CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM

Renewable Energy Technologies

ELECTROSYNTHESIS OF DEVICE QUALITY SEMICONDUCTOR FILMS

FEASIBILITY ANALYSIS

December 2001
P500-01-022

Gray Davis, *Governor*

CALIFORNIA ENERGY COMMISSION

Prepared By:
Hal Clark
Grant Program Administrator
San Diego State University Foundation

Prepared For:
California Energy Commission
Energy Innovations Small Grant Program

Researcher:
Interphases Research
Thousand Oaks, CA

Philip Misemer
Grant Program Manager

Terry Surles
Deputy Director
Technology Systems Division

Steve Larson
Executive Director

LEGAL NOTICE

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which $2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to $75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
  - Appendix A: Final Report (under separate cover)
  - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email
eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at
http://www.energy.ca.gov/research/index.html.

Executive Summary

Introduction

This project devised a Copper Indium Diselenide (CIS) deposition method that is simpler, less expensive, and more effective than the prevailing methods. The *Electrochemical Molecular Layer Epitaxy* (EMLE) method was developed in order to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large photovoltaic (PV) modules. The project targeted the energy problem of reducing the capital equipment cost for photovoltaic (PV) modules production in order to make the cost of PV power systems competitive for California ratepayers. It developed this new non-vacuum approach to fabricate high quality thin-film materials for PV modules that could lower the manufacturing costs by over 50% and increase the PV module efficiencies.

The project addressed the PIER subject area of Renewable Energy Technologies. Within that field, this project addresses the cost of manufacturing solar photovoltaic (PV) systems. Worldwide PV markets have been expanding, with sales projected to exceed $12 billion by 2010. PV could provide a large portion of the state's electricity needs without negative impact to the environment, but this potential is limited due to the high initial cost of PV systems. In order to mitigate costs, subsidized buy-down programs have been introduced so that PV power can compete in the current energy market.

This EISG project explored a means to manufacture PV devices at lower cost. It created a non-vacuum fabrication method, specifically targeting the commercially important Copper Indium Diselenide (CIS) PV cell. CIS technology is important because when fabricated with complex, expensive laboratory scale vacuum methods, CIS cells are more reliable and efficient relative to other thin film PV types. Unfortunately, currently existing low-cost non-vacuum methods, suitable for large-area cell manufacturing result in low-grade films, which require further cost-intensive vapor phase treatments. The *Electrochemical Molecular Layer Epitaxy* method integrates the low-cost, large area features of electrodeposition with the atomic level, or nanoscale control of vapor phase epitaxial methods to produce high quality CIS films at ambient conditions from aqueous solutions. The project impacts both the positively doped CIS (*p*-CIS) state of the art solar cell, as well as the new flexible, lower cost negatively doped CIS (*n*-CIS) solar cell being developed.

Objectives

1. Design, assemble and test new apparatus and control software for nanoscale-controlled electrodeposition that eliminates need for vacuum processing.
2. Identify critical deposition parameters.
3. Synthesize binary precursor films.
4. Analyze the thin-films with electrochemical and surface analytical characterization.
5. Extend the investigation to produce ternary CIS absorber layer.
6. Begin a process of commercial readiness

Outcomes

1. A new non-vacuum electrodeposition apparatus, including process control software, was successfully designed, assembled and tested. The introduction of an unconventional thin layer flow cell was the key element that facilitated a precise electrodeposition process.
2. The effects of the standard EMLE deposition parameters of temperature, electrolyte composition, deposition potential, and timing parameters were identified, along with the effect of electrolyte volume.
3. The CuSe superlattice films (binary precursor films) were grown using three different methods, which enabled the identification of the process parameters.
4. A series of samples comprising 500-800 layers deposited on Mo/glass were analyzed and their composition determined. Film composition was tabulated as a function of the process parameter values.
5. This project led to a new method to produce a commercially valuable ternary CIS film, $CuInSe_2$. The results offer valuable insights into the role of process parameters allowing the identification of a new means to incorporate less noble metals in CIS film as required for high efficiency PV cells.
6. A US Patent was granted on May 8, 2001, based on the concepts underlying the new method.

Conclusions

While a fully functioning production line is still five years away, this project advanced the science toward using non-vacuum, electro-deposition for the production of thin film CIS PV cells.

1. The new electrodeposition apparatus and methodology represents an important advancement in electro-deposition process technology. It could allow the substitution of inexpensive electro-deposition hardware for the expensive vacuum deposition processing hardware currently needed to produce CIS thin film PV. Major gains were made in fine control of the electro-deposition process.
2. The new electrodeposition methodology, applied to the task of producing CIS thin film PV, has the potential to eliminate vacuum processing, reduce processing temperature, eliminate the need for multiple electrolytes, and eliminate the need for post annealing step. These potential advantages must be demonstrated in a subsequent development phase.
3. The original objective of this project was to produce a binary precursor film of CuSe using the new EMLE process, however, early success in producing the binary film allowed for the project to be extended to include the successful fabrication of a ternary Cu-In-Se material that constitutes the solar cell absorber layer.
4. Characterization of the fabricated binary and ternary samples confirmed the feasibility of the deposition process to produce high quality layers. This result should support the fabrication of CIS PV films with conversion efficiencies comparable to films produced using the existing expensive process.
5. The results of this research support the conclusion that through the commercialization of the new electrodeposition apparatus and methodology that the fabrication cost of electronic grade CIS films could be reduced by at least 50% for large PV modules.

This EISG project has been timely and instrumental in launching an alternate thin film deposition technology with the potential for lower manufacturing cost. The research team learned how to provide fine control of the electro-deposition process. The EMLE method compares well against other low-cost methods for CIS deposition that are being developed for the current *p*-CIS solar cell, as well as for a new flexible, lower cost *n*-CIS solar-cell. Nearly all other methods need an expensive, hazardous high-temperature selenization second step to produce device quality CIS films. The results are particularly important for the production of low-cost, high-volume flexible solar cells, based on *n*-CIS technology.

Further, the results of this project include a new process representing entry into the field of nanotechnology. This approach of electrodeposition controlled at the atomic level presents a relatively simple, rapid and inexpensive process to create a broad spectrum of complex semiconductor superlattices, heterostructures and quantum well devices. The new findings and their anticipated contribution to photovoltaics and nanotechnology are very important.

Benefits to California

The project performed R&D on technology that holds many potential benefits to California electricity ratepayers and the state economy. The project technology has the potential to:

- Provide California ratepayers with a viable cost-effective PV technology.
- Realize an affordable, reliable, state-of-the-art, clean and safe renewable energy resource for California residents.
- Provide a timely cost-effective renewable energy option for distributed generation to California utilities and ensure energy diversity, quality and reliability in the electricity markets.
- Lead to new in-state jobs and higher tax revenues, thus boosting California's vitality and the overall economy.
- Provide a new developmental entry into the high potential nanotechnology field.

Recommendations

The success of the feasibility study warrants further development of the new deposition method to fabricate a complete solar cell. The next stage will advance the project to:

- Extend the functionality of the design, build and test a prototype deposition apparatus and control system suitable for use in fabrication of a complete *n*-CIS solar cell.
- Advance the EMLE process to optimize the methodology for depositing all components of n-CIS PV cells.
- Automate the equipment and process and produce a quantity of *n*-CIS PV cells for operational evaluation and analysis.
- Because there currently exists a complete infrastructure supporting the manufacture and distribution of the positively doped CIS (*p*-CIS) PV cell, it is also recommended that this project advance the process to synthesize the components of *p*-CIS PV cells.
- Develop a preliminary production readiness plan to produce commercially viable PV module manufacturing equipment.

The EISG project results provide the bases and the directions for future R&D to fabricate a complete PV device. The method will evolve into an inexpensive, integrated system for large-scale manufacturing of efficient PV modules. The scale-up will take advantage of the existing automation and process lines designed for the electroplating industry. The final process will be user-friendly, robust and readily amenable to scale-up for mass production of PV modules.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: http://www.energy.ca.gov/research/innovations and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

Development Stages:	Development Activities:
Stage 1: Idea Generation & Work Statement Development Stage 2: Technical and Market Analysis Stage 3: Research & Bench Scale Testing Stage 4: Technology Development and Field Experiments Stage 5: Product Development and Field Testing Stage 6: Demonstration and Full-Scale Testing Stage 7: Market Transformation Stage 8: Commercialization	Activity 1: Marketing / Connection to Market Activity 2: Engineering / Technical Activity 3: Legal / Contractual Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis Activity 6: Production Readiness / Commercialization Activity 7: Public Benefits / Cost

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator's assessment was based on the following supporting details:

Marketing/Connection to the Market. The reaction of the scientific and PV industry communities to this technology has been enthusiastic. The project has not submitted a preliminary business plan and no commercializer has been chosen. However, business-planning information does exist, projecting market share growth to 2.85% in six years. Further, letters of commitment of funding from commercializers are reportedly in place.

Engineering/Technical. The project met the proposed goals. Following early successes with the deposition apparatus, it was decided that the effort and approach would be extended from a binary compound to a more complex and technologically important ternary material. The ternary material selected for study was $CuInSe_2$ which is used for the solar cell rather than its precursor compound CuSe which was initially studied. The results from this extended effort did affirm the viability and practical utility of the EMLE approach to fabricate tangible PV energy conversion devices.

Legal/Contractual. The Awardee holds patents on the EMLE process as well as on the *n*-CIS technology.

Environmental, Safety, Risk Assessments/ Quality Plans. Although the Final Report addresses the issue of Quality Planning, drafts of various planning documents are evidently not available. Initial drafts of the following Quality Plans are needed prior to initiation of Stage 4 development activity; Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and

Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety. This information can be prepared as separate documents or as a single document with multiple sections, and it may be a small document at this stage, but it should be created. Significant planning information should be recorded within the Manufacturability, Cost and Maintainability Analyses section, probably multiple pages of information.

Strategic. This product has no known critical dependencies on other projects under development by PIER or elsewhere.

Production Readiness/Commercialization. As previously indicated, a commercializer has not been selected. There are reportedly multiple candidates whose commitment is indicated by letter of intent.

Public Benefits. The PIER program has four public benefit goals. The applicable goal for this research project is:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.

This project potentially reduces the cost to manufacture PV cells. Lower cost cells could lead to lower cost PV generation systems. Cost effective PV systems can increase the application of this technology and thus reduce the environmental impact of electric generation in California.

This project researched advancements in science meant to reduce the manufacturing costs of CIS PV cells. The National Renewable Energy Laboratory published a paper titled "Issues in Thin Film PV Manufacturing Cost Reduction", authored by Ken Zweibel. Table 5 - Modified is adapted from Table 5 of this paper, after a private communication with the author. It shows estimated capital costs for various thin film semiconductor deposition processes. The advancements achieved in this project are expected to facilitate semiconductor deposition cost reductions of CIS, column SE, which are presently about $26/m^2. These reductions could result in costs similar to those shown for Electrodeposition CdTe, or about $1.80/m^2 to $4.00/m^2.

Table 5 - Modified			
Process (status)	**SE ($/m^2)**	**Companies**	**Initial Cost ($M) for 100 MW @ 10% Eff.**
Sublimation of CdTe (commercial)	$4.4	First Solar	$31M
Electrodeposition CdTe (pilot line)	$1.8 - $4	BP Solar	$10M - $25M
In-Line a-Si GD (commercial)	$30	Solarex, USSC	$210M
Box Carrier (Batch) a-Si (commercial)	$4	EPV	$28M
High-Rate a-Si (experimental)	$14		$99M
High-Rate CIGS Evaporation (experimental)	$26	Global Solar	$186M
Silicon-FilmTM (experimental)	$2.4	Astro-Power	$16M

Reductions in semiconductor deposition process costs would lead to reduced manufacturing facility costs (shown in the right-hand column of Table 5) and, ultimately, reduced PV module costs.

The estimated module manufacturing cost drop as the production volume and module efficiency increase. As seen from Table A, assuming a low 10% efficiency and low production volume for near term manufacturing, and using the published value of $1.8/m^2 from Table 5, the anticipated manufacturing costs are about $80/m^2. Further development to 15% efficient module and increased production volume, could lower the manufacturing costs to below $30/m^2.

Further costs reductions are anticipated for production of PV modules based on n-CIS since it uses fewer materials and processing steps.

Table A. Manufacturing cost estimate for PV modules based on CIGS films using InterPhases approach

Manufacturing capacity	2MW production	20MW production	Higher Capacity
10% efficiency	$80/m^2	$58/m^2	<<$50/m^2
15% efficiency	$52/m^2	$37/m^2	<<$30/m^2

Note that the above analysis does not place a monetary value on the reduced environmental impact resulting from utilization of this system over alternative manufacturing methods. Neither does it value the improved reliability anticipated from modules produced by this method.

Program Administrator Assessment

After taking into consideration: (a) research findings in the grant project, (b) overall development status as determined by stages and gates and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow on funding within the PIER program.

Receiving follow on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation and (c) successful evaluation of the proposal.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)