

Appendix A to FAR 99-01

**ENERGY INNOVATIONS SMALL GRANT
(EISG) PROGRAM**

EISG FINAL REPORT

**ELECTROSYNTHESIS OF
DEVICE QUALITY SEMICONDUCTOR FILMS**

EISG AWARDEE

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Abstract

This project developed a new approach to lower manufacturing cost, simplify fabrication and increase photovoltaic efficiencies of thin-film solar cells based on CuInSe_2 and its alloys (CIS). Currently, CIS modules fabricated with low-cost, non-vacuum methods exhibit lower efficiency than the vacuum deposited laboratory scale cells. Further, these modules require additional cost-intensive, hazardous, high-temperature selenization. The project developed a revolutionary electrochemical approach for relatively rapid and inexpensive synthesis of electronic grade CIS films, which avoids the high-temperature treatment. The method entailed building a superlattice of semiconductor monolayers by electrodeposition from a single electrolyte. This nanoscale deposition approach extends the utility of epitaxial methods to module fabrication with simpler apparatus and practical deposition rates.

The EISG project designed, constructed, implemented and tested new deposition apparatus. It investigated the reaction mechanisms, identified process parameters and used the data to synthesize CuSe films. The investigation was further extended to synthesize the ternary CIS absorber layer. The layer composition-process parameter correlations revealed crucial information and provided directions to advance the new method for the synthesis of morphologically homogenous, stoichiometric films. The project results can lead to an efficient, reliable and affordable photovoltaic energy conversion device for California ratepayers.

The new approach combines the low-cost, scale-up and environmental advantages of electrodeposition with the atomic level control of epitaxial deposition. The PIER-EISG support provided a timely resource to launch an exciting new enabling technology for thin-film photovoltaics. Its success could propel the CIS photovoltaics into the electric generation market and help alleviate California's electrical power shortage without damaging the environment.

Keywords: photovoltaics, CuInSe_2 , electrodeposition, low-cost synthesis, thin-film, nanoscale.

Executive Summary

Introduction

The project targeted an important energy problem of facilitating the implementation of low-cost photovoltaic (PV) power for California ratepayers. It developed a revolutionary new approach to fabricate high quality thin-film materials for PV modules that could lower the manufacturing costs by over 50% and increase the PV efficiencies. The project addressed the PIER subject area: Renewable Energy Technologies.

The current energy crises afflicting California has once again focused attention on PV to provide a cheap renewable non-polluting solution to an otherwise intransigent problem. 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 causing irreparable damage to the environment. PV is not widely used primarily due to the initial installation costs of PV systems currently at ~\$7 per Watt (W), due to the high module manufacturing cost of ~ \$4W. Thus the state subsidized buy down programs have been introduced so that PV power can compete in the current energy market.

This EISG studied the feasibility of reducing the high cost of PV systems with an innovative concept to lower the PV manufacturing costs below \$1W. It creates a revolutionary fabrication method, specifically targeting the commercially important copper indium diselenide (CIS) PV module. CIS cells are most reliable and efficient relative to other thin film PV cells when fabricated with complex, expensive laboratory scale vacuum methods. Unfortunately, low-cost non-vacuum methods, suitable for large-area module manufacturing, lead to low-grade films, which require further cost-intensive vapor phase treatments.

The project devised a CIS deposition method that is simpler, less expensive, but more effective than the prevailing methods. The method integrates the low-cost, large area features of electrodeposition with the atomic level control of vapor phase epitaxial methods to produce high quality CIS films at ambient temperature and atmosphere from aqueous solutions. The project impacts both the current positively doped CIS (*p*-CIS) solar cell, as well as the new flexible, lower cost negatively doped CIS (*n*-CIS) solar cell being developed by InterPhases.

Objectives

1. Design, assemble and test new apparatus for nanoscale deposition that eliminates the 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. Produce ternary CIS absorber layer.

Outcomes

1. The project developed a fundamentally new electrochemical process to fabricate semiconductor compounds, engineered on nanoscale.
2. It evolved beyond the initially proposed objective 3 to produce precursor films, to a new objective 5 that produced the commercially valuable CIS films.
3. It decisively established the technical feasibility of the new process from the following developments:
 - A new system was designed and constructed, in conjunction with a new process control system. The configuration, geometry and operation for each of the system components were optimized.
 - The distinguishing features of the new deposition process were identified relative to conventional electrodeposition. The effects of a range of process parameters on the deposit properties were investigated.
 - The special features of the new method were utilized to synthesize CIS thin-films controlled at molecular level, which were then characterized.
4. The results reveal crucial information and provide directions to advance the new method to produce efficient, reliable and affordable solar energy conversion devices.
5. A US Patent was granted on May 8, 2001, based on the concepts underlying the new method.

Conclusions

1. The EISG project advanced the R&D on a radically new concept for thin-film deposition.
2. It developed a practical method to synthesize compound semiconductors; it can potentially simplify the synthesis of electronic grade CIS films and reduce the fabrication costs by at least 50% for large PV modules.
3. We exceeded the proposed project goals, extending the approach to a more complex, technologically relevant CIS ternary material; the results offer valuable insights into the role of process parameters and identify a new parameter for single-step synthesis of multinary compounds.
4. The process is strategically placed against other low-cost methods for CIS deposition that are being developed. Nearly all these methods need an expensive, hazardous high-temperature selenization second step to produce device quality CIS films. Our approach produces high quality films directly in the first step at low temperature, thus avoiding the undesirable second step.
5. The project developed enabling technology to fabricate a critical component for the current *p*-CIS solar cell, as well as for a new flexible, lower cost *n*-CIS solar-cell, being developed by InterPhases.

The PIER-EISG award has been timely and instrumental in launching a revolutionary thin film deposition technology. It led to extremely important and some unexpected results, which we are eager to explore, to create high efficiency PV cells. The results are particularly important for the production of low-cost, high-volume flexible solar cells, based on InterPhases *n*-CIS core technology for building integration and electric vehicles.

Further, this award has enabled our new process to enter the high impact field of 'nanotechnology' at the ground level. This nanoscale electrodeposition approach presents a relatively simple, rapid and inexpensive process to create a broad spectrum of complex semiconductor superlattices, heterostructures and quantum well devices. In view of the importance of the new findings and the anticipated contribution to photovoltaics and nanotechnology, the project definitely warrants further development.

Benefits to California

The project develops public interest R&D that holds many potential benefits to California electricity ratepayers and the state economy. The project technology targets at least three PIER program areas. It has the potential to:

- generate an affordable, reliable, state-of-the-art, clean and safe renewable energy resource for California residents.
- provide California ratepayers with a viable cost-effective PV technology.
- propel the highly promising CIS PV technology into the electricity generation market.
- resolve the current California energy crisis and meet future energy needs without damaging the environment.
- 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.
- forestall the widely unpopular proposal to build new fossil fuel power plants and increase oil drilling in Alaska.
- lead to new in-state jobs and higher tax revenues, thus boosting California's vitality and the overall economy.

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:

- Design, build and test a prototype deposition apparatus and control system.
- Advance the new process to synthesize the components of *p*-CIS PV cells.
- Develop the method to deposit the components of InterPhases *n*-CIS PV cell.
- Automate the equipment and process for large volume production.
- Develop a preliminary production readiness plan to produce a commercially viable product.

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 in the electroplating industry. The final process will be user-friendly, robust and readily amenable to scale-up for mass production of PV modules.

Introduction

Background and Overview

The Project targets an important energy problem, facilitating the implementation of low-cost photovoltaic (PV) power to California ratepayers. It develops a revolutionary new approach to fabricate high quality thin-film materials for PV modules that will lower the manufacturing costs and increase the PV energy conversion efficiencies.

The project serves at least three of the PIER program areas of interest: (1) Renewable Generation (2) Energy-Related Environmental Research and (3) Strategic Energy Research.

The current energy crises afflicting California has once again focused attention on PV to provide a cheap, renewable, non-polluting solution to an otherwise intransigent problem. PV can provide a large fraction of the state's electricity needs without causing irreparable damage to the environment. PV can cut our utility bills and eliminate insecurities about the current rolling blackouts and electricity price increases. It can conserve our dwindling fossil fuel reserves, reduce toxic emissions and hazardous waste. PV is less widely used primarily due to the initial installation costs of PV systems. The PV module costs remain high particularly for the high efficiency devices.

The EISG project develops innovative concepts to lower the manufacturing costs and increase the efficiencies of thin-film PV modules. It develops a revolutionary electrochemical approach to fabricate high quality absorber films, specifically targeting the commercially important PV modules based on copper indium diselenide and its alloys (CIS). CIS modules exhibit lower efficiency than the laboratory scale CIS cells. The problem is that the complex, expensive laboratory scale methods used to make efficient small cells are not available to module manufacturers.

Lowering CIS PV costs requires a non-vacuum deposition method with low capital investment that is also scaleable, material and energy efficient, high-throughput, amenable to automation and simple to use. Electrodeposition offers these features, but like most low-cost, large-area deposition methods leads to low grade films, requiring further vapor phase treatments. This hybrid approach is neither economical nor suitable for coating large area modules. Nevertheless, a hybrid of electrodeposition/vacuum evaporation led to over 14% efficient cells [1].

Electrodeposition could be a promising approach if the high temperature vapor phase steps were avoided. Chemical and electrochemical atomic layer epitaxy were recently introduced to synthesize binary compounds on single crystals from separate solutions [2-5]. The method is however impractical for manufacturing large photovoltaic modules; such devices need low-cost, large-area, high-throughput deposition. Also, the atomic layer epitaxy is unsuitable for deposition of copper selenide (CuSe) and many other compounds, because it leads to the redissolution of one metal (Cu) during deposition of the next (Se).

Project Objectives

The overall project objective was to develop a distinctly different approach: *electrochemical molecular layer epitaxy* (EMLE) to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large PV modules [6,7].

Specific EISG project objectives:

- Design, assemble and test new apparatus for the EMLE deposition.
- Identify critical deposition parameters.
- Develop the EMLE approach to deposit high quality CuSe film.
- Analyze the thin-films by electrochemical characterization and surface analysis.

The economic objectives:

- Lower capital equipment costs.
- Simplify the deposition process for large area modules.
- Lower fabrication cost for high quality CIS PV modules.

New objectives that emerged during the project:

- Develop the EMLE approach to synthesize the ternary CuInSe₂ absorber layer.
- Extend the scope of EISG project objectives 1-4 to investigate the reaction mechanisms, synthesis and characterization of CuInSe₂ films.

The Project Approach section discusses the reasons for the new direction.

Report Organization

This report is organized to briefly:

- Outline the concepts underlying the new EMLE approach
- Describe new deposition apparatus
- Investigate the reaction mechanisms
- Report the results of the synthesis and characterization of the first Cu-In-Se films synthesized by the EMLE method and
- Present conclusions and suggestions for future work.

Project Approach

The EMLE approach entails the successive electrodeposition of monolayers of a compound from a single electrolyte to form a superlattice [6,7] as shown in Fig. 1. The approach is designed to produce morphologically homogenous films with self-regulating, computer synchronized sequence of flow, equilibrium and deposition from a thin electrolyte layer in a flow cell.

The approach is based on fundamental concepts regarding the nucleation process during electro-deposition. It integrates fundamental electrochemistry concepts of underpotential and diffusion layer deposition with a new concept of molecular layer formation to create a remarkably simple but powerful technique that could lead to cutting edge thin-film technology.

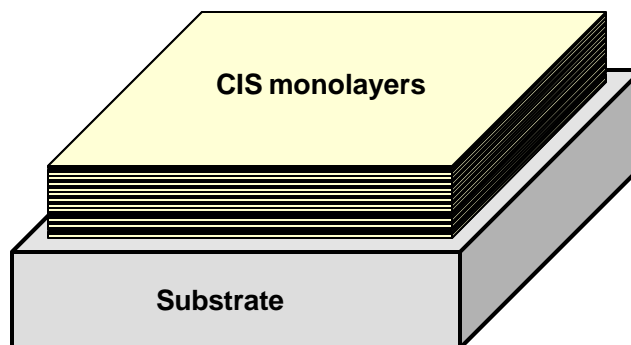


Figure 1. Multiple CIS monolayers formed on a substrate by the EMLE method.

Project Work Plan

The project work plan included design and development of (i) the new deposition apparatus and (ii) the EMLE deposition process. The following tasks (1-4) were performed to determine the feasibility of the EMLE approach:

1) Design and test new apparatus for molecular layer electrodeposition.

The major effort during the project period was devoted to this task to design, construct and assemble the several components of the deposition equipment and develop the control software for its efficient operation.

2) Identify the deposition parameters using electrochemical methods.

Electrochemical techniques, including rotating ring-disk voltammetry, multipulse amperometry, coulometry and potential pulse techniques were used to accomplish this task

3) Design control steps and instrumentation to develop the EMLE approach for CuSe film.

Using the results of task 2, the software was programmed to deliver effective sequences of control steps to generate voltage pulses and delay times as appropriate. An electronic circuit was designed to work in unison with the program.

4) Characterize the films using electrochemical and surface analytical methods.

Rotating ring-disk electrode methods were used to identify the various reactions. Electron microprobe analysis was used to characterize the EMLE synthesized films.

The deposition system development, modifications and improvements and the testing procedures undertaken are summarized in the 'Project Outcomes' section for brevity and clarity.

Project Scope Expansion

Although the long-range project goal was to synthesize the CuInSe_2 absorber material for the PV modules, the EISG project planned to demonstrate the EMLE method feasibility with a less complicated binary compound, CuSe. However, in the final quarter two issues, the new federal initiatives and certain project results led to some changes in the project direction and scope.

The EMLE project presented a timely response to new federal initiatives. It addressed National goals as described in "*National Nanotechnology Initiative: Leading to the Next Industrial Revolution*". The last Administration made Nanotechnology a top priority and emphasized its profound impact on our economy and society in the early 21st century. This EISG award has enabled our EMLE concept to enter this high impact field at the ground level. In view of the far-

reaching effects of the EMLE approach, the design, compilation and implementation of the new experimental apparatus were prioritized relative to the materials.

Following new developments in the deposition apparatus, we decided to extend the EMLE effort to the synthesis of the ternary material CuInSe_2 that is the actual component of the solar cell rather than its precursor CuSe . Even though this effort was not part of the EISG proposal, the results affirm the viability and practical utility of the EMLE approach to fabricate a tangible PV energy conversion device. This final report primarily describes the work done on tasks 1-4 during the 6th quarter, on the ternary Cu-In-Se system.

Project Outcomes

Task 1 - Design and Testing and Optimization of Deposition Apparatus

Task 1 designed, developed and implemented rather complex and elaborate apparatus based on a set of new concepts for the deposition of compound semiconductor films. The final version of the deposition equipment for EMLE is shown in Fig. 2. Its principal components include:

1. A thin layer flow cell, constructed with the assistance of Eltron Research.
2. A three-way solenoid distribution valve and a Masterflex peristaltic pump comprising a variable speed L/S pump drive, an 'Easy-Load' pump head, tubing, connectors and adapters, for delivery and exchange of solutions with the deposition chamber.
3. Electrolyte reservoirs and waste electrolyte container connected to the deposition chamber through feed lines.

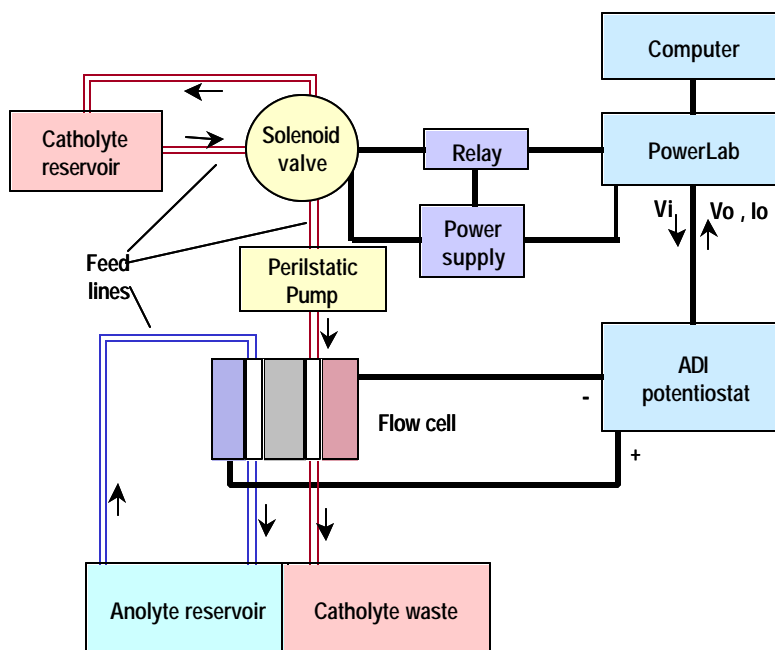


Figure 2. Schematics of experimental set-up developed for EMLE synthesis

4. Powerlab potentiostat recording-control unit and process control software to synchronize the delivery, equilibration, deposition and monitor the deposition parameters.

The flow cell is the central element of the experimental apparatus. It provides a large surface area electrode and a narrow gap for solution flow through the cathode compartment. The narrow gap confines the reactant ions within a thin solution layer, which establishes equilibrium instantly with the electrode surface. It provides each reactant ion immediate access to the electrode surface for uniform nucleation, promoting epitaxy. Quiescent deposition avoids mass transport and flow pattern complications, thus preventing 3-dimensional nucleation and polycrystallinity.

A separator membrane separates the anode compartment. The anolyte is circulated through a separate circuit to prevent interference from anode reaction products. The solenoid valve controls the flow of the catholyte into the cell. The pump speed regulates solution flow rate. A delay time introduced after each filling equilibrates the electrolyte. The catholyte flushes out after the deposition of a molecular layer. The anolyte solution is circulated in a closed circuit to prevent gas accumulation in the anode compartment. The substrates used were Mo/glass, C, Au or Pt coated Cu foils. The counter electrode was Mo/glass, Pt or Ti foil. SCE or a Cu wire measuring the solution redox potential served as reference electrodes.

Task 2 - Deposition Parameters and Reaction Mechanism for Cu-In-Se system

Many alternate reaction paths and products can occur in an electrolyte comprising Cu, In and Se ions. The compounds formed depend primarily on the reaction potential and to a large extent on the relative metal ion concentration ratio in the electrolyte. Controlling the kinetics of competing reactions is essential to obtain a stoichiometric film. The EMLE approach controls kinetics by limiting the solution volume in addition to the standard parameters, e.g., temperature, electrolyte composition and deposition potential [6].

The standard experimental parameters for EMLE deposition: temperature, electrolyte composition, deposition potential, equilibration time and layer deposition time, were investigated by conducting *in-situ* coulometric and voltammetric studies of redox reactions for Se, Cu and In based electrolyte systems using (a) a conventional cell, as well as (b) the thin layer deposition cell [Appendix I]. Distinctly different features between the 2 deposition systems were identified. EMLE for CIS films takes advantage of these unique features, the self-limiting reactions and the low free energy of -254 kJ/mol [13] for CIS formation to control the film stoichiometry

Task 3 - EMLE synthesis of CuSe and CuInSe₂ thin-films

The voltammetric data obtained in Task 2 provided the process parameters for CIS deposition. The CIS films were grown with a synchronized solution flow, equilibration and deposition sequence. Molecular layer deposition was monitored by tracking the current transients during deposition. This information derived was used to control the electrolyte flow (or stirring) rate and equilibration time.

The Task 3 results were in agreement with the voltammetric data of Task 2. Distinct differences were observed in the current output generated in bulk solution in a conventional cell and in the thin layer flow cell. The differences were manifested primarily during the anodic segment of the waveform which we attribute to the dissolution of specific binary phases in the two situations.

Task 4 - Characterization of Electrosynthesized Films

This first study of EMLE synthesis explored a variety of experimental parameters for EMLE deposition, including: electrolyte composition, deposition potential waveform, equilibration time, layer deposition time, temperature, stirring or flow rate between layer deposition. The composition of a series of samples comprising 500–800 layers was determined with electron microprobe analysis. The number and types of monolayers deposited during each pulse are deduced from the net charge density/pulse and charge density for monolayer of Se, CuSe, Cu₂Se and CuInSe₂ monolayers. The samples had excess of CuSe phase as anticipated for electrodeposition from bulk electrolyte. The CuSe content was related to the deposition potential, the deposition technique and the charge layer.

Task 5 - Final Report

A synopsis of the results of Tasks 1 through 4 are presented in this report. A detailed technical report is included in Appendix I. It contains a description of the deposition mechanism for the various elements and compounds, the deposition process and an analysis of the deposited films.

Conclusions and Recommendations

Conclusions

The EISG project demonstrated the feasibility of a new low temperature deposition approach for compound semiconductor thin-films. The project results have been very promising, substantially advancing the R&D on a very new EMLE concept for thin-film synthesis. The results suggest that the EMLE approach has the potential to simplify the synthesis of electronic grade CIS films and reduce fabrication costs for large PV modules. The key conclusions that support our assessment are drawn from the results presented in the 'Project Outcomes' in section 3 and Appendix I:

1. A practical new deposition system was developed, for the EMLE synthesis of CIS films at room temperature. It included the construction, assembly and implementation of new apparatus, and the optimization of the configuration, geometry and operation for each of the system components.
2. Voltammetric investigations reveal that different reaction mechanisms for CIS formation are prevalent in bulk electrolytes and in a thin solution layer. Elucidation of reaction mechanisms identified the distinctly different process parameters associated with the new system, relative to conventional electrodeposition apparatus. These parameters provide the crucial molecular level control necessary to synthesize homogenous films for CIS PV devices in the next development stage.
3. This first study of applying EMLE concepts to thin-film synthesis provides valuable insights into the role of various deposition conditions that could lead to a practical method for the deposition of a ternary compound.
4. The results of composition and process parameter correlation reveal important information and provide directions for the EMLE synthesis of morphologically homogenous CIS layers.

5. The EMLE method offers many advantages over conventional electrodeposition. It avoids the post-annealing step needed for conventionally electrodeposited films. It also eliminates the use of multiple electrolytes, rinse cycles and elaborate deposition apparatus required for atomic layer epitaxy. Thus, it extends the utility of epitaxial deposition to fabricate devices with simpler apparatus and practical deposition rates.
6. The new research results offer the first indication for the viability of the EMLE technology for commercial fabrication of PV modules.
7. The work performed has exceeded the proposed project goals, extending the approach from a binary compound to a more complex, technologically relevant CIS ternary material. The first feasibility study provides valuable insights into the role of various process parameters.
8. The first demonstration of the EMLE synthesis of CIS films has been a major milestone for thin-film deposition technology. The EMLE project results received enthusiastic reviews from the PV community at the recent national ACS (S. Diego) and MRS (S. Francisco) conference symposia.
9. The EMLE project is strategically placed against the low-cost methods for CIS deposition under development at other companies. Our approach offers several competitive advantages, primarily because it deposits high quality semiconductor films directly in the first step at low temperature. Thus, it avoids the expensive and hazardous second step of high-temperature selenization. Nearly all other low-cost deposition methods need the second undesirable step to convert poor quality precursors into semiconducting films.

The PIER-EISG award has been well-timed and instrumental in launching this revolutionary technology. The project method has evolved successfully beyond the initial proposed approach with the implementation of new experimental set-up, state-of the art electrochemical equipment and software. Extending the project scope from depositing binary CuSe compounds to a ternary CIS compound led to the most important result for this project — a new means to incorporate the less noble metals in CIS film as required, for high efficiency PV cells.

Further, this award has enabled our EMLE concept to enter the high impact field of 'nanotechnology' at the ground level. The EMLE approach could potentially be an enabling technology for nanomaterial synthesis. In view of the importance of the new findings and the anticipated contribution to photovoltaics and nanotechnology, the project definitely merits further development.

Recommendations

The recommendations for the next stage for this project include optimizing the EMLE method to produce high quality thin-films and extend the approach to other materials to produce high efficiency solar cells. Specific objectives have to be accomplished to advance the EMLE technology to the next stage:

1. Design and build a prototype deposition system. The new deposition apparatus design and operation will evolve from the specifications and cost goals stated for the completed project. Further modifications are necessary to the experimental apparatus, the control circuitry and fine-tuning of the deposition cell dimensions.

2. Identify the process parameters to synthesize stoichiometric absorber films for the *p*-CIS cell, e.g., CuInGaSe_2 , $\text{CuInGa}(\text{SSe})_2$.
3. Identify the process parameters to synthesize stoichiometric absorber films for the *n*-CIS cell (e.g., CuIn_3Se_5) to produce high efficiency PV cells.
4. Identify process parameters and equipment configurations to construct complete PV devices.
5. Determine composition, microstructure and opto-electronic properties of the electrosynthesized films and their relation to process parameters.
6. Develop the preliminary production readiness plan, including the critical production process, equipment, facilities and person-power needed to produce a commercially viable product.

The EISG project results provide the bases and directions for future R&D for the EMLE synthesis of device-quality absorber layers and other cell components to fabricate the complete PV device.

In addition, the EMLE method will evolve into an integrated system for manufacturing efficient inexpensive PV modules [6]. The method is rapid, user-friendly and amenable to large-scale fabrication of PV modules. Its scale-up takes advantage of the existing automation and process lines in the electroplating industry and commercial modular flow cell units, as shown in Fig. 3. These cells can be stacked to fabricate several PV modules simultaneously. The CIS PV module can thus be batch-processed at a low-cost of $< \$1/\text{Wp}$, as envisioned in Stage 1.

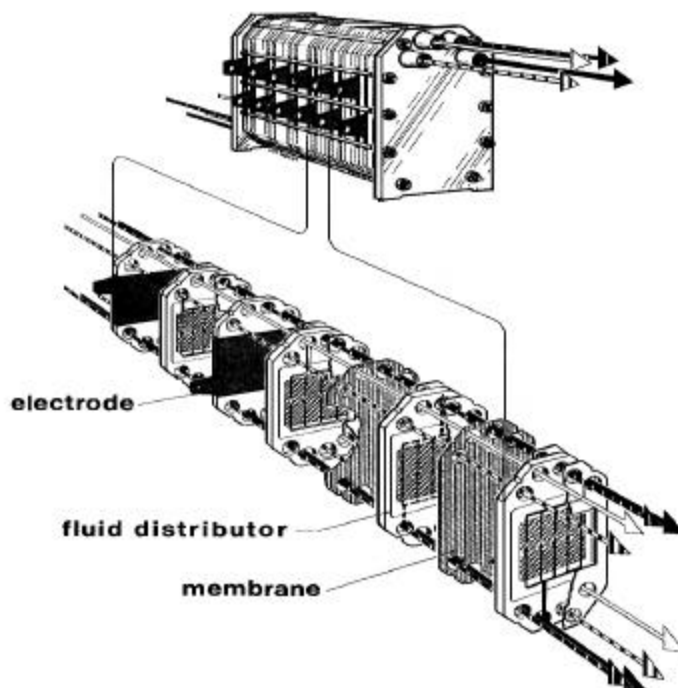


Figure 3. Commercially available equipment for EMLE synthesis of PV modules.

The project presents an inexpensive, user-friendly, environmentally benign high throughput process for manufacturing PV modules. It simplifies manufacturing and reduces module fabrication costs to $< \$1$, facilitating the implementation of low-cost PV power to California ratepayers. This project introduces a new fabrication method that can dramatically reduce the initial outlay for PV modules. This method, when combined with InterPhases core technology for *n*-CIS flexible solar cell fabrication further reduces costs. The *n*-CIS cell configuration uses fewer components, fewer processing steps and less packaging than the current *p*-CIS cell. It also uses an unconventional production approach that allows large-scale batch processing with the same equipment used in the laboratory. Its affordability and

versatility will allow new applications in building integration and electric vehicles. Current cost projections suggest a module cost of \$0.83 for a 2MW and \$0.58 for a 20MW production capacity.

At 2200 sun peak hours/year, California offers the best climate for PV. But at present PV needs substantial subsidies and rebates to compete with utility power, Columns 1 and 2 in Table I [18]. InterPhases' low cost technology expects to reduce PV costs to compete with utility electricity prices for existing buildings, without the \$3 buy-down subsidy. It would be even more economical for use in new construction where the flexible solar cell would replace conventional building elements (roof tiles, facades, windows, shading devices). In this case our technology can be cost competitive without the 15% tax rebate.

Table I. Economic analysis of grid-connected PV for CA with 2200 sun peak hours/year

Option	Current PV Technology		InterPhases Technology	
	1. No credit	2. CA buy-down + 15% tax rebate + 20-year payback	3. BIPV for old construction + 15% tax rebate + 20-year payback	4. BIPV for new construction + 20-year payback
Module cost (\$/W)	\$4	\$4	\$1	\$1
Installed cost (\$/W)	\$7.00	\$7.00	\$4	\$3.55
Capital recovery factor	0.13	0.05	0.05	0.05
Subsidy	0	\$3.00 + 15%	15%	0
Electricity price	\$0.14/kWh	\$0.14/kWh	\$0.14/kWh	\$0.14/kWh
PV electricity cost	\$0.41/kWh	\$0.134/kWh	\$0.134/kWh	\$0.134/kWh

The EISG grant provided a well-timed resource to initiate the EMLE project. It helped launch an exciting new PV technology that could resolve the energy problems facing California without causing irreparable damage to the environment. The project leads to an affordable, non-polluting electricity-generating device for California ratepayers. PV affordability provides a timely cost-effective energy option to the California utilities during the current energy crises. It can eliminate the need to build additional pollution-causing power plants or import natural gas, and reduce hazardous chemical waste disposal in California's landfills.

In addition to the cost benefits, PV electricity provides non-tangible public benefits in terms of clean environment, improved health and safety. The EMLE project technology offers even further environmental benefits, both to the utility worker and to the California ratepayer. The safe, simple, electrochemical manufacturing greatly minimizes hazardous toxic vapor-phase reactants, organic solvents and solid waste. It will impact the local and state economies and expand the RD&D knowledge base.

Since the start of this EISG contract, California has received the following benefits:

The project has created a new scientific information base, which impacts the material science, PV and energy policy-making entities. A new U.S. Patent based on the concepts proposed for the

EMLE project was granted on May 8, 2001. New information about a novel method for producing low-cost solar cells, derived from EISG project results, has been disseminated to the PV industry and scientific community at two California-based technical conferences. The PI presented the following papers:

- "Solution-based Processes for Processing CuInSe₂ Thin Films", Symposium on "Thin Film", American Chemical Society Meeting, S. Diego, April 1-4, 2001.
- "Molecular Level Approach for Low Temperature Synthesis of CuInSe₂ Films," Symposium H, 'II-VI Chalcogenide Semiconductor Materials', Materials Research Society Conference, S. Francisco, April 14-20, 2001.

The papers generated very enthusiastic response within the scientific community and the PV industry.

The EMLE project has far-reaching effects for the development of the exciting new field of nanotechnology. The EISG project has enabled our nanoscale processing EMLE technology to enter the nationally important area at ground level.

The anticipated savings in the California subsidies alone far outweigh the California Energy Commission cost outlay of \$75,000 for this project by several orders of magnitude. The anticipated non-tangible benefits from the project further enhance the public benefit-cost ratio.

Development Stage Assessment

Table II displays the Stage Activity of our EISG project, which has been completed to Stage 3 (Research and Bench Scale Testing).

Table II. Project Development Stage Activity Matrix

Stages Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Development	5 Product Development	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								

Marketing Activity

Cost effective CIS PV technology can meet the needs of a rapidly changing energy marketplace. The EISG project impacts the manufacturing cost for the established *p*-CIS PV technology as well as the InterPhases *n*-CIS technology. *p*-CIS technology is in pilot plant stage at several PV

companies. The CIS companies are excited at the prospect of expensive vacuum methods with our low-temperature CIS deposition method with its many potential benefits. They encouraged us to speed up its commercial availability

Our *n*-CIS flexible solar cell is even more affordable and versatile. It can penetrate new markets for building integration, electric vehicles, mobile and space systems. Funding commitment letters of intent from our potential commercializers are in place. InterPhases plans joint ventures with the PV industry to manufacture and market the *n*-CIS cell. Its current business plan includes a 2 year development phase leading to a 100kW pilot plant, the construction of a 2MW plant in 2004 and a 20MW plant in 2006 for large scale manufacture of *n*-CIS PV. The plan projects worldwide PV market shares of 0.4% in 3 years and 2.85% in 6 years. In the interim period, the company plans to license spin-off technologies generated from this project.

Engineering/Technical stage

As noted, this effort is a critical component of a larger project that features a new flexible, low-cost *n*-CIS solar cell, which was developed exclusively by InterPhases with private and government funds. Previously completed technical milestones include:

- 12% efficient & stable *n*-CIS solar cell.
- *n*-CIS thin-film cell fabrication method.
- Electrodeposition methods for CIS and CuISe₃.
- New CuIn₃Se₅ absorber with solar-matched bandgap for *n*-CIS cell.

The EISG project established an important technological milestone in the progression of the *n*-CIS project to the energy market. It demonstrated the technical feasibility of a new simpler and cost effective deposition method and system. The special attributes of the new method were exploited to synthesize CIS films. The next development stage 4 will exploit the EISG project results in the fabrication of *n*-CIS PV cell. In contrast to the current *p*-CIS PV technology, InterPhases' *n*-CIS flexible cell reduces the number of components and processing steps. This reduces its development period and simplifies large scale manufacturing. Three key patents, 30+ technical publications and successful demonstration of six SBIR grants from NSF, DOE and BMDO validate the *n*-CIS technology. It justifies advancing to Stage 4.

Legal / Contractual

A U.S. Patent application based on the concepts underlying the EMLE project was filed on Feb. 8, 1999. The patent, No. 6228243, entitled, "Electrochemical synthesis of crystalline compounds or alloys", was granted on May 8, 2001. Two previous patents, US Patent 4,601,960 (1986) and US Patent 5,286,306 (1994) cover certain portions of the total *n*-CIS project.

Risk Assessment / Quality Plans

The EISG project is specifically designed to simplify PV module manufacturing and lower costs for the established *p*-CIS cell and our *n*-CIS cell. Most importantly, the method eliminates the hazardous cyanide etching and selenization steps required with all other CIS deposition methods.

The project offers safe and simple electrochemical manufacturing, which greatly minimizes hazardous toxic vapor-phase reactants, organic solvents and solid waste.

Nevertheless, a Quality Plan will be developed that identifies quality control criteria, including technical performance, safety and environmental performance, in accordance with California and federal regulations. A life cycle analysis will be performed in the Stage 5 development. No potential risks are known at this time. Stage 4 will identify and report any new risks that may arise during the prototype system testing in accordance with Commission requirements and in close collaboration with PIER staff.

Strategic

The project has no known dependencies on other projects under development by PIER or elsewhere. It is strategically placed with respect to the existing thin-film technologies. It offers a unique technology to circumvent current energy problems in California and is not dependent on other PIER projects.

Production Readiness

The EMLE project presents the industry with an inexpensive, user-friendly, environmentally benign route for high volume production of PV modules. Process development in stage 4 will lead to production readiness. Collaboration with our partner CIS Solartechnik, GmbH, for electrodeposition of CIS modules is presently underway for 'building integrated PV' application. When developed, the EMLE method will already have a marketing vehicle in place for this technology. The revolutionary attributes of the EMLE project present an exciting opportunity to investors. Other potential commercializing partners include the electric utility companies and the CIS PV industry. The partnerships with the PV industry will strengthen the project and facilitate the final market transfer of the technology. We plan to select a commercializer and obtain commercializing partner commitment in stage 4. Advancing the project to stage 4 will greatly enhance the project's commercial viability and success.

Public Benefits / Costs

The electricity consumer is the end user and thus ultimate beneficiary of the project technology. The project will accelerate the commercialization of environmentally safe and reliable PV energy conversion products into the marketplace. It will thus provide access to a clean, affordable, inflation-proof resource to tap into the sun's energy which in turn will impact the quality of life in California.

The benefits offered by the EMLE technology far outweigh the California Energy Commission cost outlay for the project. The savings in subsidies, lower energy prices, numerous environmental benefits and scientific innovation will have far-reaching effects well into the future and significantly increase the public benefit-cost ratio. Further development of project technology to stage 4 will demonstrate its full potential.

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Appendix I

Details of Project Outcomes

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Task 1 - Design and Testing and Optimization of Deposition Apparatus

Task 1 is the key task for this project. It designed, fabricated and assembled a completely new experimental set-up for EMLE deposition. This involved design, development and implementation of rather complex and elaborate apparatus based on a set of new concepts for the deposition of compound semiconductor films. The final version of the deposition equipment for EMLE is shown in Fig.1. Its principal components include:

1. A thin layer flow cell, constructed with the assistance of Eltron Research.
2. A three-way solenoid distribution valve and a Masterflex peristaltic pump comprising a variable speed L/S pump drive, an 'Easy-Load' pump head, tubing, connectors and adapters obtained from Cole-Palmer Instrument Co, for delivery and exchange of solutions with the deposition chamber.
3. Electrolyte reservoirs and waste electrolyte container connected to the deposition chamber through feed lines.
4. Powerlab potentiostat recording-control unit, and process control software from ADInstruments to synchronize the pumping, delivery, equilibration, deposition and monitor the deposition parameters.

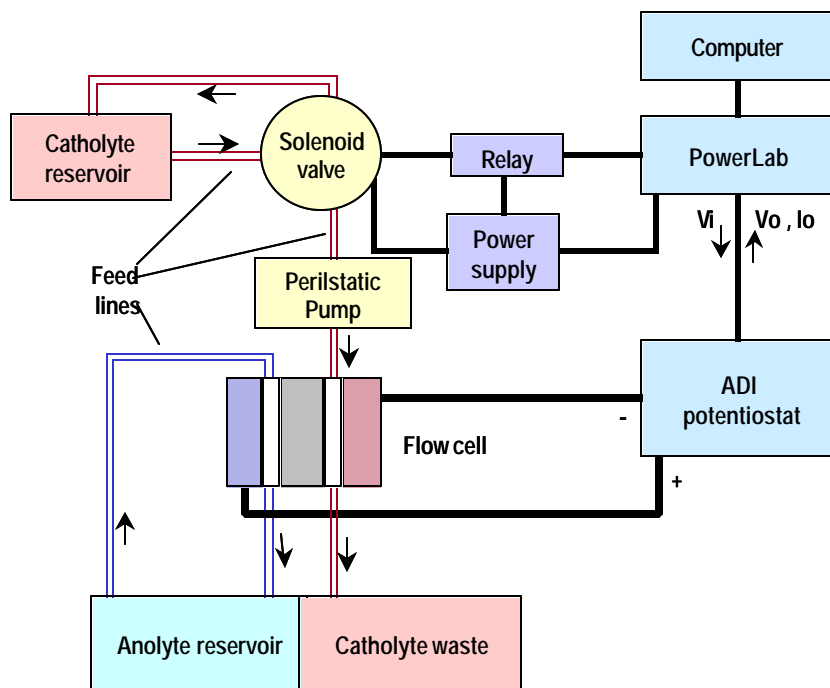


Figure 1. Schematics of experimental set-up developed for EMLE synthesis

The flow cell is the central element of the experimental apparatus. It provides a large surface area electrode and a narrow gap for solution flow through the cathode compartment. The narrow

gap confines the reactant ions within a thin solution layer, which establishes equilibrium instantly with the electrode surface. It provides each reactant ion immediate access to the electrode surface for uniform nucleation, promoting epitaxy. Quiescent deposition avoids mass transport and flow pattern complications, thus preventing 3-dimensional nucleation and polycrystallinity.

A separator membrane separates the anode compartment. The anolyte is circulated through a separate circuit to prevent interference from anode reaction products. The solenoid valve controls the flow of the catholyte into the cell. The pump speed regulates solution flow rate. A delay time introduced after each filling equilibrates the electrolyte and avoids mass transport effects. The catholyte flushes out after the deposition of a molecular layer. The anolyte solution is circulated in a closed circuit, to prevent gas accumulation in the anode compartment. The substrates used were Mo/glass, C, Au or Pt coated Cu foils. The counter electrode was Mo/glass, Pt or Ti foil. SCE or a Cu wire measuring the solution redox potential served as reference electrodes.

The earlier part of the project period was devoted to testing the experimental set-up and configuring the PowerLab software: Echem, Chart and Scope, for EMLE application. A series of voltammetric experiments were also performed with the various electrode materials in Cu^{2+} and $\text{Se}^{4+}/\text{Cu}^{2+}$ solutions in the thin layer and conventional electrochemical cells.

Task 2 - Deposition Parameters and Reaction Mechanism for Cu-In-Se system

Many alternate reaction paths and products can occur in an electrolyte comprising Cu^{2+} , In^{3+} and Se^{4+} ions. The compounds formed depend primarily on the reaction potential (E) and to a large extent on the relative metal ion concentration ratio, $[\text{Cu}^{2+}]:[\text{In}^{3+}]:[\text{Se}^{4+}]$ in the electrolyte.

Fig. 2 illustrates some likely pathways to CIS film formation in an acidic electrolyte containing $[\text{Se}^{4+}] \approx [\text{Cu}^{2+}] < [\text{In}^{3+}]$. The film formation reactions in the ternary system take place in two potential steps, E_1 and E_2 . The Cu^{2+} and Se^{4+} species reduce simultaneously to CuSe at E_1 when the $[\text{Se}^{4+}]/[\text{Cu}^{2+}]$ ratio is ~ 0.8 [8]. Cu_2Se or Se may co-deposit when $[\text{Se}^{4+}]/[\text{Cu}^{2+}] < \text{or} > 0.8$, respectively. The CuSe film reduces to Cu_2Se and Se^{2-} at a more reducing potential, E_2 . The Cu_2Se and Se^{2-} react with the In^{3+} from the solution *via* homogenous chemical reaction C, to form a CuInSe_2 film.

Alternately, the Se^{2-} may chemically react with the Se^{4+} in the electrolyte to form Se^0 (C'') or react with In^{3+} to form In_2Se_3 (C').

Controlling the kinetics of competing reactions is essential to obtain a stoichiometric film. The EMLE approach controls kinetics by limiting the solution volume in addition to the standard parameters, e.g., temperature, electrolyte composition and deposition potential [6].

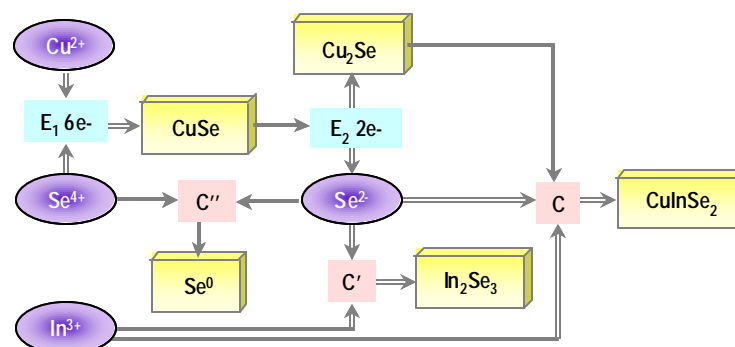


Figure 2. Mechanism of formation of Se , CuSe , Cu_2Se and CuInSe_2 films from a solution containing Cu^{2+} , In^{3+} and Se^{4+} ions.

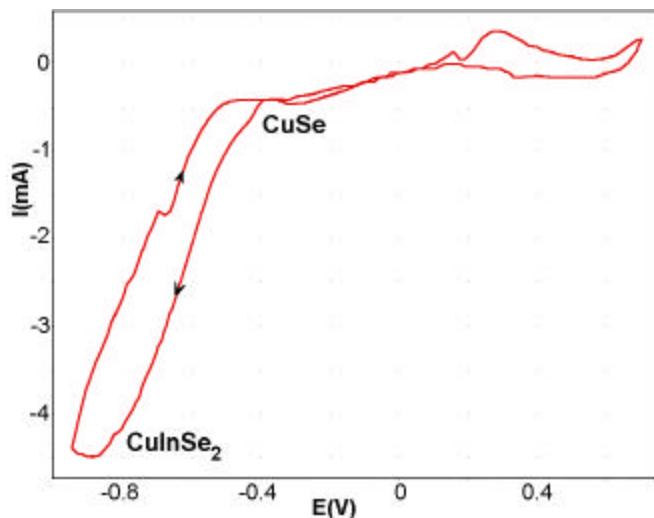


Figure 3. Voltammogram in 5mM Cu^{2+} +15mM In^{3+} +8.6mM Se^{4+} + 0.3M K_2SO_4 at a C disk rotating at 400 rpm, scan rate 10 mV/s.

Cu-In-Se system in sulfate solutions. The cyclic voltammogram in Fig. 3 was obtained in a conventional large volume (200ml) cell at a carbon rotating disk electrode. The curve shows two reduction steps at E_1 and E_2 to form CuSe and CuInSe₂. During the cathodic scan the CuSe formed at E_1 converts to CuInSe₂ at E_2 . Upon reversing the scan direction, the CuInSe₂ film continues to grow in the region $-1.0 < E < -0.6\text{V}$. A CuSe layer forms on top of the CuInSe₂ film in the region $-0.5 < E < 0\text{V}$. This Cu_xSe film dissolves during the anodic segment at $0 < E < 0.4\text{V}$. The dissolution of CuInSe₂ starts at $E > 0.6\text{V}$.

Fig. 4 shows the cyclic voltammograms obtained in the limited volume of the flow cell cathode

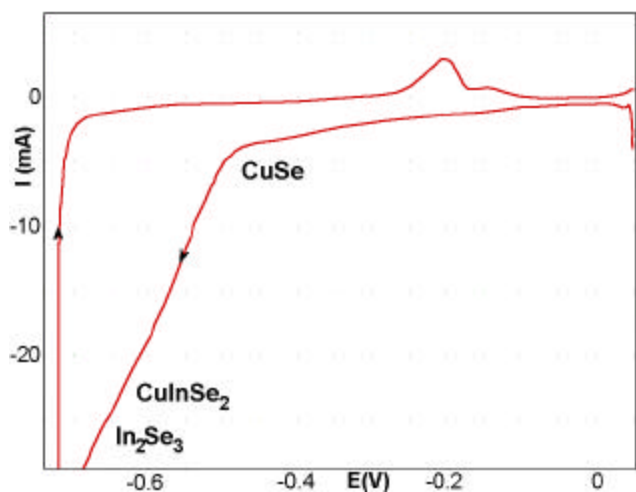


Figure 4. Voltammogram in 3mM Cu^{2+} +10mM In^{3+} +5.6mM Se^{4+} + 0.3M K_2SO_4 at a Au substrate in thin layer cell, scan rate 10 mV/s.

The standard experimental parameters for EMLE deposition: temperature, electrolyte composition, deposition potential, equilibration time and layer deposition time, were investigated by conducting *in-situ* coulometric and voltammetric studies of redox reactions for Se^{4+} , Cu^{2+} , $\text{Se}^{4+}/\text{Cu}^{2+}$ and $\text{Se}^{4+}/\text{Cu}^{2+}/\text{In}^{3+}$ electrolyte systems using a conventional cell, as well as the thin layer deposition cell. An important result involves the underpotential formation of CuSe at potentials nearly 500mV positive of the Cu-Se codeposition potential. This appears possible even on an ordinary platinized Ti surface following Se formation during anodic oxidation.

The voltammograms in Figs. 3 and 4 distinguish the processes occurring in bulk solution and a thin electrolyte layer for the

compartment containing a $\text{Cu}^{2+}/\text{In}^{3+}/\text{Se}^{4+}/\text{K}_2\text{SO}_4$ solution. The anode compartment was filled with the supporting electrolyte. The current-voltage curve was obtained under quiescent conditions. The curve segment going cathodic from 0V shows a 2-step reduction as in Fig. 3 for CuSe formation at $-0.2\text{V} < E < -0.4\text{V}$ and CuInSe₂ formation at $E < -0.5\text{V}$. On scan direction reversal, the current output appears different from that in Fig. 3. Film growth is arrested as the thin solution layer depletes of more noble metal ions and the reduction reaction proceeds to form In_2Se_3 .

EMLE for CIS films thus, takes advantage of self-limiting reactions and the low free

energy of -254kJ/mol [13] for CIS formation to control the stoichiometry. Theoretical treatment for compound formation has been presented by Kroger [14]. A monolayer of compound can deposit at a more positive potential than (I) one or (II) both component elements of the compound. Thus CIS monolayer forms at a more positive potential than at least one component element, e.g., In. Under the experimental condition used in the flow cell, deposition of In_2Se_3 and then In eventually takes place as the Cu^{2+} and Se^{4+} ions become depleted. The Cu, In and binary phases can be re-dissolved anodically at a less positive potential than that for ternary CIS and Se films.

Task 3 - EMLE synthesis of CuSe and CuInSe_2 thin-films

CuSe: The CuSe superlattice films were grown using (a) Conventional cell under quiescent condition, (b) Conventional cell with intermittent stirring, and (c) Thin layer cell using flow, equilibration and deposition sequence. The process parameters — potential limits, substrate pre-anodization, scan rate and temperature — were identified from voltammetric investigations.

CuInSe_2 : The voltammetric data for $\text{Cu}^{2+}/\text{In}^{3+}/\text{Se}^{4+}$ redox reactions in Figs. 3 and 4 provided the process parameters for CIS deposition. The CIS films were grown with a computer controlled flow, equilibration and deposition sequence. The molecular layers were deposited from a 0.3M K_2SO_4 solution containing 3mM Cu, 10mM In and 5.6mM Se at pH 2. The films were grown under quiescent conditions from bulk solution or thin solution layer. Molecular layer deposition was monitored by tracking the current transients during deposition. This provided information on the nucleation, growth kinetics, dissolution and conductivity of the layers. The information was used to control the electrolyte flow (or stirring) rate and equilibration time.

Fig. 5 shows typical waveforms at a Mo/glass electrode using a conventional cell with intermittent stirring between layer deposition. A 1s digital pulse to a mechanical stirrer and delay periods of 4s and 0.5s simulate the flow and equilibration steps for the conventional cell. This pulse was synchronized with the 0.5s applied potential pulse, which alternated between the equilibrium potential (E_0) and CIS formation potential (E_2). This generated a current output with an initial value of 15mA decaying to $\sim 5\text{mA}$. A small anodic current, observed as the voltage pulse switched to E_0 , probably dissolved the binary phases in the film.

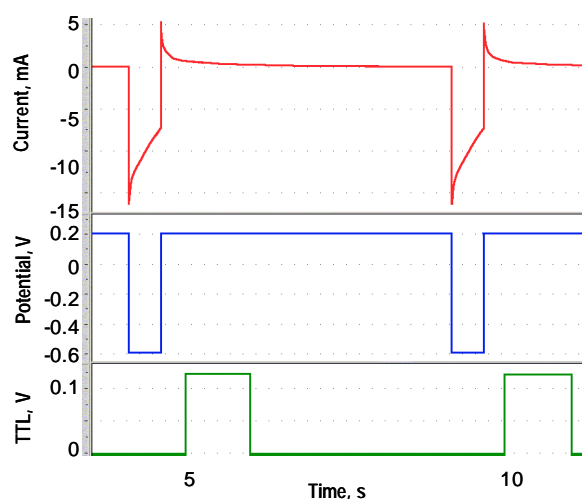


Figure 5. Current output generated with synchronized potential pulses, digital pulsed stirring and equilibration in bulk solution.

Fig. 6 shows similar waveforms obtained for EMLE in a flow through cell. The substrate was 9cm² Pt coated Cu plate. A 1s digital pulse to the solenoid valve, Fig. 1, initiated solution flow to the cell and solution equilibrated at 4s and 0.5s. This pulse was synchronized with the 0.5s applied potential pulse, which alternated between E₀ and E₂. This generated a current output with an initial value of 30mA decaying to ~ 18mA. Relatively large anodic current spike and small anodic peaks were observed at E₀ (0V), indicating dissolution of binary phases, as anticipated from Fig. 4.

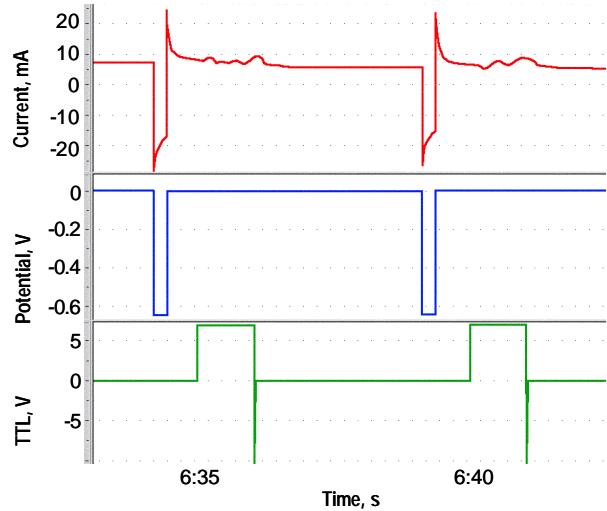


Figure 6. Current output generated with synchronized potential pulses, digital pulsed solution flow, equilibration in flow cell.

Task 4 - Characterization of Electrosynthesized Films

This first study of EMLE synthesis explored a variety of experimental parameters for EMLE deposition, including: electrolyte composition, deposition potential waveform, equilibration time, layer deposition time, temperature, stirring or flow rate between layer deposition. A series of samples comprising 500-800 layers were deposited on Mo/glass by varying waveforms and process parameters. The film composition was determined with electron microprobe analysis using a 10 keV electron beam.

Table I lists the process parameters, E, Q (charge/pulse), stirring, temperature and film composition for samples synthesized by EMLE from bulk electrolyte. As predicted by the voltammogram in Fig. 3, the films were multiphase and Cu rich. The number and types of monolayers deposited during each pulse are deduced from the net charge density/pulse and charge density for monolayer of Se, CuSe, Cu₂Se and CuInSe₂ monolayers.

Table 1. CIS Deposition Parameters & Composition Analysis

Sample No.	E(dep) V	E(eql) V	Q mC/cm ²	Stir	T °C	Atomic Ratio			No. of Monolayers			
						Cu	In	Se	CuInSe ₂	CuSe	Cu ₂ Se	Se
E206	-0.7	Off	3.4	n	25	3	1	7	1.2	1.6	0.0	0.6
E208	-0.7	Off	2.8	y	25	2	1	4	1.8	0.8	0.0	0.2
E208'	-0.7	Off	1.5	y	60	5	1	5	0.5	0.6	0.4	0.0
E209	-0.6	Off	5.5	n	50	2	1	3	3.2	2.3	0.0	0.0
C2151	-0.6	0.2	5.4	y	50	9	1	27	0.6	2.8	0.0	2.0
C2152	-0.6	0.2	8.6	y	50	22	1	60	0.5	5.1	0.0	3.1
C2153	-0.7	0.2	6.6	y	50	3	1	10	2.0	2.4	0.0	2.3
C2161	-0.7	0.2	4.8	y	50	7	1	12	1.0	3.2	0.0	0.6

The series E samples were deposited at (E_2). No potential was applied during equilibration. This waveform generates a cathodic current without anodic spike. Thus E series films contain less CuSe and negligible quantity of Se phase. Intermittent stirring between layer deposition increased the CuSe content in the film. The small amount of Se is a byproduct of reaction C', Fig. 2, that prevails at room temperature.

The C series samples were deposited with potential waveform switching between E_2 and E_0 values. The anodic spike observed at E_0 leads to decomposition of Cu_xSe to $CuSe + Se$. The CuSe content may be minimized by decreasing the value of E_2 and Q. Experiments underway plan to characterize the CIS films synthesized in the flow cell. These are anticipated to be Cu-poor, according to Fig. 4.