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**DEVELOPMENT OF PHOTOELECTROCHEMICAL CELLS BASED ON
COMPOUND SEMICONDUCTORS AND NONAQUEOUS ELECTROLYTES**

Semiannual Report for the Period May 1—October 31, 1981

By
R. D. Rauh

March 1982

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EIC Laboratories, Inc.
Newton, Massachusetts

U.S. Department of Energy

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**Semiannual Report
May 1, 1981 to October 31, 1981**

**R. D. Rauh, Principal Investigator
M. E. Langmuir, Program Manager
R. A. Boudreau, Senior Scientist
M. A. Parker, Staff Scientist**

**EIC Laboratories, Inc.
111 Chapel Street
Newton, Massachusetts 02158**

March, 1982

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I. INTRODUCTION AND SUMMARY

The objectives of our present research program are: 1) to optimize the electroless chemical bath process for deposition of cadmium chalcogenide thin film photoelectrode; 2) to explore additional thin film and polycrystalline semiconductor photoelectrodes in promising electrolyte systems developed previously; and 3) to initiate a device optimization program to scale up high efficiency electrochemical photovoltaic cells. Device optimization requires the development of test capabilities including: 3.1) laser spot scanning; 3.2) a long term test facility for diurnal cycling of test cells under a variety of conditions; 3.3) fabrication and testing of various practical cell and electrode geometries; and 3.4) continued work on improving the photoelectrode and counter electrode materials used in fabrication of the cells.

The following major achievements have been recorded during the current semiannual reporting period:

- A reproducible procedure for chemical bath deposition (CBD) of CdSe has been documented in detail, allowing a consistent production of photoelectrode yielding 5.5-6.5% conversion efficiency in alkaline polysulfide electrolyte (employing a tungsten halogen lamp/KG-2 filter solar simulated light source).
- The CBD films of n-CdSe on Ti have achieved an efficiency of ~10% under both solar simulated and real sunlight conditions using an $\text{Fe}(\text{CN})_6^{-3/-4}$ electrolyte at pH 13. For an initial current density of 16 mA/cm² (~80 mW/cm² illumination), a decrease of ~25% is observed after 3 hours illumination.
- Research was completed on developing a stable $\text{Cu}^{+}/^{+2}$ redox electrolyte in CH_3CN , which contains excess Cl^- , to promote photochemical stability. For poly-n-GaAs, best results were obtained for electrolytes containing ~0.5M CuCl, 0.05M CuCl₂, 1M tetrabutylammonium chloride, viz: at 80 mW/cm², $j_{\text{sc}} = 19 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.74\text{V}$, $P_{\text{max}} = 3.78 \text{ mW/cm}^2$, $ff = 0.27$ and $\eta = 4.8\%$ ($\eta = 8.1\%$ at 8 mW/cm² irradiation).
- Five encapsulated sealed cells have been tested with 15 cm² photoelectrodes comprised of CBD CdSe on Ti.

The cells are frontwall illuminated with various configurations for ion flow to the rear-placed Ni/CoS electrode. For one design, an efficiency of 4.3% was achieved under 63 mW/cm² real solar illumination.

- Laser spot scanning has been developed as a technique for evaluation of both large area geometrical effects and microscopic photoelectrode morphological effects on the performance of PECs.

II. CONTINUED DEVELOPMENT OF THIN FILM AND POLYCRYSTALLINE PHOTOELECTRODES

A. Refinement of CdSe Chemical Bath Deposition (CBD)

Kainthla and co-workers (1) have described the deposition of CdSe films by a chemical bath "electroless" method. The method, described in previous reports, involves the selective precipitation of CdSe on catalytic surfaces from an alkaline bath containing Na_2SeSO_3 and $\text{Cd}(\text{NH}_3)_4^{+2}$ as the reacting species. As Se^{-2} is slowly released via hydrolysis, viz

the Se^{-2} reacts rapidly with free Cd^{+2} . Reaction (1) is apparently base catalyzed, and occurs preferentially on hydroxylic surfaces.

The manuscript in Appendix A describes our work on optimizing this procedure for the preparation of CdSe photoanodes yielding >6% conversion efficiency* in polysulfide-based regenerative photoelectrochemical cells. The principal modifications may be summarized as follows:

- Repeated depositions were employed to achieve films of >2 μ thickness, necessary for efficient sunlight absorption. Intervening annealing was only necessary following the first deposition ($\sim 0.4\mu$ thick), in order to enhance adherence of the remaining layers. A terminal thickness is only reached for each deposit because of a depletion of reactants due to competitive precipitation in the bulk of solution. In a large scale process, the ratio of substrate surface area to solution volume would be maximized. Furthermore, a flow system would be employed with automated control of reagent concentration and filtration of CdSe not bound to the substrate.
- A sealed, deoxygenated system was employed. The earlier procedure employed a >10-fold excess of NH_4OH above the Cd^{+2} concentrations. Since it was carried out in an open beaker under heating, the NH_3 would evolve until the equilibrium (2) favored significant free Cd^{+2} :

* Tungsten halogen illumination with Melles Griot KG-2 filter.

By conducting experiments in sealed tubes, we determined that an NH_4OH concentration of only $\sim 0.2\text{M}$ was necessary for producing specular CdSe films. Using the composition of Kainthla et al. (1) in a sealed tube, no CdSe formation occurred even at 90°C .

- A coating of $\text{Cd}(\text{OH})_2$ was applied to the substrate before deposition. This not only enhances the catalysis of SeSO_3^- hydrolysis, but also favors the reproducibility of formation of the hexagonal CdSe structure and of specular adherent films. Even with optimized bath compositions, areas of undesirable powdery deposits are sometimes observed if substrates are not pretreated in this way.
- A stoichiometric excess of Na_2SeSO_3 and a bath temperature of $90\text{--}100^\circ\text{C}$ are employed to increase the deposition rate to an average of $\sim 0.02\mu/\text{minute}$, about 50% greater than with stoichiometric Na_2SeSO_3 and at 77°C , as employed earlier (2,3).
- A series of post-deposition treatments were employed to "activate" the deposits. These consisted of i) annealing at 550°C in air for 30 minutes; ii) etching for 20 sec in 9M HCl; iii) dipping in 2M aqueous ZnCl_2 for 10 sec; iv) lacquering the unilluminated portions of the electrode to minimize dark current losses.

Depositions have been carried out on numerous substrates - glass, Ni, Ti, indium-tin oxide and tin oxide coated glasses, stainless steel, with areas up to 150 cm^2 and of varying shapes (e.g., louvered, corrugated) for incorporation into prototype PECs. Indeed, the process is quite independent of substrate material, size and shape, unlike electrodeposition, for example.

B. Performance of CBD CdSe Photoanodes

1. CdSe/Polysulfide Cells

The performance of 1 cm^2 CBD CdSe on Ti as a photoelectrode in 1M Na_2S_2 , 1M NaOH electrolyte is described in Appendix A. High efficiency electrodes on Ti have been produced by the CBD method with open circuit photovoltages (V_{oc}) ranging from 0.5 to 0.7V, but with similar values of P_{max} (and hence, similar efficiencies of $\sim 6\%$). The processing variables affecting V_{oc} within this range have not yet been determined. Efficiencies are generally lower on stainless steel because of higher dark current losses, possibly relating to effects of pinholes. Preliminary results on ITO also indicate reduced efficiencies compared to Ti, but problems with adherence with increasing CdSe thickness have been encountered on this very smooth material. Table 1 summarizes the figures of merit of the best CBD-CdSe films on several substrates.

TABLE 1

FIGURES OF MERIT OF CBD CdSe FILMS. LIGHT SOURCE IS 100W
TUNGSTEN-HALOGEN LAMP WITH A MELLES GRIOT KG-2 FILTER.
ELECTROLYTE IS 1M Na₂S₂, 1M NaOH. NO STIRRING. T = 25°C.

Film	Light Intensity	j _{sc} (mA/cm ²)	V _{oc} (volts)	P _{max} (mW/cm ²)	Fill Factor	Efficiency η (%)
2.5μ CdSe on Ti	80 mW/cm ²	17.7	0.67	5.0	0.42	6.3
2.5μ CdSe on Ti	67 mW/cm ²	15.4	0.65	4.2	0.42	6.3
2.0μ CdSe on SS	70 mW/cm ²	12.5	0.34	1.9	0.45	2.7

2. CBD CdSe Electrodes in Aqueous Fe(CN)₆^{3-/4} Electrolyte

Frese (4) has reported high photovoltages and fill factors for n-CdSe in aqueous Fe(CN)₆^{3-/4} which they attribute to the fast electron transfer rate for this redox couple. They further claim that at pH 13 the stabilizing effect is at a maximum within the short times of their experiments (~5 min) and at intensities of 60-80 mW/cm².

We have tested three CdSe electrodes in this electrolyte at 40 and 80 mW/cm². The results are listed in Table 2 and the initial current voltage curves are shown in Figure 1. The 2.3μ thick CdSe film deposited by the CBD method gives results equivalent to the twinned crystal, i.e., η ≈ 10%. Similar CBD films in polysulfide at room temperature have efficiencies of about 5-6%. The electrodeposited (ED) film, though thicker, has an efficiency of only 3.8%, apparently due to pinholes, since the dark current-voltage curve looks similar to that of a metal electrode.

The opposing dark reaction in this electrolyte is also of high rate and not as "forgiving" as the dark reaction in polysulfide which is very sluggish on a titanium substrate. Thus, the ferri/ferrocyanide electrolyte is a good medium for the quick evaluation of the quality of thin film electrodes.

Photocurrent-time plots of the electrodes are shown in Figure 2. At 80 mW/cm², the short circuit photocurrent of the CBD film dropped steadily during three hours of operation to 55% of the original current. Renewing the electrolyte had no effect. The ED film behaved similarly, losing 24% over three hours. The twinned crystal was run for two hours at 40 mW/cm² and also suffered a loss of 36%. Presumably the decrease was due to anodic dissolution of CdSe to Cd²⁺ and Se⁰ which built up on the electrode surface. Red amorphous Se⁰ was observed only on the twinned crystal. The PEC parameters for all three electrodes after the photocurrent-time experiment are shown in Table 3. The thin film electrodes increased while the crystal electrode decreased in photovoltage.

TABLE 2
HALF CELL PEC PARAMETERS FOR n-CdSe ELECTRODES
IN AQUEOUS $\text{Fe}(\text{CN})_6^{-3/-4}$ at pH 3

<u>Electrode</u>	<u>Light Intensity</u> (mW/cm ²)	<u>V_{oc}</u> (volts)	<u>j_{sc}</u> (mA/cm ²)	<u>P_{max}</u> (mW/cm ²)	<u>ff</u>	<u>η</u> (%)
n-CdSe (ρ = 0.13)	80	-0.94	14.79	7.76	0.56	9.7
twinned crystal	40	-0.86	7.29	3.67	0.58	9.2
etched in 4:1 HCl:HNO ₃						
n-CdSe (CBD)	80	-0.87	16	7.91	0.56	9.9
2.3μ film on Ti	40	-0.87	8.51	4.36	0.59	10.9
etched 20 sec in 9M HCl						
n-CdSe (ED)	80	-0.89	11.98	3.05	0.29	3.8
4.1μ film on Ti	40	-0.84	6.37	1.74	0.33	4.4
etched 20 sec in 9M HCl						

TABLE 3
PEC PARAMETERS FOR n-CdSe ELECTRODES IN AQUEOUS $\text{Fe}(\text{CN})_6^{-3/-4}$
AT pH 13 AFTER X COULOMBS AT 80 mW/cm² ILLUMINATION

<u>Electrode</u>	<u>No.</u>	<u>V_{oc}</u> (volts)	<u>j_{sc}</u> (mA/cm ²)	<u>P_{max}</u> (mW/cm ²)	<u>ff</u>	<u>η</u> (%)
CdSe	79	-0.88	9.45	4.58	0.55	5.7
Twinned Crystal						
CdSe (CBD)	142	-0.94	7.48	4.45	0.64	5.6
CdSe (ED)	102	-0.91	8.7	-	-	-

Fig. 1. Half cell curve of merit of n-CdSe photoelectrodes at 80 mW/cm² W-I lamp intensity. Electrolyte: 0.5M K₄Fe(CN)₆; 0.05M K₃Fe(CN)₆ in 0.1N NaOH.

Fig. 2. Half cell short circuit photocurrent decay in aqueous $\text{Fe(CN)}_6^{3-/4-}$ at pH 13.
 — 2.3 μm CdSe CBD Film at 80 mW/cm^2 ; — — — 4.2 μm CdSe ED film at 80 mW/cm^2 ;
 — · — twinned CdSe crystal ($\rho = 0.13 \Omega\text{-cm}$) at 40 mW/cm^2 .

Additional experiments on the crystal electrode showed that when etched in aqua regia until a visible layer of Se^0 was formed, there was no change in photocurrent density or PEC parameters with time at 40 mW/cm². Because of the use of pyrex cells, the CTTS photoreaction of ferrocyanide

was not expected to occur. This was confirmed by use of a 515 nm cutoff filter which did not alter our results for the well etched single crystal.

C. Nonaqueous Electrolytes - Studies with Poly-GaAs

Two new high performance nonaqueous electrolytes have been examined during this reporting period: 1) the $\text{Cu}^+/\text{Cu}^{2+}$ redox electrolyte in CH_3CN , Cl^- solution and 2) the $\text{Fe}(\text{ClO}_4)_3/\text{Fe}(\text{ClO}_4)_2$ electrolyte in $\text{CH}_3\text{CN} \cdot x\text{H}_2\text{O}$ developed by Rockwell International (5). Our investigation during this period has centered around polycrystalline GaAs electrodes in these electrolytes.

The development of the $\text{Cu}^+/\text{Cu}^{2+}$ redox electrolyte is discussed in detail in Appendix B. In summary, the oxidation of Cu^+ becomes increasingly more facile with increasing complexing strength of the anion. The NO_3^- and ClO_4^- ligands are very weak in CH_3CN . However, the Cl^- ligand is tightly bound to the Cu^+ and Cu^{2+} ions. The CuCl_3^{-2} species, which predominates in a large Cl^- excess, oxidizes at +0.1V vs. SCE, sufficiently negative to stabilize n-GaAs against photocorrosion.

The principal advantages of this redox system are its high solubility and low light absorption. In 1M tetrabutylammonium chloride in CH_3CN , CuCl , the salt with limiting solubility is soluble to ~0.5M. The Cu^+ species have essentially no visible absorption, while the CuCl_4^- and CuCl_3^{-2} species absorb at $\lambda_{\text{max}} \approx 450$ nm, $\epsilon_{\text{max}} \approx 2 \times 10^3$. The concentrations are high enough to carry the significant current densities necessary for practical PEC operation. For polycrystalline GaAs at 80 mW/cm² solar intensity, our best figures of merit to date are $j_{\text{sc}} = 19$ mA/cm², $V_{\text{oc}} = 0.74$ V, $P_{\text{max}} = 3.78$ mW/cm², $\text{ff} = 0.27$ and $\eta = 4.8\%$. At 8 mW/cm², the efficiency is 8.1%, due primarily to an improved fill factor at the lower current density ($\text{ff} = 0.55$).

The same polycrystalline electrodes were investigated in an electrolyte containing 1.95M $\text{Fe}^{\text{II}}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, 0.05M $\text{Fe}^{\text{III}}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, 0.5M tetrabutylammonium perchlorate in CH_3CN . Typical half-cell j-V scans in the dark and under 80 mW/cm² illumination are shown in Figure 3, giving an energy conversion efficiency of around 7%. In the dark, the n-GaAs has an open circuit voltage of ~-0.4V vs. V_{redox} , indicating a significant corrosion process. A further indication of corrosion is a reduction in cell efficiency after 30 min operation under short circuit conditions at 80 mW/cm² illumination. As seen in Figure 3, this is due primarily to a decrease in short circuit current, possibly indicating a decrease in surface area or the growth of a resistive surface layer.

Fig. 3. Half cell curves of merit of polycrystalline n-GaAs photoelectrode at 80 mW/cm² W-I lamp intensity. Electrolyte is Fe^{+3/+2} in wet CH₃CN. Broken line was recorded after 30 minutes operation at short circuit. V_{oc}(photo) = 1.07 and 1.09V, for solid and broken line curves, respectively.

A comparison of the two electrolytes indicates that each has its advantages and shortcomings. While the Cu-electrolyte results in stable photocurrents over at least 4 hours operation at 10 mA/cm², significant decreases are observed for the GaAs/Fe^{+2/+3} system over shorter times. However, the high V_{OC} and fill factor of the Fe^{+2/+3} cell results in a higher efficiency, probably arising from extremely favorable electrokinetics.

III. DESIGN, CONSTRUCTION AND TESTING OF PRACTICAL CELL STRUCTURES

A. Development of Laser Spot Scanning as a Diagnostic Tool for PECs

A laser spot scanner has been constructed for the diagnosis of photoelectrode surfaces as well as of configurational variables in practical devices. Both He-Ne and tunable dye laser light sources have been employed. The system and some initial applications are described in Appendix C. To date, we have used the scanner in the following experiment.

- Documentation of the positive effects of anodization, HCl etch and ZnCl_2 treatment on the photoresponse of n-CdSe electrodes.
- Separation of photocurrent arising from subband gap excitation and from band-to-band excitation using scanning light sources of different wavelengths.
- Employed time-resolved laser spot scanning to trace out areas of high trap density on the photoelectrode surface.
- Used spot scanning to identify areas of high loss (reduced efficiency) in sealed practical devices (see below).

B. Practical Cell Studies

During this reporting period various large area photoelectrode designs were tested for their performance capabilities. Four of the five designs tested were illustrated in a previous report (2). The fifth design, referred to as the "basket weave," is illustrated in Figure 4. The basket weave design features good electrolyte access between electrodes without suffering from the loss of photoactive area due to the presence of holes or slots.

The five photoelectrodes of different geometries were prepared at the same time by the CBD method. All gave similar results in a half cell at 20 mW/cm^2 indicating that the deposits were of similar quality (see Table 4A). The electrodes were then placed in the restricted geometry of a $3 \times 5 \text{ cm}$ plexiglass cell with a CoS coated Ni-exmet counter electrode behind the photoelectrode. The cells were filled with aqueous polysulfide electrolyte and sealed. Their respective performance characteristics were measured at 20 mW/cm^2 tungsten-halogen lamp intensity and at 63 mW/cm^2 in sunlight. In addition, photocurrent laser scan maps were recorded using a He-Ne laser. The results are shown in Table 4B and 4C

Fig. 4. Basket weave cell.

TABLE 4

CdSe PHOTOELECTROCHEMICAL SOLAR CELLS
Chemical Bath Deposited Films
Cell Area: 15 cm²

Design	V _{oc} (volts)	j _{sc} (mA/cm ²)	P _{max} (mW/cm ²)	V _{Pmax} (volts)	ff	0.4 I _{d.c.} (mA/cm ²)	η (%)
A. 20 mW/cm ² Tungsten Halogen (Half Cell)							
I. Perpendicular* Counter	0.49	3.6	0.83	0.31	0.47	-0.5	4.1
II. Slant Louver	0.48	3.7	0.86	0.30	0.48	-0.6	4.3
III. Planar Perforated	0.49	3.6	0.83	0.31	0.47	-0.5	4.1
IV. Corrugated Perforated	-	-	-	-	-	-	-
V. Basket Weave	0.46	4.3	0.88	0.30	0.44	-1.0	4.4
B. 20 mW/cm ² Tungsten Halogen (Full Cell)							
I. Perpendicular Counter	0.38	2.3	0.40	0.27	0.46	-1.5	2.0
II. Slant Louver	0.43	3.5	0.78	0.28	0.50	-0.5	3.8
III. Planar Perforated	0.41	4.9	0.83	0.24	0.41	-0.9	4.1
IV. Corrugated Perforated	0.40	2.9	0.60	0.26	0.52	-1.0	3.0
V. Basket Weave	0.42	4.1	0.86	0.27	0.50	-0.7	4.3
C. 10 a.m., Sunday, October 7, 1981, Newton, MA - 18°C 63 mW/cm ² Insolation (Full Cell)							
I. Perpendicular* Counter	0.51	8.2	1.92	0.32	0.46	-1.5	3.0
II. Slant Louver	0.55	9.1	2.24	0.32	0.45	-0.5	3.6
III. Planar Perforated	0.55	13.1	2.42	0.33	0.34	-0.9	3.8
IV. Corrugated Perforated	0.44	8.1	1.80	0.30	0.50	-1.0	2.9
V. Basket Weave	0.50	12.0	2.70	0.32	0.45	-0.7	4.3

* 10 cm² cell.

and Figures 5-9. It should be noted that the experiment was run at 18°C, and higher efficiencies can be expected at 50°C.

Conclusions regarding each of the formats tested:

I. Perpendicular Counter Electrode - $\eta = 3\%$ at 63 mW/cm²

The electrode surface appeared to have been damaged while transferring the electrode from the half cell to the solar cell. The increased dark current and the many pinholes apparent from the scan map suggest this to be so. The large dead area caused by the slots through which the counter electrode projects may limit the utility of this format. It should be tested again with a pinhole-free electrode.

II. Slant Louver Electrode - $\eta = 3.6\%$ at 63 mW/cm²

This is a new design in which the louvers slightly overlap to maximize light absorption area. As a result, the scan map shows very little loss area compared to an earlier design discussed in a previous report (2). The low dark current shows that this design does not suffer from the large edge to surface ratio and that it may be possible to decrease the width of the louvers and the angle of bend still further to reduce iR drop between photo and counter electrode.

III. Planar Perforated Electrode - $\eta = 3.8\%$ at 63 mW/cm²

This is the simplest of all electrodes to construct. It has the highest photocurrent density (13.1 mA/cm²) and the lowest fill factor of the group. The low fill factor may be improved by increasing the number of holes and decreasing their size and by increasing the electrolyte volume between the electrode and the cell window. In this particular model, the photoelectrode was very close to the window and the polysulfide flow was restricted. Polysulfide access is necessary to carry out the reaction

the rate of which is known to have an effect on the fill factor in these cells.

IV. Corrugated, Perforated Electrode - $\eta = 2.9\%$ at 63 mW/cm²

Flattened, this electrode was twice the area of the planar electrode, III, yet it produces only 61% of the short circuit

Fig. 5. Photocurrent scan of Cell I - perpendicular counter electrode.

Fig. 6. Photocurrent scan of Cell II - louvered electrode.

Fig. 7. Photocurrent map of Cell III - planar perforated electrode.

Fig. 8. Photocurrent scan across corrugations of Cell IV - corrugated perforated electrode.

Fig. 9. Photocurrent scan of Cell V - "basket weave" electrode. A series of alternating over- and underlying slats.

current. It was bent into large corrugations resulting in three valleys and two hills with the hills being close to or perhaps touching the cell window. The holes were located on the sides of the hills. This cell had the largest fill factor (0.50), probably due to the low current density. The scan map which was produced by scanning across the corrugations shows a definite loss at the hill tops which again may be attributed to lack of access to sufficient volumes of electrolyte. The highest photocurrent occurs in the valleys where electrolyte volume is not restricted. Another electrode with smaller corrugations should be tested. This electrode may prove particularly effective under high light flux.

V. Basket Weave Electrode - $\eta = 4.3\%$ at 63 mW/cm²

The newest design gives the best overall performance. There are no loss areas due to performance or slots and the losses due to shadowing of the lower plates by the upper plates are minimal. The slots are essentially hidden by the upper plate.

IV. FUTURE WORK

The following experiments are either planned or in progress, and will be reported for the next semiannual period:

- A project of computer modeling and analysis of ionic transport in photoelectrochemical cells has been initiated, and the results will be used as a guide in cell design.
- Further experiments are being conducted on CBD-CdSe, including:
 - a) Capacitance measurements, to determine N_D and the Fermi level energy, to correlate with V_{oc} .
 - b) Thermionic emission analysis of dark currents in $Fe(CN)_6^{-3/-4}$ and S_x^{-2} electrolytes, to compare barrier heights and correlate with V_{oc} .
 - c) Analysis of the effects of CdS and Se overlayers, produced electrochemically or by CBD, on the efficiencies of lifetimes of CBD-CdSe photoelectrodes in $Fe(CN)_6^{-3/-4}$ electrolytes.
- Extended lifetime tests are being conducted for sealed cells subject to diurnal cycling.
- Several high power panels of sealed PECs connected in series are being constructed and tested.

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APPENDIX A

PAPER SUBMITTED TO
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CHEMICAL BATH DEPOSITION OF THIN FILM CADMIUM
SELENIDE FOR PHOTOELECTROCHEMICAL CELLS

CHEMICAL BATH DEPOSITION OF THIN FILM CADMIUM
SELENIDE FOR PHOTOELECTROCHEMICAL CELLS

R. A. Boudreau and R. D. Rauh*
EIC Laboratories, Inc., 111 Chapel Street, Newton, MA 02158

ABSTRACT

Chemical bath deposition provides an attractive, low cost method of producing cadmium chalcogenide thin films. Intimate contact between the bath solution and the substrate material permits uniform deposition on substrates of complex geometry, presently difficult with spray pyrolysis, vacuum evaporation, or electrodeposition techniques. For CdSe, rigorous control of deposition conditions promotes the formation of a hexagonal, specularly reflecting deposit rather than a less desirable sphalerite (cubic) powdery deposit. Scanning electron microscopy reveals a small grained layered plate morphology similar to that produced by the evaporation method. Specularly reflecting CdSe films can be formed over large area substrates at a thickness optimal for their use as photoelectrochemical cells (PEC). Employing polysulfide as the redox couple, conversion efficiencies as high as 6.8% have been achieved in our laboratory for these films using a tungsten-halogen white light source.

INTRODUCTION

Cadmium selenide has shown great promise as a semiconductor material for photoelectrochemical solar cells (PECs) (1,2). In aqueous polysulfide electrolytes, solar conversion efficiencies of 8.4% (3) and 6.5% (4) have been reported for single crystal and vacuum evaporated thin film CdSe,

*Electrochemical Society Active Member.

Key Words: chemical bath, cadmium selenide, thin film, photoelectrochemical cell.

respectively. CdSe thin films for PECs have also been prepared by spray pyrolysis (5) and electrodeposition (6). In a recent communication (7), we demonstrated that PEC devices could be fabricated with CdSe films derived from a chemical bath method. Pursuing further refinements of the deposition process, we have found that this method produces CdSe films yielding cell efficiencies comparable to any of the other methods, but that careful control of plating conditions were necessary for achieving reproducibility of morphology and photovoltaic properties. Compared to the other methods, the bath process is uniquely suited for depositing a uniform film over large substrates of complex geometry, as might be found in production scaled solar panels. The substrate need not be conductive, have a high melting point, or be combustion resistant. Film formation is truly a deposition of CdSe rather than a codeposition of separate elements. Chemical bath deposition (CBD) is a low technology process, requiring no high vacuum, high power supply, or expensive equipment.

The chemical bath method has been used in the past to make polycrystalline films of PbSe (8,9), ZnSe (10), CdSe (9) and CdS (11). In each case, thin film formation proceeds simultaneously with the precipitation of the respective chalcogenide. The precipitation is controlled by slowly generating ions that are in equilibrium with a chalcogenide precursor and a cation complexing agent, usually NH_3 . The reactions are highly dependent on temperature and complexing agent concentrations. For the case of cadmium chalcogenides, the following reactions apply:

For CdSe, the compound AX is either sodium selenosulfite (Na_2SeSO_3) or selenourea. The symbol A' represents the oxidized counterpart to AX, while X represents the appropriate chalcogen. Reactions (1) and (3) provide for slow generation of reacting ions. Ammonia complexation prevents the precipitation of excess $\text{Cd}(\text{OH})_2$ in the alkaline media.

The CdSe CBD process, as originally engineered by Kainthla and co-workers (9), was not addressed at the reproducible preparation of efficient photoelectrochemical films. Attempts to use the process directly in photoelectrode fabrication leads to several problems including: (a) the deposition of films having a terminal thickness too low for efficient solar collection, (b) the deposition of weakly photoactive, poorly structured films, and (c) the uncontrolled evolution of NH_3 during deposition, making conditions difficult to reproduce. The work described below addresses these problems, further refining CBD as a process for producing large area CdSe semiconducting films which yield efficient photoelectrochemical devices.

EXPERIMENTAL PROCEDURES

All chemicals were reagent grade. Titanium and stainless steel substrates were prepared by abrading with emory cloth and cleaning with chromic acid. Indium tin oxide (Nesatron) conductive glass substrates ($\rho = 8\Omega/\square$) were prepared by cleaning in dilute HCl. CdSe film thickness

was determined by weighing, using the literature density and the geometric area of the deposit. Photoelectrochemical evaluation of the films was carried out in an aqueous polysulfide electrolyte (1M NaOH, 1M Na₂S, 1M S).

All current-voltage measurements were made using a Wenking LT 73 potentiostat coupled with a ramp function generator and X-Y plotter. Counter electrodes consisted of CoS coated Ni screen or CuS coated brass (12). Solar radiation was simulated with a 100W tungsten halogen lamp employing a KG2 Melles Griot infrared filter. Half cell electrochemical potentials were determined versus a platinum wire reference. Full cell measurements were made by connecting the high performance counter electrode to both the counter and reference inputs of the potentiostat. Light intensities were calibrated and measured using an EG&G Model 450-1 Radiometer.

CdSe Deposition. The deposition bath was prepared by mixing 30 ml of 0.13M Na₂SeSO₃ reagent, 1.0 ml of 7M NH₄OH and 3.0 ml of 0.5M Cd(CH₃COO)₂ in that order. The sodium selenosulfite reagent was freshly prepared by filtering a 500 ml solution containing 95g of Na₂SO₃ and 5g of finely powdered amorphous black Se that had been stirred for several hours at exactly 65°C under nitrogen bubbling to dissolve the selenium. The excess Na₂SO₃ enhanced the Se dissolution rate, and had little discernible effect on the resulting films. After mixing, the deposition bath turned yellow in color, probably indicating the onset of colloidal CdSe precipitation.

The abraded and cleaned substrates to be used for CdSe deposition were soaked in a warm paste of Cd(OH)₂ for 5 minutes and lightly rinsed

in distilled water just before use. The substrates were added, and the bath solution was heated rapidly in a stoppered glass container with a 90°C constant temperature bath. While heating, the deposition bath developed a red CdSe precipitate. Occasionally, the bath was swirled to prevent the precipitate from adhering to the substrate. By placing the substrate in the bath so that the desired face of the substrate pointed downward, precipitate adherence was minimized. After 30-60 minutes of deposition, the CdSe film appeared as a transparent red coating on surfaces exposed to the bath. The substrates were then removed from the bath, rinsed with distilled water, and heat treated for 15 minutes at 500°C.

Following the heat treatment, which improved film adherence, the substrates were treated again with $\text{Cd}(\text{OH})_2$ paste, rinsed, and plated again. No intervening heat treatments were necessary for subsequent depositions to sustain film adherence. After the final deposition, a final heat treatment of 550°C for 30 minutes in air was used to activate the films. Air was a necessary ingredient for the heat treatment, and higher heat treatment temperatures resulted in excessive film vaporization and damage while lower temperatures resulted in incomplete film restructuring and lower photoresponse. The heat treatments converted the reddish films to a dark grey color. Following the final annealing, the CdSe films were etched for 20 seconds in 9M HCl at room temperature and rinsed. A post etch treatment to reduce dark current losses consisted of dipping the electrode in 1M ZnCl_2 (13), allowing the zinc solution to dry on the electrode, and then rinsing with distilled water.

The ammonia concentration and reagent freshness were critical to good film formation. If a yellow color did not form in the solution prior to heating, the ammonia concentration was too high, but if excessive white $\text{Cd}(\text{OH})_2$ precipitated, the concentration was too low.

CBD Process Optimization. The procedure of Kainthla and co-workers (9) for bath deposition of CdSe was carried out in an open vessel and employed a large excess of NH_4OH . This excess gives rise to an induction period for CdSe precipitation, while enough NH_3 evaporates from the hot bath to allow the release of some Cd^{+2} ions. No deposit forms if the vessel is sealed.

Using the published procedure (9), the resulting films were, in our hands, of irreproducible morphology, which may be related to an uncontrolled NH_3 effusion rate. The deposits were sometimes specular and sometimes powdery in nature. On glass substrates, the as-deposited specular films appeared clear red or orange in transmitted light and shiny dark brown in reflected light. In contrast, the powdery films appear translucent pink in transmitted light and light brown in reflected light. After annealing, the mechanically softer powdery deposits appeared flat black and etched rapidly in HCl , while the specular films possessed a metallic sheen and etched slowly. The electron micrograph in Figure 1A shows that the specular deposits are large grained and exhibit widely spaced cracks. The electron micrograph of a powder deposit, Figure 1B, reveals smaller grains and smaller cracks.

In order to remove the NH_3 effusion step and bath contact with the open atmosphere, further experiments were conducted in sealed tubes. The

A

B

Fig. 1. Scanning electron micrographs of chemically deposited CdSe. Sample annealed at 500°C for 15 minutes in air. Magnification, 2500X. A) Specularly reflecting deposit; B) Powdery deposit.

bath composition was held constant except for the NH_4OH concentration, which was varied from 2M to below 0.1M. The deposit began to appear at $\sim 1.5\text{M}$ NH_4OH , gradually thickening as the NH_4OH concentration was lowered. At the higher NH_4OH concentrations, the powdery morphology was observed. Only below $\sim 0.3\text{M}$ NH_4OH did the desired transparent red deposits occur in these sealed tubes. Our modified procedure employs 0.2M NH_4OH , at which concentration a small amount of $\text{Cd}(\text{OH})_2$ precipitate forms at room temperature.

Even with the optimized bath composition, substrates that were not thoroughly cleaned often developed inhomogeneous mixed powder and specular deposits. Homogeneous specular deposits could be enhanced by pretreating the substrates with a paste of $\text{Cd}(\text{OH})_2$. It has been suggested by Kainthla and co-workers (9) that $\text{Cd}(\text{OH})_2$ provides nucleation sites for CdSe , and promotes the formation of hexagonal over the thermodynamically less favorable cubic crystal structure.

Adapting the process for producing films of thickness >1 to 2μ is, of course, critical to photovoltaic application. It was found that by carrying out the deposition in sealed tubes at 90°C with a stoichiometric excess of Na_2SeSO_3 , an optimized average growth rate of $\sim 0.02\mu/\text{min}$ could be achieved without adversely affecting the specular morphology. Under these conditions, the bath becomes depleted of active reagents in ~ 20 min due to competing homogeneous CdSe precipitation. Thus, the deposit could, in principle, be continually thickened by periodically renewing the reagents. Figure 2 shows how the thickness of the CBD film develops with successive depositions, with intervening anneals. The heat treatments

Fig. 2. Thickness of CBD CdSe film following successive depositions with intervening heat treatments at 500°C.

are most important in the early depositions, as they not only improve film adherence, but also photovoltaic activity.

CdSe Photoelectrochemical Cells - Employed as a photoelectrode in polysulfide, half cell characteristics for 1 cm² CdSe films were measured as a function of deposit thickness. Figure 3 shows that for films on titanium substrates at 57 mW/cm² insolation, solar conversion efficiency increases linearly with thickness up to a thickness of 2.5 microns. The output voltages were typically 0.1V higher than voltages observed for films prepared by other techniques, although voltages were highly dependent on film morphology (see below). Deposits on stainless steel displayed open circuit voltages ~0.1V lower than comparable films on titanium, primarily as a result of increased cathodic dark current. Deposits on stainless steel and titanium showed little difference in their short circuit photocurrents. The best films to date, possessing an area of 1 cm², displayed a conversion efficiency of 6.8% at 50 mW/cm² insolation on titanium at room temperature.

Figure 4 shows half cell characteristics for a typical 1 cm² electrode as a function of light intensity. The efficiency increased as the light intensity was reduced until a point was reached where the cathodic dark current proportionately contributed a large influence. Concentration polarization or a limiting dissolution rate of anodically formed neutral sulfur decreased the photoanode efficiency at high light intensities.

Deposit structure and morphology were critical to the performance of these films. The powdery films display very high cathodic dark currents

Fig. 3.. Effect of film thickness on photoelectrochemical cell characteristics of chemical bath deposited CdSe on Ti. Test conditions: 67 mW/cm² tungsten-iodide lamp with KG-2 filter, unstirred aqueous polysulfide (1M NaOH, 1M Na₂S, 1M S), room temperature.

Fig. 4. Half cell current-voltage characteristics for a 1 cm^2 CBD CdSe deposit on Ti as a function of light intensity. Test conditions: tungsten-iodide lamp with KG-2 filter, unstirred aqueous polysulfide, room temperature.

and consequently low solar conversion efficiencies. One typically observed a dark current of $\sim 5 \text{ mA/cm}^2$ for powdery deposits as compared to $\sim 1 \text{ mA/cm}^2$ for specular deposits at -0.4V vs. Pt/redox. The difference may arise from the film defects or differences in surface area. The observed dark current losses represent a catalyzed reduction of polysulfide by the CdSe deposit. The reduction is represented by:

The catalysis mechanism is presumably similar to that operating at the surface of the CoS and CuS counter electrodes when the current is flowing in the normal direction for generating power (13). When bare Ti substrates were measured in place of the photoelectrodes, there was only about 0.1 mA/cm^2 of dark current. The poor catalytic behavior of bare Ti probably explains why we observe essentially no detrimental effects arising from the presence of pinholes on Ti. The PEC is thus more "forgiving" to the effects of pinholes than would a solid state photovoltaic device.

The use of conducting glass substrates enabled the construction of chemically deposited backwall PECs. These PECs operated by illuminating the semiconductor through the transparent substrate material rather than from the top. Backwall PECs possess the advantage of allowing the use of stabilizing opaque electrolytes such as polysulfide selenide and permits the counter electrode to be placed very close to the semiconductor electrolyte interface. The CdSe backwall cells of 4 cm^2 area and $\sim 1.5 \mu$ film thickness produced 8 mA/cm^2 short circuit current and an open circuit voltage of $\sim 0.4\text{V}$ vs. Pt/redox under 67 mW/cm^2 insolation with polysulfide electrolyte. The beneficial acid etch and zinc treatments were not employed

as they tended to shear the deposits from the very smooth conductive glass.

The CBD method is useful for homogeneously coating large area electrodes with irregular surfaces, as might be found in practical photoelectrochemical cell designs. Preliminary measurements on CBD CdSe/polysulfide cells possessing photoelectrodes of 100 cm² area resulted in measured efficiencies that were about half those found for 1 cm² electrodes. Losses appear to relate to restricted ion flow to some segments of these large electrodes, and to the impedance of electrode structure itself. The design and scaling of practical photoelectrochemical cells will be a subject of a future publication.

SUMMARY

The procedure of Kainthla and co-workers (9) for the chemical bath deposition of CdSe has been modified to produce high efficiency photoanodes for photoelectrochemical solar cells. These modifications include (a) operation at a lower NH₄OH concentration in a sealed cell, to improve morphological reproducibility; (b) employing a Cd(OH)₂ substrate coating, to promote specular deposits of hexagonal crystal structure; (c) depositing at a higher temperature and with excess Na₂SeSO₃, to improve the deposition rate; and (d) layering successive deposits to achieve practical film thicknesses. Using the modified procedures, CdSe films on Ti substrates may be routinely produced which yield >6% solar conversion efficiencies in photoelectrochemical cells with a polysulfide electrolyte.

ACKNOWLEDGMENT

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APPENDIX B

PAPER PRESENTED AT THE
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PHOTOELECTROCHEMICAL CELLS BASED ON n-GaAs AND THE
Cu(II)/Cu(I) REDOX COUPLE IN ACETONITRILE

PHOTOELECTROCHEMICAL CELLS BASED ON n-GaAs AND THE
Cu(II)/Cu(I) REDOX COUPLE IN ACETONITRILE

M. E. Langmuir, M. A. Parker and R. D. Rauh
EIC Laboratories, Inc., 111 Chapel Street, Newton, MA 02158

ABSTRACT

In acetonitrile, the potential of the Cu(II)/Cu(I) redox couple is very dependent on the coordinating strength of the anion present. In the presence of perchlorate or nitrate, the potential is not within the GaAs band gap, and the redox couple does not stabilize GaAs with respect to photodecomposition. Chloride ion, which coordinates with both cations, shifts the potential within the gap and stabilization of the semiconductor can be obtained. It is important that Cu(II) be present as the tetrachloro complex to prevent loss of Cu(II) from the PEC by a photoreduction to Cu(I). Present conversion efficiency for a poly-GaAs electrode in Cu(II)/Cu(I) tetrabutylammonium chloride, acetonitrile electrode at 80 mW/cm² is 4.8%.

INTRODUCTION

The use of nonaqueous electrolytes in photoelectrochemical cells has some promise for extending the voltage range of stabilizing redox species beyond that possible in water. Numerous examples exist where redox couples incapable of sustaining stable photocurrents at semiconductor/aqueous liquid junctions are capable of stabilizing the semiconductor in acetonitrile (1,2), propylene carbonate (3) or alcoholic electrolytes (4,5).

The strong solvation (or solvent coordination) of the Cu(I) ion renders it much more stable in acetonitrile than in water. The fact that the oxidizing power of Cu(II) salts in CH₃CN decreases with increasing complexing strength of the anion is well known and agrees well with the formal potentials given in Table 1 for the Cu(II)/Cu(I) couple in the presence of ClO₄⁻, NO₃⁻ and Cl⁻. The Cu(II) perchlorate salt is soluble in acetonitrile up to 0.2M, but is virtually undissociated at room temperature while the Cu(I) perchlorate salt is totally dissociated (6). With NO₃⁻, only Cu(II) forms a complex (7) and with Cl⁻ a number of chloro complexes are possible for both oxidation states. The stepwise formation constants and extinction coefficients of the four Cu(II) and two Cu(I) complexes generally found to be stable in acetonitrile are given in Table 2 (8).

In this paper, we present studies of the requirements for stabilization of the n-GaAs photoelectrode by the Cu(II)/Cu(I) redox couple in acetonitrile.

EXPERIMENTAL PROCEDURES

Materials. Semiconductor electrodes were prepared as previously described (1) from large grain polycrystalline GaAs naturally doped n-type with $N_D = 8 \times 10^{16} \text{ cm}^{-3}$, obtained from Laser Diode Corp. The crystal was matte etched in 1:1 $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ before each use.

Electrolyte solutions were prepared under Ar in a Vacuum-Atmosphere dry box using Burdick and Jackson (UV) acetonitrile ($<0.004\%$ H_2O) without further purification. Solutions of anhydrous nitrate and perchlorate salts of Cu(I) were prepared by quantitative reaction of pure copper metal with the corresponding anhydrous silver salts. Cu(I) chloride solutions were prepared directly from the anhydrous CuCl salt (99.9% pure, Alfa). The Cu(II) salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and supporting electrolytes, TMAC, TEAC, TBAC (Southwestern Chemical) and TBAP were vacuum dried at 70°C for several days before storage in the dry box. The total dryness of the chloride salts was confirmed by titration of weighed samples with standard AgNO_3 solution.

Concentrations of the various Cu(II) chloride complexes in the electrolyte solutions were determined spectrophotometrically. Potentials of the redox couples were measured with a Hewlett-Packard high impedance voltmeter on a Pt electrode versus a 0.01M AgNO_3 (CH_3CN)/Ag reference electrode (E° vs. $\text{SCE}_{\text{aq}} = +0.273\text{V}$) (11). Photoelectrochemical cell measurements were made in a cell described elsewhere (1) in which the current-voltage characteristics could be measured as a half-cell using a Pt wire pseudoreference electrode, or as a two-electrode "solar cell." Stirring could be provided if desired. All current-voltage curves were recorded at a scan rate of 20 mV/cm^2 unless otherwise stated.

The light source for PEC measurements was a 100W tungsten halogen lamp with a Pyrex collimating lens system and KG-2 infrared filter. This system closely approximates the AML spectrum. Intensity was measured with an EG&G Radiometer calibrated with an Optronics Laboratories, Inc. standard tungsten halogen lamp. Intensity was varied by use of neutral density filters. All intensities are reported as intensities at the cell face and are not corrected for cell reflectance or solution absorbance.

RESULTS AND DISCUSSION

Results of initial experiments with the Cu(II)/Cu(I) redox couple in acetonitrile are shown in Table 3. With no redox couple present, the photocurrent decayed rapidly due to the formation of an insoluble oxidation product on the GaAs surface. Similar behavior was found in the presence of the perchlorate and nitrate electrolytes. However, in the saturated TMAC solution of the copper chlorides, which contained $\sim 0.1\text{M}$ Cl^- , the photocurrent remained steady even without stirring at low light intensity and at higher intensity could be maintained with

stirring. This indicated that the Cu(I) chloride species was competing effectively for holes at the photoelectrode at low intensity, but that at high intensity the Cu(I) oxidation was mass transfer limited due to its low concentration. The observation of a brown oxidation product (CuCl_2 or CuCl_3^-) streaming from the GaAs surface confirmed this interpretation of the initial observations. To increase the concentration of Cu(I) in solution, it was necessary to find a chloride source which was more soluble in acetonitrile than TMAC. Tetrabutylammonium chloride (TBAC) proved satisfactory, being soluble to more than 2M. The solubility at 25°C of CuCl in 1M TBAC was determined to be 0.43M. Most solutions for the subsequent photoelectrochemical cell (PEC) measurements were prepared as 0.4M CuCl and 1M TBAC with varying concentration of anhydrous CuCl_2 added.

At $\text{Cl}^-:\text{Cu(I)}$ concentration ratios of 2-100, the major Cu(I) species is known to be $[\text{CuCl}_2\text{L}_2]^-$.^{*} Addition of CuCl_2 to make the solutions 5-100 mM in Cu(II), resulted in the mixture of Cu(II) chloro species shown in Figure 1A as determined spectrophotometrically, and the change in redox potential shown in Figure 1B. The shift of the redox potential to more negative values as the concentration ratio of $\text{CuCl}_4^{2-}:\text{CuCl}_3^-$ increased, reached a minimum at +0.07V vs. SCE_{aq} . This equilibrium rest potential is well within the n-GaAs band gap, as shown in Figure 2, and allows stabilization of the photoelectrode.

The photoanode reaction in these solutions is presumably reaction (1),

followed by the relatively slow solvent displacement by chloride ion (reactions (2) and (3)) to give the equilibrium Cu(II) chloro species according to the stepwise formation constants given in Table 2.

The counter electrode reactions must be reduction of the CuCl_3^- and/or CuCl_4^{2-} to the corresponding tri- and tetrachloro Cu(I) species, followed by rapid displacement of Cl^- by acetonitrile to give the equilibrium Cu(I) species, i.e., CuCl_2^- :

* $\text{L} = \text{CH}_3\text{CN}$. In all copper complexes in acetonitrile, L coordinates through the nitrile nitrogen to the copper ion in competition with the other ligands. The copper ions are always tetrahedrally coordinated, and L takes up the positions not occupied by Cl^- . For simplicity, we have omitted the L from the ion notation except when absolutely necessary for clarity.

Evidence for reactions (1 through 7) comes from polarographic data (12) and from cyclic voltammograms taken at scan rates as high as 11V/sec (13). At very fast scan rates, it was possible to detect the tri- and tetrachloro Cu(I) species by their reductions to Cu^0 at peak potentials (E_p) $\approx$ -1.8 and -2.6 volts vs. Ag^+/Ag , respectively, in a solution which initially contained only CuCl_4^- and excess chloride. For the CuCl_2^- species, E_p for reduction to Cu^0 lies at -1.1 volts. At slow scan rates (20 mV/sec), this reduction peak and the corresponding stripping peak are found in the voltammograms. However, at scan rates greater than 5 V/sec and a negative limit of -1.5V, they are no longer detectable, because the equilibria (6) and (7) cannot occur before the reduction to Cu^0 . The stripping peak is found again when the negative limit is set beyond the cathodic peaks for CuCl_3^{-2} and CuCl_4^{-3} .

Because of the equilibria following the electron transfer reactions, for both anodic and cathodic reactions, the electrolyte system may be considered electrochemically "nonreversible"; however, the whole system is chemically reversible and completely regenerative in the dark and in the absence of oxygen.

PEC parameters were determined using the solutions of the compositions shown in Figure 1A. Figure 3A shows a typical linear short circuit current versus intensity plot for the n-GaAs/Cu(II/I) chloride half cell. At the concentrations shown, the half cell did not appear to be mass transfer limited. Also typical was the linear increase in open circuit photovoltage with log intensity shown in Figure 3B. At 80 mW/cm² light intensity on the cell face, the flat band potential was not reached (see also Figure 1). If the energy levels are correct, the V_{oc} should reach about 1V at saturation. Figure 4, which illustrates a series of current-voltage curves at different intensities, shows decreasing power conversion efficiencies with increasing light intensity, primarily resulting from decreasing fill factors (0.34 at 80 mW/cm² and 0.55 at 8 mW/cm² irradiation). This decrease is true of many other semiconductor/electrolyte PEC cells and is due to the many interacting factors which affect the fill factor adversely at high light intensities, i.e., diffusion of the electroactive species to the site of the photohole, electron transfer rate, diffusion of the product away from the semiconductor surface to avoid the reverse dark reaction, etc.

We have also compared half cell PEC parameters at 80 mW/cm² for our poly n-GaAs electrode in (0.8M saturated Na_2Se , 0.1M Na_2Se_2 , 1M NaOH) electrolyte and in the 0.4M Cu(I), 0.05M Cu(II), 1M TBAC in acetonitrile and found that the matte-etched electrode gave the same value for power

conversion efficiency ($\eta = 4.8\%$). In the case of the polyselenide, the V_{oc} and short circuit were smaller but the fill factor was greater. Ruthenium ion treatment (14) increased the η to 6.8% for the polyselenide electrolyte but had no effect on the PEC parameters in the acetonitrile electrolyte.* Apparently the rate of electron transfer or mass transfer in the latter case is not fast enough to take advantage of the increased effective lifetime of photoholes caused by ruthenium adsorption at recombination sites (15).

Determination of Stability. The half cell short circuit current as a function of time was studied under a variety of conditions to determine the stability of the GaAs to photodecomposition in the electrolyte. In solutions where $CuCl_4^{2-}$ was the dominant Cu(II) species, the photocurrent at 0 to 80 mW/cm² AM1 insolation was quite stable over a four hour period. However, in solutions where the $CuCl_3^-$ concentration was significant, one of two things occurred: i) the short circuit current increased with time as the solution absorbance due to Cu(II) species decreased. Eventually the Cu(II) concentration was so small that the reduction of Cu(I) to Cu⁰ became the dominant reaction at the platinum counter electrode rather than the reduction reactions (4) and (5). At the same time, brown $CuCl_2$ or $CuCl_3^-$ could be seen streaming from the photoanode; or ii) after a period of steady photocurrent, the short circuit photocurrent decreased while a reddish-brown film grew on the face of the GaAs crystal.

Cu(II) Loss. The disappearance of Cu(II) chloride species in the first case was due to photoreduction of the $CuCl_3^-$ species in acetonitrile solution according to reaction (8) which has recently been investigated

by pulsed laser photolysis (16) and by introduction of chloro radical scavengers into the solution (17). Following absorption of a photon, the charge transfer to metal (CTTM) occurs with homolytic cleavage of the metal-chlorine bond.

In the presence of free chloride ion, chloro radical is formed:

Cl_2^- does not react with acetonitrile (18) nor does it undergo its usual bimolecular reaction (10),

* In the polyselenide electrolyte, the following figures of merit were obtained at 80 mW/cm²: No Ru treatment, $V_{oc} = 0.60V$, $j_{sc} = 14.5$ mA/cm², $ff = 0.44$, $\eta = 4.8\%$; with Ru treatment, $V_{oc} = 0.73V$, $j_{sc} = 14.1$ mA/cm², $ff = 0.53$, $\eta = 6.8\%$.

in acetonitrile since no second order decay process was found for $\text{Cl}_2^{\cdot -}$ disappearance (19). Rather, it may (a) reoxidize Cu(I) to Cu(II) in a reverse dark reaction, or (b) oxidize or chlorinate impurities in the electrolyte, or (c) react with GaAs if it reaches the semiconductor surface before being quenched by the other two processes. An important fact for our purpose is that the absolute quantum yield measurements (17) show that only the CuCl_3^- species has a significant CTM quantum yield, $\phi_{\text{Cu(I)}} = \phi_{\text{Cl}_2^{\cdot -}} = 0.28$. For the $\text{CuCl}_4^{=}$ species, on the other hand, $\phi_{\text{Cu(I)}} = \phi_{\text{Cl}_2^{\cdot -}}$ is less than 10^{-3} . Thus, the difficulties encountered because of the photoreduction of the Cu(II) species to Cu(I) can be avoided by working in solutions of high enough chloride concentration to convert all of the Cu(II) to $\text{CuCl}_4^{=}$.

We have shown this to be true in an experiment in which the electrolyte was prepared 0.2M in CuCl, 0.05M in CuCl_2 and 1M in TBAC, and all of the Cu(II) was present as $\text{CuCl}_4^{=}$. At both 40 and 80 mW/cm² irradiation intensity for four hours, there was no detectable change in $\text{CuCl}_4^{=}$ concentration. At 40 mW/cm², we also observed no change in short circuit current output of the PEC and no change in the matte-etched surface of the GaAs electrode. At 80 mW/cm², some pitting and polishing of the surface occurred during the four hours of operation. Apparently at 0.2M $\text{CuCl}_2^{\cdot -}$, diffusion and electron transfer rates do not keep up with photohole production at high intensity, and some lattice oxidation occurs followed by reaction with Cl^- causing dissolution.

Film Formation. We observed film formation on the photoanode to occur at high light intensities under conditions of quiescent electrolyte and when there was little excess free chloride. Under each of these conditions, there seemed to be an induction period during which the short circuit current was steady, followed by a decrease in current as the reddish-brown layer spread across the crystal surface and grew thicker and finally, a steady state current was reached. The film was not removed by stirring the electrolyte in the presence of light but was eventually removed in the dark. The film was soluble in neat acetonitrile, and in moist air appeared to turn colorless. These observations are consistent with identification of the film as $\text{CuCl}_2(\text{L}_2)$ which forms under high current conditions in the same manner as I_2 films form on MoSe_2 photoelectrodes. The mechanism for the I_2 precipitation in the latter case has been well-documented by Tributsch, Sakata and Kawai (20). The induction period exists until the buildup of CuCl_2 oxidation product at the electrode surface exceeds the solubility of CuCl_2 and nucleation occurs on the crystal face. The film is then quickly propagated across the crystal surface causing a decrease in light intensity at the surface. Lack of access of free chloride to the surface to convert CuCl_2 to CuCl_3^- prevents dissolution of the film. The low steady state current following film formation appears to be due to lattice oxidation, since pitting of the electrode under the film has been observed.

Film formation has been prevented by operating at lower light intensities or at the maximum power voltage (rather than at short circuit) to reduce the current density and in so doing the concentration of photoproduct at the surface and/or by employing those means which encourage rapid removal of CuCl_2 from the photoanode surface, including efficient stirring and high free chloride concentration which increases the overall rates of reactions (2) and (3).

CONCLUSION

We have shown that complexation of Cu(II)/Cu(I) ions with chloride in acetonitrile shifts the redox potential to a position within the band gap of GaAs and stabilizes the n-GaAs photoanode. Furthermore, complexation in solutions of high chloride concentration where Cu(II) is present as CuCl_4^- is favored because of (a) less solution absorbance, (b) reduced probability of anodic film formation, and (c) essentially no photoreduction of CuCl_4^- as opposed to the lower Cu(II) chloride complexes.

Our best PEC figures of merit to date at 80 mW/cm^2 at room temperature with a cell using polycrystalline n-GaAs are: $j_{\text{sc}} = 19 \text{ mA/cm}^2$, $V_{\text{oc}} = -0.74\text{V}$, $P_{\text{max}} = 3.78 \text{ mW/cm}^2$, $ff = 0.27$ and $\eta = 4.8\%$. Presumably these values can be improved with use of a better quality single crystal n-GaAs electrode and operation at higher temperatures. Very long term stability has not yet been demonstrated for this cell, but obviously will be influenced by current density, redox concentration, and the catalytic nature of the GaAs surface toward Cu(I) oxidation.

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Fig. 1. A: Molar concentrations of major Cu(II) species at constant CuCl (0.4M) in acetonitrile. B: Equilibrium rest potential on Pt. Open symbols in 1M TBAC, filled symbols in 2M TBAC.

Fig. 2. Potential diagram of n-GaAs in CH₃CN.

Fig. 3. Half-cell parameters vs. light intensity for the cell:

poly-GaAs | CuCl_2 (0.05M), CuCl (0.32M) | Pt
0.8M TBAC, CH_3CN

W-I lamp, KG-2 filter, stirred electrolyte. A, short circuit photocurrent; B, open circuit photovoltage.

Fig. 4. Half cell current-voltage curves at different intensities.

TABLE 1
FORMAL POTENTIALS OF THE $\text{Cu}^{+2}/\text{Cu}^{+1}$ AND $\text{Cu}^{+1}/\text{Cu}^{+2}$
REDOX COUPLES IN ACETONITRILE

<u>Couple</u>	<u>Anion</u>	<u>E vs. SCE</u> (V)	<u>E vs. Ag^+/Ag</u> (V)	<u>Reference</u>
$\text{Cu}^{+2}/\text{Cu}^{+1}$	ClO_4^-	+0.95	+0.650	(9)
			+0.679*	(10)
	NO_3^-	+0.695	+0.395	(9)
	Cl^-	+0.56**	+0.26	(9)
$\text{Cu}^{+1}/\text{Cu}^0$	ClO_4^-	-0.30	-0.60	(10)
	NO_3^-	-0.30	-0.60	our value
	Cl^-	-0.42**	-0.72	our value

*Corrected for liquid junction potential.

**Refers to the dichloro species.

TABLE 2
STEPWISE FORMATION CONSTANTS OF Cu(I) AND Cu(II) CHLORIDE
COMPLEXES IN ACETONITRILE, AND THEIR LONG
WAVELENGTH EXTINCTION COEFFICIENTS

	<u>Stepwise Formation</u> <u>Constant</u>	<u>Long λ_{max}, nm</u>	<u>ϵ</u>
Cu(I)	$K_{\text{CuCl}} = 10^{4.9}$	no absorbance in the visible	
	$K_{\text{CuCl}_2^-} = 10^{5.9}$	no absorbance in the visible	
Cu(II)	$K_{\text{CuCl}^+} = 10^{9.7}$	296	4×10^3
	$K_{\text{CuCl}_2} = 10^{7.9}$	no distinguishing peak	
	$K_{\text{CuCl}_2^-} = 10^{7.1}$	462	1.69×10^3
	$K_{\text{CuCl}_3^-} = 10^{3.7}$		$\sim 2.86 \times 10^3$
	$K_{\text{CuCl}_4^{-2}} = 10^{3.7}$		

Taken from Ref. 8.

TABLE 3

PEC PARAMETERS FOR n-GaAs/Cu²⁺/+1, CH₃CN/Pt HALF CELLS

<u>Electrolyte</u>	<u>E vs. Ag⁺/Ag</u> (V)	<u>Light Intensity</u> (mW/cm ²)	<u>V_{oc}</u> (V)	<u>j_{sc}</u> (mA/cm ²)	<u>η</u> (%)	<u>Remarks</u>
0.09M CuClO ₄ 0.01M Cu(ClO ₄) ₂ in 0.09M TBAClO ₄	+0.60	53	-0.75	-	-	Photocurrent decays rapidly with or without stirring.
0.1M CuNO ₃ 10 ⁻⁴ Cu(NO ₃) in 0.1M TBABF ₄	+0.35	11	-0.42	-	-	Photocurrent decays rapidly with or without stirring.
0.048M CuCl 0.005M CuCl ₂ in saturated TMAC* (~0.1M)	-0.2**	5.3	-0.708	2.3	15.1	Photocurrent steady without stirring.
Same as above	-0.2**	53	-0.79	11.9	3.7	Photocurrent decays unless solution stirred.

* TMAC = tetramethylammonium chloride.

** Approximate potential for oxidation of CuCl₂⁻ species.

APPENDIX C

PAPER PRESENTED AT THE
160th ECS MEETING IN DENVER, COLORADO

LASER SPOT SCANNING OF PHOTOELECTROCHEMICAL CELLS

LASER SPOT SCANNING OF PHOTOELECTROCHEMICAL CELLS

M. E. Langmuir, R. H. Micheels, R. A. Boudreau and R. D. Rauh
EIC Laboratories, Inc., 111 Chapel Street, Newton, MA 02158

ABSTRACT

Laser scanning of the photoelectrode in a photoelectrochemical cell is a powerful diagnostic tool for assessing the effect of surface modifications of the semiconductor electrode on cell performance. Photocurrent scan maps of photoelectrodes with external and/or white light bias allow the study of the effect of iR losses in the cell under operating conditions. A dye laser adds versatility to the system by permitting wavelength dependent responses to be mapped. The possibility of time resolved measurements, using a pulsed laser source, is also discussed.

INTRODUCTION

The method, which involves the recording of photocurrent or photovoltage developed in a semiconductor as a spot of light is raster scanned over the semiconductor surface, has been referred to in the literature by a variety of descriptive names including scanning light spot analysis (SLS) (1), scanning light microscopy (SLM) (2) and simply, laser scanning (3). The scanning has been accomplished by translating the laser beam in both x and y directions with oscillating mirrors (2,3) or by translating the stage on which the semiconductor or solar cell is mounted (1). The scanner which we describe here is of the former type. By simply changing the position and focal length of the focusing lens, resolution may be varied to study single grain boundaries in polycrystalline semiconductors, or to map losses in large area solar cells. The use of laser scanning to study grain boundaries has been described elsewhere (2,4) and will not be treated here. In this paper, examples are given of the utility of the method for the study of 1) surface modifications of a thin film CdSe photoelectrode and 2) losses in photoelectrochemical cells (PECs) which can be ascribed to cell design.

INSTRUMENTATION

The laser spot scanner system, pictured in Figure 1, is based on two galvanometer scanners (General Scanning G100-PD) and a 3.5 mW HeNe laser source attenuated with neutral density filters and focused with a plano-convex lens. Lenses of varying focal lengths were used for different resolution and scan range requirements. For high resolution studies, a 50 mm focal length lens, L_1 , placed after the scanner mirrors, was used which produced a spot with an 11μ (1/e) diameter. For large cells a 200 mm lens, L_2 , placed before the scanner mirror,

was used instead. The scanner mirrors were driven in a raster pattern by two ramp generators through two scan control amplifiers (General Scanning CCX-101-1). Photocurrent was amplified and monitored with a potentiostat (Amel 551) for fast scan rates and a picoammeter (Keithly 480) for slow scan speeds. Photovoltage was monitored with a 100 kHz bandwidth amplifier. The two-dimensional raster scanned photocurrent and photovoltage images were either displayed on an oscilloscope, used in the x-y mode, for rapid scanning, or on an x-y chart recorder for slow scans. The oscilloscope images were produced by modulating the CRT beam intensity with the photocurrent or photovoltage signal. When the x-y recorder was employed, a "X-modulation" scheme was used in which the photocurrent or photovoltage signal is superimposed on the X-position input to the recorder with an op-amp adder, allowing quantitative measurements to be made. A pen lifting circuit was also used with the chart recorder to blank the retrace in the Y-scan direction.

In order to obtain additional information from spot scanning, a N_2 pumped, pulsed dye laser (Molelectron DL II) was employed as a scanner light source. The laser wavelength was tuneable over the range 360-940 nm and the pulse width was about 5 nsec. The pulsed photovoltage signal was averaged with either a boxcar integrator or a lock-in amplifier depending on the signal decay time.

STUDY OF SURFACE MODIFICATIONS OF THE PHOTOELECTRODE

The effect of surface modifications of electrodeposited CdSe on Ti foil are shown in Figure 2. A 1 cm², 4 micron thick film was subjected to the following treatments in succession: A, annealing at 600°C in air for 15 minutes; B, a 2-second etch with conc. HCl; C, anodization for 3 seconds in 0.1N H₂SO₄ at 4.5V. The PEC parameters after each treatment were measured in aqueous polysulfide electrolyte at 45 mW/cm² intensity with an IR filtered tungsten-halogen lamp (see Table 1). Figure 2 shows the corresponding laser scan maps and a photograph of the electrode surface after treatment C.

The annealed electrode had a low photoresponse with a slow time constant. After the HCl etch, the response was rapid and almost a factor of 10 higher, although some bare spots appeared as indicated by the small dips in the photoresponse. The drastic reduction of the PEC parameters after anodization were attributable to cracking and flaking off of the film as shown by a comparison of the scan map and the corresponding photograph of the electrode surface.

Often, the changes in photoresponse with surface modification are subtle and the measurements of PEC parameters are very sensitive to experimental conditions such as light intensity at the photoelectrode and reproducible positioning. If several surface modifications can be made on one electrode and recorded on one scan map, this difficulty is obviated. Figure 3 is an example of an array of etch "steps" on a single chemical bath deposited CdSe film on titanium. Virtually no

difference was observed at short circuit, but when the cell was held at -0.4V , i.e., close to the open circuit voltage, the etch steps could be discerned. Thus, changes in collection efficiency with surface modification should be measured at small band bending. The use of forward bias has also been shown to be advantageous to detect defects in solid state photocells (3).

Much interest has been shown recently in the ZnCl_2 treatment of CdSe and CdS photoelectrodes (5-8). The treatment apparently suppresses the opposing cathodic current at the photoelectrode and thereby enhances the photocurrent and the open circuit photovoltage. To investigate whether it had any effect on subgap states usually present on polished CdSe crystal surfaces, a 1 cm^2 single crystal was given the localized combination of surface treatments shown in Figure 4A. At a bias voltage of -0.45V vs. a CoS counter electrode in aqueous polysulfide electrolyte, the photocurrent on the polished half of the electrode was very small compared to that on the etched half. Figure 4B shows the scan map of the etched portion of the crystal. An increase in photocurrent of $\sim 10\%$ is observed when the beam crosses into the region of ZnCl_2 treatment (indicated by an arrow in Figure 4B).

To determine whether ZnCl_2 had any effect on subgap states, the HeNe CW laser was replaced with a N_2 -pumped dye laser and a lock-in amplifier. The normalized action spectra of a polished and etched portion of the crystal are shown in Figure 5A. The response for the polished area is at least a factor of 10 smaller than that of the etched area and shows a subband gap absorption maximum at about 760 nm in agreement with similar spectra reported by Heller et al. (9). Using 760 nm pulsed light from the dye laser we recorded two single photovoltage scans to cover each of the 4 quadrants of the crystal and repeated the scans in the same positions with 588 nm pulsed light. The average power at the two wavelengths was approximately $20\text{ }\mu\text{W}$ at 760 nm and $100\text{ }\mu\text{W}$ at 588 nm , and the beam diameter was about $50\text{ }\mu\text{m}$ in these experiments. The scans at 760 nm do indicate that the subband gap response is decreased by etching and the 588 nm response is increased by etching. The ZnCl_2 also appears to diminish slightly the subband gap response in both polished and etched regions.

To further characterize the different regions of the crystal, the time resolved rise and decay of the photovoltage signals caused by band gap and subband gap excitation were recorded on an oscilloscope triggered by the laser pulse. The subband gap excited photovoltage rise and decay times are not affected by etching but the rise time of the band gap response is much faster in the etched than in the polished area. In principle, it should also be possible to map the fast and slow response areas using a boxcar integrator to record the signal.

Although we cannot yet interpret with any certainty the observed spectral and kinetic differences in photovoltage response, the

sensitivity to surface treatment indicates the participation of charge traps, at or near the solid-liquid interface, which act as recombination sites for holes and electrons. Excitation of charge from these traps to the conduction band, for example, could result in the well-defined subband gap response. The different mechanisms of filling and emptying these traps under sub- and supraband gap excitation may explain the observed differences in photovoltage transients.

STUDY OF CELL DESIGN

With additional modification of the basic scanner to provide for white light illumination of the photoelectrode while scanning with the chopped HeNe beam, it was possible to detect areas of iR drop in PECs as well as surface defects in the photoelectrode. This method has been used to analyze two possible practical frontwall cell formats for thin film CdSe electrodes shown in Figure 7.

Cell I is a structure with holes in the planar photoelectrode, to enable ion flow to the rear-placed counter electrode. The photoelectrode is of $\sim 15 \text{ cm}^2$ nominal area, produced by chemical bath deposition of CdSe on Ti foil. The scan map of a portion of this cell, shown in Figure 9, was obtained using a secondary white light bias to enhance iR effects. In addition to revealing the dead areas resulting from the perforations, the map shows pinholes and several areas of enhanced photocurrent scratches in the substrate, where the film is perhaps thicker or of greater roughness. Cell polarization and iR effects show up as slightly enhanced photocurrents immediately adjacent to the holes, and as a general negative curvature of the scans in areas between the holes.

Cell II contains a 100 cm^2 CdSe photoelectrode, prepared by electrodeposition on a louvered Ti substrate. In this case, the slots beneath the louvers provide the path for ion flow. Figure 8 shows a scan map of the illuminated portion of the electrode scanned vertically across 3 of the louvers. At the right side of Figure 8 is a cross-sectional view of the louvers. Maximum photocurrent occurs where the distance between the photoelectrode and the counter electrode is a minimum, i.e., at the flat edge. Areas of maximum loss are, of course, the slits between the louvers, indicated by A. This suggests that 1) the louvers should be narrower to produce more edges, 2) the angle of bend should be smaller, and 3) a different design in which the louvers overlap slightly would decrease the loss area. Other areas of loss marked B and C are due to bare spots on the Ti substrate.

CONCLUSION

We have demonstrated that laser spot scanning is a useful tool for studying the preparation of surfaces of semiconductors employed in photoelectrochemical cells. Spot scanning is also an aid in designing practical geometries for such devices. Clearly, however, the spot

scanning technique using liquid-semiconductor junctions goes beyond the parochial concerns of solar cell studies. The technique can be employed in the rapid evaluation of bulk and surface properties of semiconductors without the need of prior processing. The potential exists for interpreting localized responses to light in terms of diffusion length, surface recombination velocity, minority carrier lifetime and surface state density, for example, so that surface profile of these properties may be constructed on as-grown semiconductor materials. Hence, this measurement technique can be used to evaluate semiconductors for a variety of device applications where lateral homogeneity is important. Spatial resolution is limited by the diffraction limit of light, and has not been tested to date in laser spot scanning studies, but remains a fertile area for further study.

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TABLE 1
PEC PARAMETERS AS A FUNCTION OF SURFACE
TREATMENT OF A CdSe FILM

<u>Treatment</u>	<u>Photovoltage</u> (volts)	J_{sc} (mA/cm ²)	P_{max} (mW/cm ²)	η (%)
A - Annealing	-0.39	2.45	0.25	0.7
B - HCl Etch	-0.45	12.5	2.1	4.6
C - Anodization	-0.43	7.3	1.4	1.0

*W-I lamp KG-2 filter, 45 mW/cm²
Electrolyte: 1M Na₂S, 1M S, 1M NaOH.

Fig. 1. Pictorial representation of laser scanner.

Fig. 2. He-Ne laser scan maps (623.8 nm) of CdSe thin film after A, annealing; B, HCl etch; C, anodization. Beam diameter $\sim 20\mu$, beam power at electrode surface $\sim 100\text{ }\mu\text{W}$.

Fig. 3. Effect of etch time in 9M HCl on chemically deposited CdSe thin film. Cell biased at -0.4V . Diagram at the left indicates etch times for scan map on right. See Fig. 2 for laser parameters.

Fig. 4. A, Diagram of various surface treatments on CdSe single crystal; B, photocurrent scan map of the etched (left-hand) portion of the crystal in alkaline polysulfide. The arrow indicates edge of enhancement of photocurrent by ZnCl_2 treatment.

Fig. 5. A, CdSe photoanode action spectrum in alkaline polysulfide electrolyte; B, single wavelength scan of segments of CdSe crystal in Fig. 4A, using N_2 pumped dye laser and phase sensitive detection.

Fig. 6. Time resolved photovoltage of CdSe single crystal.

Fig. 7. Prototype frontwall thin film photoelectrochemical cells.

Fig. 8. Short circuit photocurrent scan map of chemical bath deposited CdSe film on a perforated substrate. Beam diameter $\sim 50\mu$; laser intensity ~ 0.5 mW.

Fig. 9. Short circuit photocurrent scan of louvered cell; white light bias. Potentiostatted at 0.0V; chopped HeNe laser; lock-in amplifier. Electrodeposited film.