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Research on Photoelectrochemical Cells Based on CdSe, CdSe_{1-x}Te_x and Other Photoelectrode Materials

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RESEARCH ON PHOTOELECTROCHEMICAL CELLS
BASED ON CdSe, CdSe_{1-x}Te_x, AND OTHER
PHOTOELECTRODE MATERIALS

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ABSTRACT

Research on electrochemical photovoltaic cells incorporating thin film n-CdSe and n-CdSe_{1-x}Te_x photoanodes has resulted in efficiencies up to 7.5% using small area electrodes in polysulfide electrolytes. Efficiencies close to 10% can be achieved using alternate electrolytes in significantly less stable systems. The major limitations on the efficiency of II-VI photoelectrochemical cells are associated with the open circuit voltage and the fill factor. Research on CuInSe₂ electrochemical photovoltaic cells has resulted in efficiencies up to 11.7% using single crystal n-CuInSe₂ photoanodes in aqueous electrolytes. The n-CuInSe₂ surface and the electrolyte have been optimized to produce a highly stable semiconductor/electrolyte junction. A review will also be given on the status of photoelectrochemical storage cell research. In situ photoelectrochemical measurement techniques have been used to probe the semiconductor/electrolyte interface and have been used to support the characterization of semiconductor materials for solid state photovoltaic applications.

INTRODUCTION

The SERI Photoelectrochemical Cell Program, supported by DOE's Photovoltaics Division, was initiated in FY79. The objective of the program is to evaluate the efficiency, stability, and storage potential of polycrystalline thin film semiconductor/electrolyte systems with the ultimate goal of demonstrating the feasibility of achieving 10% (AM1) photoelectrochemical cell efficiency levels. Currently, the program consists of seven research subcontracts issued to universities and business organizations and an in house research effort conducted at SERI. In FY83 the program was supported at a total funding level of approximately \$713K, of which \$533K was subcontract support. In FY84 the overall funding level will be approximately \$550K. The three major subtasks of the program include: i) the deposition and characterization of polycrystalline thin film photoelectrode materials for photoelectrochemical applications, ii) the investigation of photoelectrochemical storage approaches, and iii) fundamental research on photoelectrochemical processes, including interface analysis and stability studies. Table 1 summarizes the research activities which were supported in FY83 and which have been carried over into FY84.

In order to achieve the objective of the Photoelectrochemical Cell Program, as stated above,

research activities have been directed toward a focused and coordinated study of II-VI polycrystalline thin film photoelectrochemical cells. II-VI single crystal and polycrystalline materials characterized in these studies have been incorporated in the investigation of photoelectrochemical storage systems. In support of storage and electrochemical photovoltaic cell research, fundamental studies have focused on understanding device performance and identifying factors limiting both thin film cell efficiency and stability. Promising new materials, such as CuInSe₂ and related compounds, have also been investigated based on evidence of superior intrinsic material properties for photoelectrochemical applications. Recently, it has been recognized that some photoelectrochemical measurement techniques offer advantages over solid state techniques in terms of their in situ non-destructive material characterization capability, simplicity, and greater sensitivity. This recognition has resulted in the increased use of photoelectrochemical characterization methods in solid state photovoltaic research, and it is expected that this trend will continue. The following discussion summarizes the status and recent progress in the Photoelectrochemical Cell Program.

II-VI POLYCRYSTALLINE THIN FILM EFFICIENCIES

Polycrystalline thin film photoelectrodes have been prepared from II-VI materials in the SERI Program by four deposition approaches, including co-evaporation (1), electrodeposition (2), chemical spray pyrolysis (3) and chemical bath deposition (4). A summary of the results obtained for polycrystalline n-CdSe and n-CdSe_{1-x}Te_x using these deposition approaches and for single crystal n-CdSe has previously been reported (5). An update of recent significant efficiency results is given in Table 2. In general, efficiencies of 5.5 to 6.5% under approximate AM1 or AM2 conditions can be obtained routinely for n-CdSe thin films deposited on titanium substrates by all four deposition techniques in electrochemical photovoltaic cells incorporating polysulfide electrolytes. Equivalent efficiencies up to approximately 7% have been obtained for co-evaporated n-CdSe thin films deposited on both titanium and tin oxide substrates in frontwall and backwall cell configurations. Equivalent efficiencies up to approximately 7.5% have also been obtained for co-evaporated n-CdSe and n-CdSe_{1-x}Te_x thin films deposited on titanium substrates. The highest efficiencies reported for n-CdSe and n-CdSe_{1-x}Te_x (x=0.2) films less than two microns in thickness are 7.5% (6) and 7.4% (1) respectively under approximate AM2 illumination conditions using polysulfide electrolytes.

In polysulfide electrolytes, the major limitations on n-CdSe electrochemical photovoltaic cell efficiencies are associated with the open circuit voltage and fill factor. The open-circuit voltage is bounded at an upper limit of approximately 0.8V by the equilibrium band bending in the space charge layer, and the fill factor is limited by recombination, resistance, and charge transfer kinetic factors. Short circuit currents are near the theoretical limit due to a combination of high quantum efficiency and field assisted charge collection in thin films, which compensates for low minority carrier diffusion lengths. Typical open circuit voltages are in the range of 0.6 - 0.74 V and typical fill factors are in the range of 0.5-0.7. Increased open circuit voltages up to 0.9-0.97 V (7, 8) have been obtained in n-CdSe cells incorporating the ferro-/ferricyanide redox couple. This couple has a potential that is more positive than that of the sulfide/polysulfide couple, resulting in an additional increase in band bending of up to 0.4 V. Fill factors can also be enhanced due to an increase in charge transfer kinetics between the semiconductor and electrolyte. Efficiencies of up to 9.9% (7) for n-CdSe thin films and 12-14% (9, 8) for n-CdSe single crystals have been reported for photoelectrochemical cells incorporating ferro-/ferricyanide.

Recently Grumman has reported an efficiency of 9.4% (AM2) for an n-CdSe_{0.20}Te_{0.80} electrochemical photovoltaic cell incorporating a polysulfide electrolyte (Table 2). The photoelectrode was sliced from a large grain polycrystalline boule grown by directional solidification (10). The tellurium rich compound had a bandgap of 1.37 eV compared to 1.74 eV for n-CdSe, but was less stable than n-CdSe or n-CdSe_{0.80}Te_{0.20}. The results are primarily significant in demonstrating the potential for achieving efficiencies near 10% for mixed II-VI materials in the polysulfide electrolyte, which has advantages in terms of stability compared to alternative aqueous electrolyte systems.

STABILITY OF II-VI POLYCRYSTALLINE PHOTOELECTRODES

Considerable research has been performed in order to understand the degradation processes occurring in II-VI photoelectrochemical systems. Using electrochemical techniques and modeling studies, SRI has developed a mechanism for n-CdSe photodegradation involving the initial photo-oxidation of the semiconductor lattice followed by the formation of decomposition products which vary as a function of the electrolyte composition. In polysulfide electrolytes, lattice oxidation is followed by ion exchange with the solution to incorporate sulfur in the semiconductor lattice, leading to surface passivation. *In situ* spectroscopic surface analytical studies by Brooklyn College have correlated the growth of segregated phases of CdSe_{1-x}S_x on the surface of n-CdSe films with photoelectrode deactivation (11). Photocorrosion is suppressed in polysulfide electrolytes by the efficient reduction of photogenerated holes by surface adsorbed sulfide, which subsequently rapidly desorbs as solvated sulfur (12). In other electrolytes, such as the considerably less stable ferro-/ferricyanide system, degradation leads initially to a conducting selenium surface film, which eventually passivates the photoelectrode as film thickness increases (13).

Significant stability can be achieved in polysulfide electrolytes by optimizing the electrolyte composition.

Grumman has demonstrated a stable co-evaporated n-CdSe thin film electrochemical photovoltaic cell at 4.8% efficiency for six months with less than a 1% decrease in power output under controlled laboratory conditions using a polysulfide electrolyte with added selenium (14). In addition, the Weizmann Institute has demonstrated complete stability of 3% polycrystalline n-CdSe cells for several months under outdoor test conditions (15). At present the stability of n-CdSe_{1-x}Te_x thin film electrodes is less than that for n-CdSe in polysulfide electrolytes. However, the Weizmann Institute has reported stability results for n-CdSe_{0.75}Te_{0.25} cells initially 3-4% in efficiency, which degrade less than 25% in five months under outdoor test conditions (16). The stability of the ternary compounds decreases as the tellurium content in the films increases.

Several approaches have been investigated in the Photoelectrochemical Cell Program to increase stability such as the use of nonaqueous electrolytes and the use of surface modification techniques, including the deposition of metal, semiconductor, polymer and oxide films on photoelectrode surfaces. These optimization approaches for stability tend to have detrimental effects on efficiency due to optical, resistance and other limiting factors. Surface modification via the use of native or extrinsic oxide conducting films to provide a diffusion barrier has proven successful with some materials, such as CuInSe₂, which will be discussed in the next section. Recently, the Weizmann Institute has reported a cation effect which has resulted in a further optimization of the polysulfide electrolyte for II-VI cells. Both the stability and efficiency of a single crystal n-CdSe photoelectrode increased in cells containing aqueous polysulfide solutions incorporating the alkali metal cation series, from Li⁺ to Cs⁺ (17). The extent of the effect is under investigation.

CuInSe₂ PHOTOELECTROCHEMICAL CELLS

Based on the successful work of Boeing on solid state CdS/CuInSe₂ cells, an internal program was initiated at SERI to investigate the efficiency and stability potential of CuInSe₂ in photoelectrochemical cells. A systematic investigation was conducted to characterize the chemical, structural and electrical properties of p- and n-CuInSe₂ and related materials in the series (Cu₂Se)_x(In₂Se₃)_{1-x}. This investigation included: i) characterization of the optical and electronic properties of single crystal and polycrystalline materials, ii) determination of the relationship between the photovoltaic behavior and the solid state chemistry of (Cu₂Se)_x(In₂Se₃)_{1-x} materials, iii) determination of degradation pathways using electrochemical and surface analytical techniques and iv) investigation and control of the surface chemistry of CuInSe₂ through surface modification techniques. Electrochemical studies indicate that the light induced decomposition of CuInSe₂ is consistent with Cu depletion of the semiconductor surface (Cu⁺ found in solution) and the formation of neutral selenium, as a surface film or solution species. However, it was found that a high degree of corrosion resistance could be generated by modifying the semiconductor surface with an InO_x film, which had little effect on the opto-electronic properties of CuInSe₂.

Through the systematic optimization of the semiconductor surface and electrolyte, highly stable n-CuInSe₂ electrochemical photovoltaic cells incorporating polyiodide electrolytes were investigated

with efficiencies up to 11.7% (under tungsten-halogen illumination of 120-145 mW/cm²) as shown in Table 2. Stability was accomplished using two approaches. First, indium was electrodeposited on CuInSe₂ and then air annealed to produce the InO_x surface barrier. Second, Cu¹⁺ and In³⁺ were effectively added to the electrolyte to reverse the decomposition equilibrium associated with CuInSe₂ photodegradation. The polyiodide electrolyte was optimized for the photovoltaic output parameters. No change in output parameters nor in the photoelectrode surface was detectable after passing 20,000 coulombs/cm² through the cell at a short circuit current density of 50 mA/cm² (18). These investigations have also resulted in the development of photoelectrochemical techniques which are useful in the characterization of CuInSe₂ for solid state applications.

PHOTOELECTROCHEMICAL STORAGE CELLS

The focus of storage research has been on the three electrode in situ photoelectrochemical storage approach, which is primarily being investigated at the Weizmann Institute. The Weizmann system, as shown in Figure 1, consists of an n-CdSe_{1-x}Te_x photoelectrode connected both to a CoS counterelectrode and a Sn/SnS storage electrode. A polysulfide electrolyte is used in the photoelectrode compartment and a sulfide electrolyte is used in the storage compartment. One of the advantages of this device configuration is that light energy can be simultaneously converted into electrical energy and stored chemical energy, yielding a highly flexible system arrangement. In the dark, the discharge reaction converting chemical to electrical energy occurs between the storage electrode and counterelectrode. Using n-CdSe_{0.75}Te_{0.25} photoelectrodes that are 20 cm² in area and up to 4% in efficiency, Weizmann has demonstrated system solar conversion efficiencies of up to 3% in 24 hour charge/discharge test cycles and has operated experimental cells under outdoor test conditions at lower efficiencies for several months. The storage cell has been subjected to six hour charge/discharge cycling for one month with no observable degradation. Weizmann has also demonstrated the internal series connection of the three electrode cells to yield linear submodules (16). The Photoelectrochemical Cell Program is coordinated so that II-VI polycrystalline thin film photoelectrode research complements and supports the in situ storage investigations.

An alternative storage approach has been investigated at IGT and the University of Texas which incorporates both n-type semiconductor photoanodes and p-type semiconductor photocathodes. The concept involves a photoelectrolysis cell which is separated from the redox cell in a four electrode ex situ device configuration. Advantages of the four electrode storage approach include the capability of generating higher photovoltages with the use of two photoelectrodes for charging the storage cell and greater flexibility in optimizing device performance, since the charge and discharge cell functions are separated. Several systems have been examined by IGT containing transition metal layer dichalcogenide photoanodes, such as n-WSe₂ and n-MoSe₂, in halide/halogen electrolytes and p-InP photocathodes in chalcogenide/chalcogen electrolytes (19). Two systems have been investigated that generate photovoltages in excess of one volt including n-WSe₂/p-InP (19) and n-CdSe/p-InP (20). Most work to date has been performed using small area single crystal

photoelectrode materials.

PHOTOELECTROCHEMICAL PROCESSES

In support of fundamental research to characterize the semiconductor/electrolyte interface, several nondestructive in situ photoelectrochemical measurement techniques have been developed which have wide ranging applications. Rockwell has demonstrated the general utility of electrochemical photocapacitance spectroscopy (EPS) for the characterization of energy levels and densities of bulk and surface states within the semiconductor bandgap. EPS has proven useful in characterizing surface states which limit the open circuit voltage in n-CdSe thin films deposited by co-evaporation and electrodeposition. The technique has also been extended to n-GaAs, p-GaAs, p-Zn₃P₂, and a-Si in support of solid state photovoltaic research and to characterize semiconductor materials for general electronic applications (21). Brooklyn College has developed the technique of electrolyte electroreflectance (EER) spectroscopy to measure the optical properties and flatband potential of semiconductor photoelectrodes, as well as to monitor changes in the energetics of the semiconductor/electrolyte interface as a function of time, potential, surface treatments, etc (22). Brooklyn College has also used Raman spectroscopy and electric field modulated photoluminescence measurements to characterize the surface composition of II-VI photoelectrodes as a function of aging (23). In the future, the use of photoelectrochemical measurement techniques to support solid state photovoltaic research will increase as the value of such techniques becomes more widely established.

CONCLUSIONS

Significant progress has been made in the Photoelectrochemical Cell Program in the past two years of research. Efficiencies of approximately 10% have been achieved for II-VI polycrystalline electrochemical photovoltaic cells in aqueous electrolytes for thin film n-CdSe and for large grain polycrystalline n-CdSe_{1-x}Te_x materials. Polysulfide electrolytes continue to be optimized for both stability and efficiency, and stability has clearly been demonstrated for time periods on the order of months. The concept of photoelectrochemical storage has been advanced and warrants continued basic research, based on the possible utility of storage to photovoltaics. During the course of the program, several photoelectrochemical measurement techniques have been developed for the nondestructive in situ characterization of semiconductor materials. These techniques will eventually find greater application in solid state photovoltaic research due to advantages in terms of simplicity, versatility and sensitivity.

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Table I. FY83/FY84 Photoelectrochemical Cell Program

Subcontractor	Principal Investigator(s)	Research Activities
Brooklyn College	M. Tomkiewicz	Electrolyte electroreflectance (EER) of the semiconductor/electrolyte interface, graded junctions, photoluminescence of II-VI thin films (aging studies).
Grumman	M. Russak	Co-evaporation of CdSe, CdSe _{1-x} Te _x , and CuInS ₂ , semiconductor/electrolyte interface analysis.
IGT	A. Sammells, P. Ang	Photoelectrochemical redox storage studies, assessment of photoelectrochemical storage approaches.
Rockwell	D. Tench, R. Haak	Semiconductor surface modification, development and application of electrochemical photocapacitance spectroscopy (EPS) to II-VI and other thin film photoelectrode materials.
SRI	K. Frese, D. Canfield	Photoelectrochemical cell corrosion studies, modeling of photoelectrode degradation processes.
Univ. of Texas	A. Bard, F. Fan	Aqueous redox systems for energy storage, surface modification of transition metal dichalcogenide films.
Weizmann Institute	J. Manassen, S. Licht	Three electrode photoelectrochemical <u>in situ</u> storage cells, storage electrode studies, stability studies.
In House Research	D. Cahen,* Y. Chen, J. Folmer, P. Ireland, R. Noufi, J. Turner	Photoelectrochemical characterization of efficiency and stability of CuInSe ₂ and related materials.

*On leave from the Weizmann Institute

Table 2. Recent Polycrystalline Thin Film and Single Crystal Efficiency Results

Cell Structure	Morphology/ Deposition Process/ Substrate	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η %	Area (cm ²)	Illumination (mW/cm ²)	Reporting Organization
n-CdSe/2.5 F S ²⁻ , 1.0 F S, 1.0 F OH ⁻ /Pt	P/CE/Ti	0.57	14.3	0.69	7.5	0.25	75 (ELH)	Grumman
n-CdSe _{0.30} Te _{0.20} / 2.5 F S ²⁻ , 1.0 F S, 1.0 F OH ⁻ /Pt	P/CE/Ti	0.54	18	0.57	7.4		75 (ELH)	Grumman
n-CdSe _{0.20} Te _{0.80} / 2.5 F S ²⁻ , 1.0 F S, 1.0 F OH ⁻ /Pt	LP/Ti	0.59	22.4	0.54	9.4	0.2	75 (ELH)	Grumman
n-CuInSe ₂ /6 M I ⁻ , 0.1 M Cu ²⁺ , 0.1 M In ³⁺ /Pt	SC	0.47	50	0.60	11.7	0.05	120 (W-Halogen)	SERI

P=Polycrystalline, SC=Single Crystal, CE=Co-Evaporation, LP=Large Grain Polycrystalline

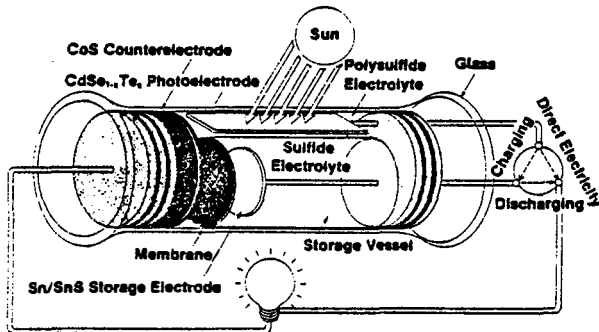


Figure 1. Schematic diagram of the three electrode in situ photoelectrochemical storage cell.