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W. L. Wallace

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1617 Cole Boulevard
Golden, Colorado 80401

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Photoelectrochemical Cells With and Without Storage Based on II-IV Semiconductor Materials

William L. Wallace

Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

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. Research on CuInSe₂ electrochemical photovoltaic cells has resulted in efficiencies up to 11.7% using single crystal n-CuInSe₂ photoanodes in aqueous electrolytes. A review will also be given on the status of photoelectrochemical storage research.

1. Introduction

The SERI Photoelectrochemical Cell Program, supported by DOE's Photovoltaics Division, was initiated in FY 79. 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 five research subcontracts issued to universities and business organizations, as shown in Table 1, supported at an overall funding level of \$550 K in FY 84. The three major subtasks of the program include: i) the deposition and characterization of polycrystalline thin film photoelectrode materials, ii) the investigation of photoelectrochemical storage approaches, and iii) fundamental research on photoelectrochemical processes.

In order to achieve the objective of the Photoelectrochemical Cell Program, as stated above, research activities have been directed toward a focused study of II-VI polycrystalline thin film materials, which can then be incorporated into the investigation of storage systems. In support of cell research, fundamental studies have focused on device performance and limitations on cell efficiency and stability. Promising new materials, such as CuInSe₂, have also been investigated based on evidence of superior intrinsic properties for photoelectrochemical applications. In addition, in situ, non destructive photoelectrochemical measurement techniques developed in the program have been used both in photoelectrochemical and solid state photovoltaic research. The following discussion summarizes the status and recent progress in the Photoelectrochemical Cell Program.

2. II-VI Polycrystalline Thin Film Efficiencies

Polycrystalline thin film photoelectrodes have been prepared from II-VI materials 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 n-CdSe and n-CdSe_{1-x}Te_x films has previously been reported (5) and an update of recent results is given in Table 2. In general for electrochemical photovoltaic cells under AM1 or AM2 conditions: i) efficiencies up to 6.5% can be obtained routinely for n-CdSe films on titanium substrates by all four deposition techniques, ii) efficiencies up to 7% have been obtained for co-evaporated n-CdSe films on both titanium and tin oxide substrates, and iii) efficiencies up to 7.5% have been obtained for co-evaporated n-CdSe and n-CdSe_{1-x}Te_x 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 in 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 0.8 V by the built-in voltage, and the fill factor is limited by recombination, resistance, and charge transfer kinetic factors. Short circuit currents are near the theoretical limit due a combination of high quantum efficiency and field assisted charge collection in thin films, compensating for low minority carrier diffusion lengths. Increased open circuit voltages, up to 0.9 - 0.97 V (7,8), and increased fill factors have been obtained in n-CdSe cells containing the ferro-/ferricyanide redox couple, which has a

more positive redox potential and faster electron transfer kinetics than polysulfide. Efficiencies up to 9.9% (7) for n-CdSe thin films and 12 - 14% (8,9) for n-CdSe single crystals have been reported for aqueous ferro-/ferricyanide photoelectrochemical cells.

Recently Grumman has reported an efficiency of 9.4% (AM2) for an n-CdSe_{0.2}Te_{0.8} photoelectrode sliced from a large grain polycrystalline boule (10) and Weizmann has reported an efficiency of 12.7% (AM1) for a single crystal n-CdSe_{0.65}Te_{0.35} photoelectrode (11) in a polysulfide electrolyte. These results are primarily significant in demonstrating the potential for achieving high efficiencies for mixed II-VI materials in the polysulfide electrolyte, which has advantages in terms of stability compared to alternative aqueous electrolytes.

3. Stability of II-VI Photoelectrode Materials

Using electrochemical techniques and modeling studies, SPI 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 (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 using a polysulfide electrolyte with added selenium (14). 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 stable 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). Both the stability and efficiency of single crystal n-CdSe and n-CdSe_{1-x}Te_x photoelectrodes increases in cells containing aqueous polysulfide solutions incorporating the alkali metal cation series, from Li⁺ to Cs⁺ (11,17).

4. CuInSe₂ Photoelectrochemical Cells

Based on the successful work of Boeing on solid state CdS/CuInSe₂ cells, an internal program at SERI investigated the efficiency and stability of CuInSe₂ in photoelectrochemical cells. A systematic study was conducted to characterize materials

in the series (Cu₂Se)_x(In₂Se₃)_{1-x} including: i) characterization of the optical and electronic properties of single crystal and polycrystalline materials, ii) determination of the relationship between photovoltaic behavior and solid state chemistry, iii) determination of degradation pathways, and iv) investigation and control of the surface chemistry of CuInSe₂. Electrochemical studies indicate that the light induced decomposition of CuInSe₂ is consistent with Cu depletion of the semiconductor surface 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.

Stable n-CuInSe₂ electrochemical photovoltaic cells incorporating polyiodide electrolytes have been investigated with efficiencies up to 11.7%. Stability was accomplished using two approaches. First, indium was electrodeposited on CuInSe₂ and then air annealed to produce the InO_x surface barrier. Second, Cu⁺ and In³⁺ were added to the electrolyte to effectively reverse the decomposition equilibrium associated with CuInSe₂ photodegradation. No change in output parameters nor in the photoelectrode surface was detected 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.

5. 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 cell consists of an n-CdSe_{1-x}Te_x photoanode 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. 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 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).

6. 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 capacitance 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:H_x in support of solid state photovoltaic research and to characterize semiconductor materials for general electronic applications (19). 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 (20). 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 (21). 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.

7. 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 1. 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 CuInSe ₂ , semiconductor/electrolyte interface analysis.
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.
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, P. 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 %	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 _{0.80} 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 SERI
n-CdSe _{0.65} Te _{0.35} / 1.8 M Cs ₂ S, 3.0 M S/Pt	SC	0.78	22.3	0.68	12.7		93.7(Sun) Weizmann

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