D) activities. CRADAs require DOE approval. CRADAs require R&D participation by industry partners.

Protection of Generated Information and Intellectual Property: Commercially valuable but non-patentable information generated under a CRADA may be protected for up to 5 years (See Article VIII of the CRADA Manual M483.1-1). Licenses to use intellectual property (IP) made or created under a CRADA are negotiated separately. The industry partner receives, in return for its collaborative participation in the CRADA research project, first right to negotiate a license for any new laboratory IP made or created under the CRADA, in a pre-negotiated field-of-use. Each party has the right to elect title to inventions made by its employees (See Article XV of the attached draft CRADA). The U.S. government retains a nonexclusive, nontransferable, irrevocable, paid-up license to practice or have practiced for or on behalf of the United States any IP created or made under the CRADA.

Financial Information: Under each CRADA the laboratory and the industry partner may provide one or more of the following: personnel, equipment, services, intellectual property, and facilities.

- The laboratory cannot pay out funds to the industry partner, but the industry may provide funds to the laboratory if it desires to do so.

Other Topics: Industry partners must agree to "substantial U.S. manufacture" of resulting products and services or provide a plan for providing net benefit to the U.S. economy that is approved by DOE (See Article XXII of the attached draft CRADA). DOE must approve all CRADAs.

Point of Contact

Proposals and technical inquiries should be directed to: Oak Ridge National Laboratory Industrial Technologies Program, indtech@ornl.gov