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**ELECTROCHEMICAL PHOTOVOLTAIC CELLS CdSe THIN FILM
ELECTRODES**

Final Report, June 1979—June 1980

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ELECTROCHEMICAL PHOTOVOLTAIC CELLS
CdSe THIN FILM ELECTRODES

Prepared for

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by

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Final Report

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ABSTRACT

This year's program has focused on developing stable, thin-film CdSe electrodes with sunlight conversion efficiency of 10% for use with aqueous polysulfide electrolytes in frontwall and backwall illuminated EPCs. The main effort has been directed towards establishing the relationships among thin-film processing, resultant electronic properties and I-V performance in order to produce electrodes with maximum power conversion efficiency.

Thus far, the most encouraging results have been obtained with CdSe thin-film electrodes produced in two ways for frontwall cells. First, films deposited on titanium at approximately 100°C with a high Se/Cd ratio and then heat treated in air at 350 - 400°C. These films usually have a very fine grained microstructure after heat treatment and the resultant electrodes exhibit fairly square I-V characteristics with fill factors of 0.6 or greater and high current output. The overall power efficiency of these electrodes is limited by relatively low output voltages. At present, power conversion efficiencies of 3 - 5% can be obtained reproducibly at simulated AM2 conditions with electrodes processed in this manner. The best efficiency in sunlight obtained to date with this type film is 5.3%.

The second type of film that has yielded very promising results is deposited on titanium at substrate temperatures greater than 400°C. The interesting feature of these electrodes is their increased open circuit voltage. However, the current output and fill factor are lower. As a result, the power conversion efficiency of these electrodes is 3 - 4%. These frontwall cell electrodes were found to have stable outputs for almost two months.

Backwall electrodes with an efficiency of greater than 4% and short circuit densities near theoretical for AM2 conditions have been produced. The main limit to higher efficiency of these electrodes seems to be the series resistance of the transparent conductor.

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1. INTRODUCTION

The overall objective of this program is to develop a stable, thin-film electrochemical photovoltaic cell with a sunlight conversion efficiency of 10%. This objective was approached primarily using the CdSe aqueous sulfide-polysulfide electrolyte and to a lesser degree the CdSe-CdTe alloy aqueous sulfide-polysulfide electrolyte system. Two types of composite electrodes have been fabricated and evaluated during the course of this year's program. These electrodes are ultimately intended for use in front and backwall illuminated EPCs, basic designs for which are shown in Fig. 1. These complete thin-film electrochemical solar cells consist of three major components: a photoactive electrode, a redox electrolyte, and a counter electrode. In both cases, power is delivered to a load (R in Fig. 1) connected in an external circuit between the photoactive electrode and the counter electrode. The differences between these cells is in the semiconductor electrode configuration. In Fig. 1a (frontwall cell), the semiconductor film is deposited on an opaque conducting substrate and must be positioned in the cell in such a way that the incident radiation can fall on the semiconductor liquid junction. In this case, a transparent window is necessary in front of the electrode and the incident radiation must pass through a layer of electrolyte before it strikes the junction. In addition, it is necessary to have free flow of electrolyte from the photoactive electrode to the counter electrode. In this configuration, semiconductor films of various thickness and a wide variety of substrate materials can be used. Figure 1b (backwall cell) shows a semitransparent photoactive electrode that allows irradiation of the junction through the semiconductor rather than through the electrolyte. In this cell, electrolyte absorption losses are eliminated and the design is somewhat simplified. However, the number of materials available as conducting substrates is limited due to the transparency requirement.

An analysis of the upper limit efficiency of cells utilizing these designs including consideration of the following: band gap factor, voltage factor, fill factor, collection factor, reflection losses and electrolyte

Fig. 1 Photoelectrochemical Conversion Cell Designs

absorption, indicates that thin-film frontwall cells with power efficiency in the range of 10 - 13% and backwall cells with efficiencies of 11 - 15% can be produced with the materials under investigation in this program.

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2. TECHNICAL PROGRESS

THIN FILM DEPOSITION

The equipment shown in Fig.2 was used to produce the thin-films evaluated during this program. The CdSe thin-films were made by the simultaneous evaporation of Cd and Se from two independently controlled resistive heated boats. Each source is controlled by a Sloan MDC 9000 Thin Film Deposition Controller which provides precise deposition rate control and thickness measurement. Titanium sheet (0.25 mm thick) and SnO₂ or In₂O₃ - SnO₂ coated glass were used as electrode substrates. Soda lime silica monitor slides were also used. The substrates are clamped onto a copper plate into which cartridge type heaters have been placed to provide substrate temperature control. The CdSe deposition was found to be uniform over an area of 50 cm². In addition, EDAX and Auger spectroscopic determinations indicate the thickness and deposition rates programmed and monitored on the deposition controllers correctly reflect the actual chemical compositions of the as deposited films.

The first phase of the thin-film deposition effort involved investigation of the following deposition parameters: Cd/Se ratio, CdSe deposition rate and substrate temperature. The film thickness was 1 to 2 μ m.

The determination of the effect of these deposition variables on the I-V characteristics of the thin-film electrodes was done by subjecting each film to a standard annealing schedule followed by potentiostatic I-V evaluation. This approach was taken to independently investigate the effects of deposition conditions on I-V performance without introducing further complications due to variation in post deposition treatment conditions.

Substrate preparation was found to be critical to obtaining thin films with good adherence. The following procedures were developed. For the SnO₂ and SnO₂-In₂O₃ coated glass and the monitor slides the following procedure: wash in soapy water and rinse in acetone, boil in soapy water, boil in hydrogen peroxide solution, rinse in deionized water, was found to

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Fig. 2 Co-evaporation Deposition System

suitably clean these substrates prior to deposition. The titanium substrates were cleaned by mechanical abrasion, followed by soaking in a chromic-sulfuric acid solution and then rinsing in deionized water. After cleaning, all the substrates were stored in deionized water until used.

The initial characterization of the CdSe thin-films was primarily done by chemical, microstructural and optical determinations and to a lesser extent electronic measurements. As the program progressed, several electronic measurement techniques were modified for use on these very thin-films and more emphasis was placed on these measurements in establishing the correlations among deposition parameters, thin-film properties and I-V performance.

The details of the x-ray diffraction and microstructural analysis of films deposited under various conditions has been presented previously (Ref 1) and only the key findings will be reviewed here. The crystallographic orientation and microstructural appearance of the as-deposited films were determined primarily by the Se/Cd vapor stream ratios at a given substrate temperature. For convenience the Se/Cd ratio in the as-deposited film is denoted as x in the formula CdSe_x , so that a film for which the Se/Cd ratio was three would be expressed as CdSe_3 . The CdSe condensation rate (based on the Cd rate) did not have a major impact on the stoichiometry or microstructure at lower substrate temperatures but did at temperatures in excess of 350°C . The combinations of x values and substrate temperatures which resulted in coherent film formation are shown in Fig. 3. The as-deposited films varied from crystalline to amorphous depending on deposition conditions. The films formed at low x values were crystalline (hexagonal) with a strong 001 growth texture that become less pronounced at higher substrate temperatures and lower deposition rates. These results are consistent with those reported for CdSe thin-films deposited from the compound (Ref 2 and 3). At high Se/Cd ratios and lower substrate temperatures the as-deposited films are amorphous. These films crystallized with a strong 001 texture upon heat treatment. In this case radical, chemical, microstructural and optical changes occur with crystallization and loss of excess Se as shown in Fig. 4, 5 and 6. This contrasts with the results obtained with films deposited at higher substrate temperature where there are no major microstructural or chemical

400	X				
300	X	X			
200	X	X	X		
100	X	X	X	X	X
25	X	X	X	X	X
	1	2	3	4	5

Se/Cd Ratio

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Fig. 3 Combinations of Substrate Temperature and Se/Cd Vapor Stream Ratios Resulting in Coherent Film Formation

As Deposited

After Heat Treatment

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Fig. 4 Microstructural Changes Observed in a CdSe₃ As-Deposited Film With Heat Treatment at 400°C for 15 min in Air

Fig. 5 Representative TGA Traces of Two CdSe_x Thin Films on Titanium in Argon

Fig. 6 Transmission Curves of Se Film, Unfired CdSe_3 Film, and Fired CdSe_3 Film

changes observed with heat treatment. In almost all cases, however, the photoelectrochemical performance of the as-deposited thin-film electrodes was poor, with most films peeling from the substrate. The post deposition heat treatment employed was, therefore, critical to developing optimum I-V characteristics as well as film adherence.

Some CdSe - CdTe alloy films were also made. In this case, the two deposition boats were loaded with CdSe and CdTe powders, respectively, and the alloy composition was obtained by controlling the relative evaporation rate of each compound. X-ray diffraction analysis of these films indicated a complete range of solid solution formation from CdSe to CdTe as well as a strong growth texture. Optical measurements indicated a large red shift in band gap of the alloy film with increasing CdTe content as shown in Fig. 7. The chemical compositions were determined by EDAX and agreed well with the expected composition. Alloy films will be made by the simultaneous evaporation of Cd, Se and Te during next year's program.

ELECTRODE EVALUATION

A major portion of this program has been directed towards establishing the correlations among thin-film processing conditions, resultant electronic properties and I-V performance so that thin-film electrodes with maximum conversion efficiency can be produced. In support of this effort a considerable amount of time has been devoted to developing reliable, reproducible electronic property measurement techniques for these very thin-films (Ref 4). In addition, an in-house developed model of the semiconductor-electrolyte junction has also been used for some data analysis (Ref 4 and 5).

It has been reported that the I-V output performance of II-VI and III-V compound EPC electrodes is significantly improved with surface etching, due to the removal of highly defective surface material (Ref 6 and 7). This was found to also be the case for many, but not all, of the thin-film electrodes evaluated during this program. The details of etching the thin-film electrodes have been presented earlier (Ref 8). While significant improvements in I-V performance were observed with etching, the results were not always

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Fig. 7 Variation of Bandgap With CdTe Content for Coevaporated CdSe - CdTe Films

reproducible due to the high reactivity of the aqua-regia based mixtures employed. Even at a $\text{HNO}_3\text{:HCl}$ ratio of 1:50 the margin for error in etching time with these very thin-films was quite small as the etchant strength was found to increase with time. We have subsequently found that a 25% HNO_3 etch provides similar electrode performance improvement but greater control and reproducibility due to a much slower etching rate. The effect of a 10 second etch on an electrode topography and I-V performance is shown in Fig. 8 and 9.

Frontwall Electrodes

In terms of achieving the program efficiency goal of 10%, thus far the most encouraging results have been obtained with CdSe thin-film electrodes produced in two ways. First, films deposited on titanium at approximately 100°C with a high Se/Cd ratio and then heat treated in the temperature range of 350 to 400°C in air. These films usually have a very fine grained microstructure after heat treatment as shown in Fig. 10 and the resultant electrodes exhibit fairly square I-V characteristics with fill factors of 0.60 or greater and high current output. The overall power efficiency of these electrodes is limited by relatively low output voltages. At present, power conversion efficiencies at simulated AM2 conditions (W-I ELH lamp discussed in Ref 4) from 3 to 5% can be obtained reproducibly with electrodes processed in this manner. The best performance in sunlight obtained to date with this type film is shown in Fig. 11, with $\eta = 5.3\%$.

The second type of film that has yielded very promising results is deposited on titanium at substrate temperatures greater than 400°C at a rate of $\sim 10 \text{ \AA/s}$ with a slight excess of Se. It can be seen in Fig. 12 that the microstructure of the films deposited under these conditions is quite different from that of the films produced at lower substrate temperatures and heat treated at 400°C for 15 min. in air (i.e., standard heat treatment) shown in Fig. 10. In particular, the average grain size is significantly larger and the film is quite columnar with grains that appear to be continuous from the surface through the film. Analysis of X-ray diffraction patterns of these films indicate they are hexagonal CdSe with the crystallites having their c-axis perpendicular to the substrate (the 002 reflection is most intense).

Before Etching

After Etching

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Fig. 8 Scanning Electron Micrographs Showing The Topographic Changes in a Thin-Film Electrode With a 10s Dip in 25% HNO_3

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Fig. 9 Current-Voltage Curves Illustrating The Improvement in Performance Found With Etching in 25% HNO_3

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Fig. 10 SEM Micrographs of CdSe_3 After Heat Treatment at 400°C , 15 min in Air

Fig. 11 Current-Voltage Curve for CdSe_3 Electrode Heat Treated at 400°C , 20 min in Air. Sunlight Intensity 76 mW/cm^2

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Fig. 12 SEM Micrographs of CdSe Thin Film Deposited at $T_s = 425^\circ\text{C}$

EDAX spectra show the films to be stoichiometric when compared to a high purity CdSe powder standard.

Even though these films are deposited at elevated temperatures they still require post deposition heat treatment to obtain optimum I-V performance as shown by the series of curves presented in Fig. 13. The interesting feature of films produced in this manner is their higher open circuit voltage, which is consistently in the range of 0.55 to 0.65 V. However, the current output and fill factor are lower than those obtained with the films discussed previously. As a result, the power conversion efficiency of these electrodes is in the range of 3 - 4% at 75 mW/cm², AM2 conditions. An I-V curve taken in sunlight is presented in Fig. 14.

Some difficulty was encountered initially with the adherence of the films processed in this manner, so that after several I-V scans the films would begin to peel. This problem was eliminated by slow cooling the films after deposition and depositing a thin (1000Å) layer of chromium on the titanium before deposition of CdSe. The Cr makes an ohmic constant with CdSe and its coefficient thermal expansion ($6 \times 10^{-6}/^{\circ}\text{C}$) is intermediate between Ti ($8.5 \times 10^{-6}/^{\circ}\text{C}$) and CdSe ($3 \times 10^{-6}/^{\circ}\text{C}$). The use of lightly sandblasted or chemically etched Ti has also minimized this problem.

While thin-film electrodes are being produced on transparent conducting substrates for use in backwall illuminated cells as well as opaque conducting substrates for frontwall cells, most of the work to date has been done with films deposited on titanium. This is due to the relative ease of electrode fabrication and wider range of processing parameters available with the metallic substrate. Even though, some very encouraging results have been obtained with the backwall cell electrodes, as will be discussed later in this section.

In order to obtain a more basic understanding of the relationships among the electrode material and interface properties that affect the photovoltaic performance of the CdSe polysulfide junction a detailed analysis of selected experimental data on the two types of frontwall electrodes just discussed was conducted.

Fig. 13 Current-Voltage Scans for CdSe Thin Film Electrodes Deposited at $T_s = 450^\circ\text{C}$ and Heat Treated at Three Temperatures • Electrode Area: 0.1 cm^2

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Fig. 14 Current-Voltage Curve for CdSe Electrode Deposited at $T_s = 450^\circ\text{C}$
Then Heat Treated at 500°C 15 min in Air, Sunlight Intensity 76 mW/cm^2

Film CE131 is representative of the high substrate temperature deposition films and CE134 typifies the low substrate temperature, high Se/Cd ratio deposition films. Their I-V characteristics for the simulated AM2 intensity distribution is given in Fig. 15. As can immediately be seen by inspection the I-V characteristics of these two films are quite different. The high deposition temperature film, CE131, has a gradual decline in current with increasing voltage and a tail at the high voltage end. The low deposition temperature film, CE134, has a flat I-V characteristic at low voltages and a sharp drop in current at higher voltages. A comparison of some of these I-V characteristics together with resistivity, and microstructure data is given in Table 1 for the two films. Some qualitative conclusions relating the resistivity values of the films to their I-V characteristics can immediately be made. The film with the higher resistivity, CE-134, shows a higher J_{SC} and lower V_{OC} than CE-131 which has a lower resistivity by more than two orders of magnitude. If it is assumed the difference in the resistivities of

TABLE 1 COMPARISON OF FILM CHARACTERISTICS FOR TWO FRONTWALL ELECTRODES (AM2 SIMULATION)

Film	Grain Size (μm)	($\Omega\text{-cm}$)	V_{OC} (V)	J_{SC} (ma/cm^2)	FF	η (%)
CE131	0.7	1.1×10^3	0.64	10	0.44	3.7
CE134	0.05	4.2×10^5	0.41	14	0.55	4.3

the two films is due primarily to changes in free carrier density, N_D , then the differences in the I-V characteristics can be explained by the following. Since the depletion width, W , is given by $1/2$

$$W = \left(\frac{2\epsilon\epsilon_0 V_{fb} - V}{q N_D} \right)^{1/2}$$

a lower N_D value would result in a large depletion width. This then would result in a higher short circuit current since more carriers would be generated in the depletion layer rather than in the bulk where recombination are more likely to occur. The initially flat I-V characteristic can also be explained as due to the high resistivity film depletion width being sufficiently large so that the condition $\alpha W \gg 1$ prevails over most of the

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Fig. 15 Current-Voltage Curves for Electrodes CE131 and CE134, $75 \text{ mW}/\text{cm}^2$ Intensity, AM2

intensity spectrum. In contrast the lower resistivity film decline of J with V can be explained by narrowing of W with increasing voltage causing greater generation of holes in the bulk with subsequent recombinations. The differences in V_{oc} of the films is also consistent with their difference in resistivities. As carrier density decreases, the Fermi level of the CdSe film is lowered. This then makes the flat band potential more positive and results in less band bending. Since the open circuit voltage is slightly more positive of the flat band potential it decreases as the Fermi level of the film decreases.

To obtain a more quantitative characterization of the effects of the film properties on the performance characteristics, the theoretical model we have developed (Ref 5) was used to analyze experimental I-V data. The variation of J_{sc} with light intensity was investigated to assure that light saturation effects would not be a factor in this analysis. The intensity levels used in this experiment were from 1 to 10 mW/cm², well in the linear range for both electrodes as shown in Fig. 16. The I-V measurements on the two films were made using monochromatic light at a wavelength of 650 nm. The data was reduced to internal quantum efficiency by using measured values of reflectance, correcting for electrolyte absorption, and measuring the incident intensity. The net photocurrent was obtained by using the amplitude of the current resulting from a chopped monochromatic source. This was done to eliminate the effects of dark current on the I-V characteristics.

The model used to fit the experimental data was obtained by solving the diffusion equation for minority carriers using boundary conditions relevant to the semiconductor electrolyte junction, that is, the photocurrent is linearly related to the concentration of minority carriers at the interface. Using this boundary condition and assuming quasi-equilibrium conditions in the depletion region current voltage relations are derived. The model takes into account losses in current due to recombinations in the depletion region and the bulk of the semiconductor.

The results of the comparison of the model calculations and the experimental I-V data are shown in Fig. 17 for the two films. The significant model parameters that were adjusted to fit the data were minority carrier

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Fig. 16 Short Circuit Current Density vs Intensity for CdSe Deposited at 450°C and 100°C on Ti Substrates

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Fig. 17 Experimental Monochromatic Current-Voltage Curves (Solid Lines) and Model Calculations for Electrodes CE131 and CE134

diffusion length, L_p , carrier density N_D , lifetime, τ , and charge transfer velocity, v_t . The other parameters such as absorption coefficient and flat band potential were obtained from experimental data. The diffusion length was obtained from the low voltage and reverse bias data (not shown) for the high temperature substrate film CE-131. The results indicate that $L_p < 0.02 \mu\text{m}$, which is a very small value. The value of N_D also obtained in this voltage region was $3.5 \times 10^{15} \text{ cm}^{-3}$. Values of $\tau = 10^{-10} \text{ sec}$ and $v_t = 5000 \text{ cm/sec}$ were obtained from the data in the region where the current decreases more rapidly with voltage. These parameters characterize the losses due to recombinations in the depletion region. The short lifetime is consistent with the small diffusion length and inferred mobility from the measured resistivity, and value for N_D . The fitted value of v_t of 5000 cm/sec is more than an order of magnitude greater than values we have obtained for the same electrolyte using a single crystal CdSe electrode (Ref. 9).

This higher charge transfer velocity for the thin films can explain the observation that the corrosion rate has been reported to be lower for thin film than single crystal electrode (Ref 10). Since the rate of corrosion involves a competition between the decomposition reaction and the redox reaction a higher value of v_t would tend to favor the redox reaction.

The low deposition temperature, high resistivity film, CE-134, was found to have a carrier density of 10^{13} cm^{-3} . This low value indicates that the film is fully depleted, that is, the depletion width extends throughout the thickness of the film. The diffusion length therefore cannot be determined since no measure of absorption in the bulk is available. However, the value of $2 \times 10^{-10} \text{ sec}$ obtained for the lifetime and the resistivity measurement indicate a diffusion length comparable to that of the high temperature films.

The parameters obtained here are not quite uniquely determined. For example, by increasing the carrier density of CE-134 to 5 times the value found and using a lifetime of 10^{-10} sec a fit within experimental error to the data could also be found. What we have done here is assume the same carrier density ratio as the resistivity ratio and that v_t of the two films are the same. Although this may not be strictly accurate the following conclusions based upon the parameters obtained can be made with a reasonable degree of confidence.

1. Both films appear to have poor diffusion lengths and carrier lifetimes. The larger grain size of the high temperature film does not appear to improve these properties. It appears then that L_p and are not limited by grain boundary recombinations but rather by point defects or stacking faults occurring within the grains (Ref 11).
2. The low temperature substrate films are highly stoichiometric with carrier densities of the order of 10^{13} cm^{-3} . This is probably due to the post deposition heat treatment of the films that initially contain a high selenium to cadmium ratio. Since the films are fully depleted high short circuit currents result. The high substrate temperature films have carrier densities of the order of 10^{15} with depletion widths of $\sim 0.4 \mu\text{m}$. This results in films with lower short circuit currents but higher open circuit voltages than the higher resistivity films.
3. The charge transfer velocities of these films are quite high compared to the single crystal. This is probably due to the larger surface area caused by highly irregular geometry of the polycrystalline material. As a result, reasonably good efficiencies are obtained despite the poor carrier lifetime. In addition this provides an explanation for the improved corrosion resistance of the thin film compared to the single crystal material.

Additional confirmation of our analysis of the CdSe thin film properties comes from the spectral response data as shown in Fig. 18. As seen from the figure the internal quantum efficiency vs. wavelength characteristics of the two films are quite different. The CE-134 film has a measured response further out into the long wavelengths at sub-bandgap energies. This can be explained as due to absorption from band tail states created by charged defects. The large depletion width makes for efficient carrier collection despite the low absorption coefficients in the sub bandgap region. As the absorption coefficient gets large when bandgap absorption due to direct interband transition takes place, the quantum efficiency reaches 100%. At shorter wavelengths the quantum efficiency decreases. This is due to photogenerated majority carrier diffusion to the interface where recombination

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Fig. 18 Spectral Response of Electrodes CE131 and CE134

with photogenerated holes takes place. This effect has not been included in the model used for analysis of the data presented here. We are however developing a model which includes diffusion effect in the depletion region which should provide us with additional tools for data analysis and interpretation.

The lower resistivity film (CE131) shows a lower quantum efficiency over the entire spectrum due to its smaller depletion width. The fall off in efficiency at short wavelengths again is attributed to diffusion of majority carriers to the interface. The peak in efficiency occurs at a shorter wavelength than the high resistivity film. This is also consistent with the higher carrier density of this film. A higher carrier density results in a greater electric field at the interface thereby making back diffusion less likely. As a result, losses due to diffusion start to occur for carriers generated closer to the interface i.e., at shorter wavelengths where the absorption coefficient is larger. At longer wavelengths the change in quantum efficiency with wavelength shows the same dependence as that predicted using the parameters obtained from the analysis of the monochromatic I-V data.

Analysis of the dark current behavior of photovoltaic devices is commonly made due to its importance in determining the fill factor, open circuit voltage, and efficiency. For the CdSe-polysulfide electrochemical photovoltaic cell however the dark current has not yet played a significant role in determining these device characteristics. This is due to the dominance of recombination mechanisms in the depletion region, bulk, and interface in determining the I-V characteristics of the device. It is conceivable, however, that as these mechanisms become less significant due to improvements in material properties the dark current will play a more significant role. We have therefore decided to analyze the dark I-V characteristics of the CdSe-polysulfide junction to gain a better understanding of the transport mechanisms involved.

The model selected for analysis of the data is the one for thermionic emission given by the following equation. (Ref 12):

$$J = fA^*T^2 \exp(-q\phi/kT) \exp(qV/nkT)$$

where ϕ is the barrier height, A^* is the Richardson constant, n is the ideality factor and f is a transmission coefficient that takes into account tunneling across the Helmholtz layer to ion acceptor states. A log I vs V plot (forward direction) for CE-131 and CE-134 is shown in Fig. 19. The linearity of the plots over most of the voltage range indicates that the thermionic diffusion model may be a valid one. From the slope and intercept at $V = 0$ the values of n and I_0 are obtained where $I_0 = fA^*T^2\exp(-q\phi/kT)$. Using a barrier height of 0.8 volts as obtained from our single crystal data, the transmission factor, f , can be found. A summary of these results is given in Table 2. The high transmission probability indicates that tunnelling through the Helmholtz layer may not be the mechanism for electron transfer. An alternate possibility may involve electron transfer to induced interface states created by absorbed ions with subsequent desorption. The ideality factors are considerably greater than unity indicating that other transport mechanisms may be dominant. Possibilities include hole injection, field emission, or multistep tunnelling through the depletion layer (Ref 13).

TABLE 2 SUMMARY OF DARK CURRENT PARAMETERS FOR TWO FRONTWALL THIN FILM ELECTRODES

Film	I_0 (mA/cm ²)	n	f
CE131	1.3×10^{-3}	3.2	>1
CE134	1.6×10^{-4}	1.29	0.4

There is insufficient data at present to determine the transport mechanisms responsible for the dark current behavior of the CdSe electrodes. Additional data such as temperature dependent I - V characteristics may give us more information to establish the dominant mechanisms.

Backwall Electrodes

CdSe thin-films were deposited on two types of transparent conductor coated glass. One conductor was chemical spray deposited, halogen doped SnO_2 with resistivity in the range of 6 to 15 Ω /square and visible transmission

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Fig. 19 Forward Bias Dark Current vs Voltage for Electrodes CE131 and CE134

around 80% the other was sputtered $\text{In}_2\text{O}_3 + 9\% \text{SnO}_2$ with resistivity of 10-20 Ω/square and visible transmission of greater than 85%. As with the metallic substrates, films were deposited on these substrates with a wide range of parameters. However, in this case the combination of thin-film properties that will yield an electrode with maximum efficiency is somewhat restricted. It is desirable to have the space charge region extend through the full thickness of the film to promote rapid carrier separation and obtain good collection efficiency (Ref 14). In addition, the film thickness should be such that all the incident light of greater than bandgap energy can be absorbed within the film. A calculation of this thickness based on the measured values of absorption coefficient listed in Table 3 (Ref 1), indicates that at 500 nm a film thickness of 0.680 μm would be sufficient to absorb 99% of the light, whereas at 700 nm a thickness of 2.37 μm would be required. This suggests a film thickness of 2-3 μm to provide an adequate amount of material for the absorption of sunlight. In order to have a space charge layer width of this order a majority carrier doping density of less than 10^{14}cm^{-3} would be necessary (assuming a voltage drop of 0.7 V across the space charge layer).

Backwall electrode performance was tested in a cell specifically designed for this purpose, pictured in Fig. 20, which allows irradiation of the CdSe through the substrate glass and transparent conductor. This cell design eliminates the electrolyte absorption loss and allows reasonably quick sample change.

TABLE 3 MEASURED OPTICAL ABSORPTION COEFFICIENT FOR CdSe THIN FILM

<u>Wavelength (nm)</u>	<u>($\times 10^4 \text{cm}^{-1}$)</u>
400	8.68
433	7.16
466	7.00
500	6.76
533	6.53
566	4.81
600	4.05
633	3.48
666	2.76
700	1.94

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Fig. 20 Cell Used For Evaluation of Backwall Illuminated Electrodes

In the discussion of the electrodes deposited on the titanium substrates would suggest, the most success with these backwall illuminated electrodes was obtained with CdSe films that had been deposited at low substrate temperatures with high x values. Films of this type (heat treated after deposition at 400°C in air) have produced electrodes with power conversion efficiencies greater than 4% at 75 mW/cm², AM2, as shown in Fig. 21. In reviewing these data, it should be noted the short circuit current density, J_{SC} , of 17 mA/cm² is almost at the theoretical limit for a material with $E_g = 1.7$ eV responding to an AM2 spectrum (Ref 15). The thickness of this particular film is 2.5 μ m (see Fig. 22) so that all the impinging radiation is absorbed within the film. The open circuit voltage of 0.453 V, while not as close to the theoretical limit as the J_{SC} , is such that $V_{OC} \times J_{SC}/Int$ still results in maximum efficiency of 10.3% at 75 mW/cm². It is the low fill factor of 0.42 that currently limits the efficiency of this electrode. The same type of film deposited on the titanium substrates, tested under the same conditions, generally has J_{SC} in the range of 12-14 mA/cm², fill factors from 0.55 to 0.65 and V_{OC} from 0.4-0.45.

The low fill factor of the backwall illuminated electrode is attributed to the series resistance drop from the electrode surface to the current collection lead (see Fig. 20 for electrode construction detail) which is on the order of 20-30 Ω , whereas the series resistance of the titanium substrate, wire combination is approximately 1 Ω . A reduction in fill factor has been shown to result when the series resistance of a solar cell is too high (Ref 14 and 15). The change in solar cell parameters with varying intensity also indicates a series resistance problem with this electrode. Although the J_{SC} changes nearly linearly with intensity as shown in Fig. 23, it can be seen in Table 4 that the fill factor and as a result η increase with decreasing intensity.

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Fig. 22 SFM Micrographs of Thin-Film Backwall Electrode. Substrate is 10Ω per Square Tin Oxide Coated Glass

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Fig. 23 Variation of J_{sc} With Intensity For Electrode of Fig. 21

TABLE 4 VARIATION OF SOLAR CELL PARAMETERS FOR ELECTRODE OF FIG. 21
WITH LIGHT INTENSITY
(UNCORRECTED FOR REFLECTION LOSSES)

INTENSITY (mW/cm ²)	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	η (%)
74	17.1	0.45	.41	4.2
39	8.8	0.43	.48	4.7
5.4	1.4	0.40	.52	5.4

The spectral response and monochromatic I-V behavior of these backwall electrodes were also investigated as part of the overall efficiency analysis. The I-V curve for this electrode at 650 nm is shown in Fig. 24. The power conversion efficiency is 9.5% and is still limited by a fill factor of 0.52. The maximum theoretical efficiency is 18.4%. The internal quantum efficiency at short circuit conditions is 0.95. Hall measurements and direct resistivity measurements on these type films (Ref 4) indicate the donor densities, N_D , are in the range of 10^{12} - 10^{13} cm⁻³, majority carrier mobilities, μ , from 10-40 cm²/V-sec and resistivities, ρ , from 10^4 - 10^5 -cm. These parameters indicate that the space charge region extends through the entire thickness of the thin-films resulting in excellent collection efficiency observed experimentally.

The spectral response of another electrode of this type is shown in Fig. 25 (corrected for reflection). The response is quite flat, with only a small fall off in the blue. There is also a sub-bandgap energy response in this spectrum indicative of the presence of band tail states within the gap. Analysis of the full monochromatic I-V curves revealed a significant variation in output power parameters, even though the quantum efficiency (ϕ) was fairly constant. These data are summarized in Table 5. This variation is due to the depth of penetration of each wavelength radiation into the thin-film. The space charge region extends through the film thickness, however the electric field is greater towards the surface. As a result, when the electrode is put into forward bias (i.e. drawing power), and the band bending is reduced, it is more difficult for holes generated away from the surface, where 450 nm radiation would be absorbed, for example, to reach the surface than for holes

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Fig. 24 Monochromatic Current-Voltage Curve For Backwall Illuminated Electrode, 650 nm Light, 5.3 mW/cm² (Uncorrected For Reflection Losses)

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Fig. 25 Spectral Response Curve For Backwall Illuminated Electrode

generated nearer the surface, as would be the case for those generated by 650 nm radiation. This effect is reflected in the observed reduction in fill factor in going to shorter wavelength radiation. This is also supported by the fact that the increase in quantum efficiency with voltage in reverse bias is greater for the shorter wavelength curves than for the longer wavelength ones, indicating the additional bias is useful in promoting more efficient carrier separation for radiation absorbed further away from the junction.

TABLE 5 SUMMARY OF MONOCHROMATIC I-V PARAMETERS
FOR BLACKWALL IRRADIATED ELECTRODE

Wavelength (nm)	Intensity (mW/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	ϕ (%)
450	1.08	0.30	0.35	0.41	4.0	93
500	2.28	0.73	0.39	0.46	5.7	97
550	4.54	1.65	0.42	0.48	7.3	98
650	7.62	3.02	0.44	0.50	8.8	95
700	7.26	2.85	0.44	0.50	8.6	87
720	6.04	2.11	0.43	0.52	7.8	74
750	5.52	0.61	0.39	0.51	2.2	23

Electrodes of this type utilizing CdSe films deposited at elevated substrate temperatures generally have higher V_{oc} than those already described but significantly lower photocurrents such that their power conversion efficiency has not exceeded 1%, this poor performance is attributed to the narrower space charge region in these films causing most of the absorbed light to be absorbed in the neutral region where the recombination losses are more dominant.

CdSe-CdTe Thin-Film Electrodes

A preliminary investigation of the performance of CdSe-CdTe alloy thin film anodes was conducted during this program. The initial composition chosen was CdSe_{0.65}Te_{0.35} due to the high efficiency recently reported for sintered polycrystalline mixtures of this composition (Ref 16). The as deposited film exhibited the expected red shift in absorption. The film was then heat treated in air at 600°C for 10 minutes. The I-V performance and spectral response curve (with a typical CdSe curve for reference) for this

sample are shown in Fig. 26 and 27. These results were quite encouraging, however, a second series of depositions of various compositions (see Fig. 7) gave much poorer results in that their photovoltaic performance was found to decrease with increasing CdTe content. As a result, the best I-V performance for this particular series of films was obtained with the 100% CdSe composition.

The difficulty with these samples seems to be related to the quality of the CdTe compound used for the depositions. The CdTe used here was obtained from a different supplier than that reported previously and the electrodes made at a composition of 100% CdTe, while having expected optical transmission properties, show no photoresponse in the potentiostatic setup. It has been reported that the quality and source (i.e., manufacturer) of II-IV compound starting material can greatly affect the performance of vacuum evaporated thin film devices (Ref 17) and we suspect this to be the case here. Additional effort in this area was suspended while a three source evaporation setup is assembled for future work.

ELECTRODE OUTPUT STABILITY

The long term output stability of the types of films (on titanium substrates) evaluated thus far was found to be quite good. The approach taken in this evaluation was to monitor the change in I-V performance of a given electrode-electrolyte combination with time under constant illumination. A 1000 W Xe-arc lamp with a Schott KG-2 heat filter was used as the light source because of its long lifetime (1500 hours).

The initial evaluation was made in 2.5 M Na₂S, 1 M S, 1 M KOH electrolyte on electrodes produced by evaporation onto titanium substrates at 100°C with a Se to Cd ratio of 3 and then subjected to the standard heat treatment. Argon was bubbled through the electrolyte, the electrode held at -0.8 V vs SCE (i.e., J_{SC} condition) and the current output monitored. Periodically the full I-V trace of the electrolyte was scanned. The initial results were excellent. This electrode was held at 12 mA/cm² for a period of 50 hours (i.e., 1500 C/cm²) which is equivalent to 7 days under normal use, with no detectable drop off in current density. The full I-V curve is

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Fig. 26 Current-Potential Scan For $\text{CdSe}_{0.65}\text{Te}_{0.35}$ Thin-Film Electrode, $I_{\text{int}} = 50 \text{ mW/cm}^2$ (Xe-arc)

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Fig. 27 Relative Photoresponse of CdSe and $\text{CdSe}_{0.65}\text{Te}_{0.35}$ Thin-Film Electrodes

virtually identical before and after this test. The output curves are presented in Fig. 28 and 29.

Initial stability evaluation of electrodes deposited at elevated substrate temperatures were not as successful in that the output current showed a significant drop with the passage of only several hundred coulombs. Inspection of the electrode revealed that the CdSe thin film had peeled from the titanium substrate causing the output to be greatly reduced. These particular samples had been deposited on very smooth titanium and not slow cooled after deposition. A second set of films were deposited using a chromium layer (1000Å) between the titanium and CdSe and slow cooled after deposition. This procedure eliminated the peeling problem and the electrode output was found to be stable with time. The electrode under study was held at approximately 8 mA/cm² for a total of 12,000 C/cm², with the I-V curve scanned periodically. There was a slight decrease in V_{OC} observed after passage of a small amount of charge as shown in Fig. 30. However, the maximum power voltage and current did not change significantly so that the efficiency of this electrode was not reduced. It should be noted that due to the reduction of V_{OC} the fill factor of this sample actually increased somewhat. The relevant performance parameters are summarized in Table 6. If this electrode were run an average of 8 hrs. a day at a 8 mA/cm² current density, passage of 12,000 C/cm² would translate into approximately 52 days of service with no measurable decrease in output power.

TABLE 6 CURRENT-VOLTAGE PARAMETERS OF CdSe ELECTRODE
UNDER LONG TERM TEST, INTENSITY 65 mW/cm²
(Xe-arc + KG-2 filter)

C/cm ²	V_{OC}	J_{SC}	$V_{P_{MAX}}$	FF	η
0	0.63	8.3	0.38	.433	3.5%
150	0.59	8.3	0.37	.435	3.3%
5000	0.58	8.2	0.37	.476	3.5%
12000	0.57	8.2	0.37	.478	3.4%

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Fig. 28 Short Circuit Current Output For CdSe_3 as Deposited Film Heat Treated at 400°C , 15 min in Air, Run in 2.5 mol Na_2S , 1 mol S, 1 mol KOH Electrolyte

- 60 mW/cm² (Xe-arc Lamp)
- 2.5 mol Na₂S, 1 mol S, and 1 mol KOH Electrolyte

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Fig. 29 Current-Voltage Curves for CdSe Thin Film Electrodes Taken Before and After Long-Term Test

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Fig. 30 Full Current-Voltage Scans Taken During Long-Term Test of CdSe Thin-Film Electrode

3. SUMMARY AND CONCLUSIONS

During this year's program photoactive CdSe and mixed CdSe-CdTe thin film electrodes with a wide range of electronic properties were produced by the co-evaporation technique and subsequent processing. These films were hexagonal and exhibited a 001 growth texture. Post deposition heat treatment was found to be necessary to obtain electrodes with optimum I-V performance. Electrodes for use in frontwall and backwall cells were produced and film thicknesses of about 2 μm were sufficient to obtain complete light absorption and good collection efficiency.

Films processed in two ways yielded the most promising results for frontwall electrodes. Films deposited with high Se/Cd ratios at low substrate temperatures followed by heat treatment in air produced electrodes with sunlight power efficiencies as high as 5.4%, with high current outputs. Analysis of these type electrodes indicated the films were highly stoichiometric, with carrier densities on the order of 10^{13} cm^{-3} , and accordingly a depletion width that extends through the entire film thickness. The transport properties of these films were found to be poor, yet the power conversion efficiency was generally from 3 to 5% due to the wide depletion width and corresponding high current output. The other type of electrode of interest was deposited at high substrate temperatures ($>400^\circ\text{C}$) near stoichiometry. These electrodes had significantly higher V_{OC} than the electrodes described above, but the J_{SC} and FF were lower so that efficiencies of 3 to 4% were recorded. These films had carrier densities in the range of 10^{15} - 10^{16} cm^{-3} and a correspondingly narrower space charge region, resulting in lower current collection efficiency. The output of both type films was quite stable with time in 2.5 M Na_2S , 1 M S, 1 M KOH electrolyte. Electrodes have been run for the equivalent of 52 days under illumination at short circuit conditions with no detectable reduction in power conversion efficiency. We have found high charge transfer velocities for these thin film electrodes in the polysulfide electrolyte which can account for their good stability.

Backwall electrodes were produced which had short circuit current densities near the theoretical limit of CdSe in an AM2 light flux. These films were lightly doped and fully depleted. Their efficiency, however, was limited to approximately 4% by poor fill factors (~ 0.4) and only modest V_{OC} ($\sim 0.4V$). The low fill factor was attributed to the high series resistance of the electrode, which is due to the sheet resistance of the semiconductor as well as the transparent conductor. The V_{OC} was limited, as in the case of the frontwall electrodes, by the low doping density minimizing the amount of equilibrium band bending present.

Finally, a preliminary investigation of CdSe-CdTe alloy thin film electrodes was conducted with mixed results. The first deposition resulted in an electrode with an efficiency of approximately 5%. However, these results could not be reproduced by subsequent co-evaporation of the compounds.

4. PLANNED FUTURE WORK

The results obtained to date indicate the following directions for future research of the II-VI compound thin film electrodes.

- o Continued investigation of the effects of various deposition conditions and post deposition treatment on the I-V performance of CdSe electrodes. Particular emphasis will be placed on improving the basic transport properties of these films so that the V_{oc} can be increased by increasing the carrier density as in the case of the high substrate temperature films, yet not reducing J_{sc} and FF significantly. To support this effort, basic electronic property and photoelectrochemical measurements as well as application of in house developed data analysis techniques will be done on an as needed basis.
- o Based on our initial encouraging results with the mixed CdSe-CdTe thin films and their potential for higher upper limit efficiency than CdSe alone, further investigation of these films will be done. A three source evaporation system will be used to allow a wide range of processing variation.
- o Backwall electrodes of CdSe and CdSe-CdTe films will be fabricated and evaluated. Particular attention will be given to reducing the series resistance of these electrodes by placement of a current collection grid between the transparent conductor and semiconductor film as well as processing variation cited above.
- o The long term output stability of the thin film electrodes, particularly backwall electrodes, will be evaluated.

The overall direction of future work remains focused on establishing the relevant relationships among thin film electrode processing, resultant material properties and photoelectrochemical performance for front and backwall II-VI compound electrodes.

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