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ELECTROCHEMICAL PHOTOVOLTAIC CELLS CdSe THIN FILM ELECTRODES

Quarterly Progress Report No. 1 for June—August 1979

By
Michael A. Russak
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September 1979

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Solar Energy

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ABSTRACT

The overall objective of this program is to obtain AM1 efficiencies in the range of 10% with electrochemical photovoltaic cells utilizing thin film electrodes. The system currently being investigated is the CdSe/aqueous sulfide-polysulfide system. This report presents the results to date of the initial CdSe deposition parameter study. The key finding has been that the ratio of Se and Cd in the "as deposited" film has marked effect on the film's chemical, microstructural, optical, and electrical properties as well as I-V performance. In addition, it has been found that electrolyte concentration and composition can have a strong effect on the I-V performance of a given electrode.

TABLE OF CONTENTS

<u>Item</u>	<u>Page</u>
Introduction.	1
Technical Progress.	2
Task I Thin Film CdSe Electrodes Preparation	2
Task II Thin Film Characterization.	4
Task III Photoelectrochemical Evaluation	15
Conclusions and Recommendations	24
Planned Future Work	25
Program Status.	26
References.	30

INTRODUCTION

The overall objective of this program is to develop a stable, thin film electrochemical photovoltaic cell with a conversion efficiency (AM1) of 10% or greater. This objective is being approached by utilizing the CdSe/aqueous sulfide-polysulfide electrolyte system employing the following methodology. Thin film electrodes are prepared by the thermal vacuum evaporation of Cd and Se using various deposition parameters. Post deposition heat treatments are applied to these electrodes and their I-V performance measured. Based on this initial I-V evaluation, selected samples are analyzed for electronic and optical properties as well as microstructural and compositional characteristics. More fundamental photoelectrochemical measurements are also done on selected samples. From this information correlations among semiconductor processing (i.e., film deposition conditions and postdeposition treatments), resultant materials properties and photoelectrochemical performance are being established.

It is anticipated that the correlations between processing and photoelectrochemical performance can then be used to produce electrodes with maximum conversion efficiency. Also, as part of the photoelectrochemical evaluation the effects of electrolyte concentration and composition on electrode efficiency and output stability are being investigated. The following tasks are being performed in carrying out this program:

- Task I Thin Film CdSe Electrode Preparation
- Task II Thin Film Characterization
- Task III Photoelectrochemical Evaluation

This first quarterly report summarizes the technical progress made in these three tasks from June 22, 1979 (actual contact start date) to September 1, 1979.

TECHNICAL PROGRESS

TASK I. THIN FILM CDSE ELECTRODE PREPARATION

CdSe thin films are being prepared by the co-evaporation of Cd and Se from two independently controlled resistive heated boats. Figure 1 shows the deposition configuration employed. Each source is controlled by a Sloan MDC 9000 Thin Film Deposition Controller which provides excellent rate control ($\pm 0.5 \text{ \AA/s}$) and thickness measurements. The substrates are clamped to a stainless steel plate (not shown in Fig. 1) which is supported approximately 45 cm from the evaporation plane. A Kanthal wire heater is mounted on the back of the substrate holder.

This system has afforded a great deal of flexibility in choosing deposition parameters and has been fairly reliable, with only about eight days of deposition time lost during this reporting period due to equipment problems.

The initial phase of this task involves the systematic variation of the following deposition parameters:

- Se/Cd ratio

- CdSe deposition rate

- Substrate temperature.

Each deposition is made onto four types of substrates: soda-lime-silica (SLS) glass slides, doped SnO_2 coated SLS glass, mechanically polished titanium sheet, and sand blasted titanium sheet (both $\sim 0.254\text{mm}$ thick). The total deposition area is approximately 50cm^2 . The deposited film thickness is uniform over this area within $\sim 5\%$, based on thickness measurements on samples taken from various locations within the deposition area. EDAX and Auger spectroscopic determinations indicate the thicknesses and deposition rates programmed and monitored on the deposition controllers correctly reflect the actual chemical compositions of the as deposited films.

The determination of the effect of the deposition variables on the I-V characteristics of the thin film electrodes is being done by subjecting each film to a standard annealing schedule followed by potentiostatic I-V evaluation. This approach has been 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. The next phase of this task, which will begin the

Fig. 1 Co-evaporation Deposition System

second quarter, will include the evaluation of various post deposition treatments on I-V performance and film properties.

Combinations of the following deposition parameters have been evaluated thus far:

Se/Cd ratios 0.9 - 5

CdSe rates 8, 13, 25 Å/s

Substrate temperatures 25, 100, 200, 300, 400°C.

Film thicknesses are in the 1 to 3 µm range. The standard heat treatment applied to the samples evaluated thus far is 400°C for 15 min. in air.

TASK II. THIN FILM CHARACTERIZATION

The initial characterization of the CdSe thin films has been primarily by chemical, microstructural, and optical determinations and to a lesser degree by direct electronic measurements. As cited under Task I a range of Se/Cd deposition ratios (i.e., x in CdSe_x) have been used in preparing films. The following discussion will focus on several specific ratios and present typical characterization data on these films before and after the standard heat treatment.

The first set of films were deposited with $x = 0.95$ (i.e., Cd rich), using a rate of 10 Å/s for Cd and 12 Å/s for Se. The "as deposited" films were somewhat cloudy and grainy in appearance. X-ray diffraction analysis indicated the presence of two distinct phases in the films; Cd and CdSe. The CdSe is most likely the hexagonal (wurtzite) phase with a strong 0001 growth texture ($d = 3.51\text{Å}$), although a mixture of the hexagonal and cubic (sphalerite) phase cannot be completely discounted due to the close registry of these two X-ray patterns. If the cubic phase is present the strength of the $d = 3.51\text{Å}$ spacing would coincide with a strong 111 growth texture. Mixtures of cubic and hexagonal CdSe as well as only hexagonal CdSe have been observed previously in vacuum evaporated CdSe films (Ref. 1). Table 1 presents the observed x-ray diffraction pattern of these films and ASTM Card File data for comparison. The effect of the standard heat treatment on these films is shown in Table 2 where it can be seen the excess Cd has oxidized to CdO. The relative intensity and location of the CdSe peaks was not affected by this heat treatment. Figure 2 shows SEM micrographs of a film

TABLE 1 SUMMARY OF X-RAY DIFFRACTION PEAKS FOR CdSe_x
FILM BEFORE HEAT TREATMENT ($x=0.95$)

OBSERVED	CdSe (Hex) (ASTM Card 8-459)		CdSe (Cubic) (ASTM Card 19-191)		Cd (ASTM Card 5-0674)	
$\underline{d(\text{\AA})}$	$\underline{d}$	$\underline{hkl}$	$\underline{d}$	$\underline{hkl}$	$\underline{d}$	$\underline{hkl}$
3.74	3.72	100				
3.53	3.51	002	3.51	111		
3.32	3.29	101				
2.82					2.81	002
2.57	2.56	102			2.58	100
2.36					2.35	101
2.15	2.151	110	2.149	220		
1.99	1.980	103			1.90	102
1.90						
1.83	1.834	112	1.833	311		

TABLE 2 SUMMARY OF X-RAY DIFFRACTION PEAKS FOR CdSe_x
FILM AFTER HEAT TREATMENT ($x=0.95$)

OBSERVED	CdSe (Hex)	CdSe (Cubic)	CdO (ASTM Card 5-0640)	
$\underline{d(\text{\AA})}$	$\underline{d}$	$\underline{d}$	$\underline{d}$	$\underline{hkl}$
3.74	3.72			
3.54	3.51	3.51		
3.32	3.29			
2.73			2.712	111
2.56	2.56			
2.35			2.349	200
2.16	2.151	2.149		
1.99	1.980			
1.83	1.834	1.833		
1.66			1.661	220

a) BEFORE HEAT TREATMENT

b) AFTER HEAT TREATMENT

79/79-001W

Fig. 2 SEM Micrographs of $\text{CdSe}_{0.95}$ Film (Bar = $1\ \mu\text{m}$)

with $x = 0.95$ before and after heat treatment. The granular nature of these films is quite evident, and it can be seen that the heat treatment results in no obvious microstructural changes.

The second series of films were deposited with $x = 1.15$ ($\text{Cd} = 10\text{\AA}/\text{s}$, $\text{Se} = 15\text{\AA}/\text{s}$). These films are not cloudy and have a reddish brown color as deposited. In this case the X-ray diffraction patterns of the unfired films showed only two major CdSe peaks at $d = 3.53\text{\AA}$ and $1.99\text{\AA}$, and an amorphous roll at low 2θ values. Tables 3 and 4 summarize the observed d spacings before and after firing. In this case there is an increase in intensity of the $d = 3.54\text{\AA}$ and $1.99\text{\AA}$ peaks as well as the appearance of the $d = 2.55\text{\AA}$ peak after firing, accompanied by the disappearance of the amorphous roll.

To further evaluate the chemistry of these samples, Auger depth profiles were done on selected films. Evaporated samples of known thickness on polished metal substrates were used to establish the ion beam sputtering rate to quantitatively define the depth profiles. A CdSe single crystal was used as a standard to establish the Se/Cd ratio of 1. Figure 3 shows an Auger depth profile of a film in this series before and after heat treatment. It can be seen clearly that before heat treatment the film is Se rich (particularly the surface) and upon firing the Se is removed and the film is nominally stoichiometric. This finding is consistent with the changes observed in the x-ray diffraction patterns. Since films of Se alone were found to be amorphous, it was assumed that the excess Se is present as an amorphous deposit and the "as deposited" films with $x = 1.15$ are two phase material consisting of CdSe and Se. This is also expected from the phase diagram of the Cd-Se system (Ref. 2) where the reported solubility of Se in CdSe is <0.002 atomic percent.

Figure 4 presents SEM micrographs of CdSe_x film with $x = 1.15$. There are no major structural changes evident in these micrographs due to heat treatment, although the fracture edge of the heat treated sample appears to have slightly more structure than that of the "as deposited" film. The heat treated films generally show more cracking than the "as deposited" films which is probably related to the loss of excess Se upon firing.

TABLE 3 SUMMARY OF X-RAY DIFFRACTION PEAKS FOR CdSe_x
FILM BEFORE HEAT TREATMENT ($x=1.15$)

OBSERVED $\overset{\circ}{d}(\text{\AA})$	CdSe (Hex) $\underline{d}$	CdSe (Cubic) $\underline{d}$
3.53	3.72 3.51 3.29 2.56 2.151	3.51 2.145
1.99 + amorphous roll	1.98 1.834	 1.833

TABLE 4 SUMMARY OF X-RAY DIFFRACTION PEAKS FOR CdSe_x
FILM AFTER HEAT TREATMENT ($x=1.15$)

OBSERVED $\overset{\circ}{d}(\text{\AA})$	CdSe (Hex) $\underline{d}$	CdSe (Cubic) $\underline{d}$
3.54	3.72 3.51 3.29	3.51
2.55	2.56 2.151	 2.149
1.99	1.98 1.834	 1.833

Fig. 3 Auger Depth Profile of CdSe_{1.15} Film

a) BEFORE HEAT TREATMENT

b) AFTER HEAT TREATMENT

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Fig. 4 SEM Micrographs of CdSe_{1.15} Film (Bar = 1 μ m)

The third case to be considered is films with $x \sim 2.5$, deposited at a Cd rate of $5\text{\AA}/\text{s}$ and Se rate of $15\text{\AA}/\text{s}$. These films have the same general appearance as those with $x = 1.15$, but their color is more reddish. In almost all cases the "as deposited" (at 25°C) films are amorphous, although some films are slightly crystalline with a small peak at $d = 3.53\text{\AA}$. Upon heat treatment major structural changes occur in the film and a very strong peak at $d = 3.53\text{\AA}$ is observed along with several other much weaker diffraction peaks. Table 5 summarizes the X-ray diffraction data and Fig. 5 shows typical microstructure of these films before and after heat treatment. The microstructural changes occurring in these films are radical. Before heat treatment the film is quite featureless, indicative of an amorphous deposit. However, after heat treatment a much more oriented structure is observed. These observations are consistent with the X-ray diffraction findings.

Films deposited with $x > 2.5$ closely resemble the films with $x = 2.5$ in appearance, chemically and structurally. They are amorphous as deposited and crystallize with a very strong 0001 texture after heat treatment.

The rate of CdSe deposition does not seem to have a significant effect on the chemical and structural properties of the "as deposited" films. An investigation of the effect of substrate temperature on film deposition for a wide range of Se/Cd ratios has not been carried out. However, the data presently available indicate for a CdSe film with $x = 1.15$, increasing the substrate temperature enhances the degree of crystallinity of the unfired film. This is evidenced by the increased intensity of the diffraction peak at $d = 1.99\text{\AA}$ with increased substrate temperature. This effect is much more pronounced for films with $x \geq 2.5$ where at room temperature the films are amorphous as deposited, and as the substrate temperature is raised the film develops a strong 0001 growth texture. It has also been observed that CdSe film adherence is better on the surface roughened Ti substrates than on the mechanically polished Ti.

Optical Properties

The transmission spectrum of a fired thin film is presented in Fig. 6. The initial Se/Cd ratio was 1.15 in this film and differences were noted between the "as deposited" and heat treated transmission curves. The curve for the unfired sample is offset slightly to the left due to the presence of the excess Se ($E_g = 2.2\text{eV}$). The effect of the Se on the optical absorption coefficient (α) of the

TABLE 5 SUMMARY OF X-RAY DIFFRACTION PEAKS FOR CdSe_x
FILM AFTER HEAT TREATMENT ($x=2.5$)

OBSERVED $\underline{d}(\text{\AA})$	CdSe (Hex) $\underline{d}$	CdSe (Cubic) $\underline{d}$	Se $\underline{d}$	Cd $\underline{d}$
	3.72			
3.53	3.51	3.51		
3.29	3.29			
3.01			3.005	
2.82				2.82
	2.56			
2.14	2.15	2.149		
	1.98			
1.83		1.833		
1.76			1.76

a) BEFORE HEAT TREATMENT

b) AFTER HEAT TREATMENT

79/79-004W

Fig. 5 SEM Micrographs of CdSe_{2.5} Film (Bar = 1 μ m)

Fig. 6 Transmission Curve of Heat Treated CdSe_{1.15} Film

thin film is shown in Table 6, where calculated α values for heat treated and "as deposited" films are presented. The α of the fired films is from 10-20% higher for the unfired film. The effect of larger amounts of Se in the unfired film on its absorption spectrum is shown in Fig. 7 which compares the transmission curves for an evaporated Se film (1), on unfired CdSe_x film with $x = 3$ (2) and the same film after heat treatment (3). It can be seen that as the film crystallizes its absorption edge shifts to longer wavelengths with CdSe formation.

Resistivity Measurements

A limited amount four point probe and through the film resistivity measurements at room temperature have been done to date. The general trends are that films with $x < 1$ are very conductive as deposited and their conductivity increases with heat treatment, whereas films with $x > 2$ have moderately low conductivities as deposited, which increase slightly upon heat treatment. Table 5 shows representative results for two films.

TASK III - PHOTOELECTROCHEMICAL EVALUATION

The routine photoelectrochemical evaluation employed for the thin film electrodes deposited under various conditions has been potentiostatic I-V measurements in the dark and at 50 mw/cm^2 in AM1 light. As in the previous section, selected data will be presented here to show the observed relation between film stoichiometry and I-V performance.

Films with $x < 1$ were found to have very poor I-V characteristics with V_{oc} in the range of 0.1 to 0.3 V, J_{sc} from 0.5 to 1.2 mA/cm^2 , $ff \sim .25$ and $\eta \sim 0.1\%$. These poor results are probably due to the very high conductivity of these films resulting in very narrow space charge regions at the junction, which accounts for low collection efficiency. Preliminary analysis of monochromatic I-V curves for these films indicates very low quantum efficiencies ($\sim 3-4\%$), short minority carrier diffusion lengths ($\sim 0.05 \mu\text{m}$) and high doping densities ($> 10^{20}$).

Films with $x = 1.15$ have better I-V characteristics with V_{oc} from 0.35 to 0.54 V, J_{sc} from 1 to 3 mA/cm^2 , ff as high as 0.4 and η from 0.2 - 1.0%. More fundamental photoelectrochemical evaluation of these films has not been completed.

TABLE 6 OPTICAL ABSORPTION COEFFICIENT FOR CdSe_x THIN FILM BEFORE AND AFTER HEAT TREATMENT ($x = 1.15$)

Wavelength (nm)	Fired ($\times 10^4 \text{ cm}^{-1}$)	Unfired ($\times 10^4 \text{ cm}^{-1}$)
400	8.68	6.82
433	7.16	5.12
466	7.00	5.49
500	6.76	4.69
533	6.53	5.10
566	4.81	4.17
600	4.05	3.80
633	3.48	3.26
666	2.76	2.39
700	1.94	1.39

TABLE 7 RESISTIVITY OF CdSe_x FILMS

x	Before Heat Treatment	After Heat Treatment
0.95	$1.7 \times 10^{-2} \Omega\text{-cm}$	$3.32 \times 10^{-3} \Omega\text{-cm}$
2.63	$8.4 \times 10^5 \Omega\text{-cm}$	$2.1 \times 10^5 \Omega\text{-cm}$

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Fig. 7 Transmission Curves of Se Film (1), Unfired CdSe₃ Film (2) and Fired CdSe₃ Film (3)

The best I-V performance to date has been recorded with films that have x values of 2 to 4, with V_{oc} in the range of 0.4 to 0.5V, J_{sc} from 4 to 9 mA/cm², ff 0.4 to 0.6 and η from 1-3%. The I-V curves representing the best performance recorded this quarter are shown in Figs. 8 (metal substrate, light through electrolyte) and 9 (transparent conducting substrate, light through film). The efficiencies of these samples are 2.5 and 3.25%, respectively. Statistically the best I-V parameters have been obtained with an x value of ~ 3 using the standard post deposition heat treatment. Monochromatic I-V curves for films with x = 3 indicate high internal quantum efficiencies, 80-85% at 700 nm. Analysis of these curves in the reverse bias region using simple depletion layer theory (Refs. 3 & 4) results in the calculation of minority carrier diffusion lengths of several tenths of a micrometer and carrier densities in the 10^{15} to 10^{16} range. Also, action spectra of these films indicate significant response at wavelengths greater than bandgap energy as well as a fall off of response towards the blue end of the spectrum. This type of response has been shown to be indicative of defective material (Refs. 4 & 5), and we attribute the modest efficiency observed with these electrodes to the defective nature and small crystallite size of the processed CdSe thin films.

As part of the photoelectrochemical evaluation task this quarter, a study of the effect of polysulfide electrolyte concentration and composition on dark current behavior and visible transmission of the electrolyte has been undertaken. Figures 10 and 11 show the variation of rest potential and transmittance at 500 nm, respectively, for the combinations investigated. The dark current data are currently being analyzed based on the following reaction paths:

and

for the anodic and cathodic reactions, respectively. This analysis will provide insight into the mechanisms that affect the I-V performance of a thin film electrode as shown in Fig. 12. Curves A and B were run on the same electrode at the same light intensity (700 nm filter). The only difference is that curves A were run in electrolyte that had 1F S whereas curves B were run in 0.01F S electrolyte. Both electrolytes were 2.5F in Na₂S and 1F in KOH.

Fig. 8. J-V Curve for CdSe Film on Metal Substrate

Fig. 9 J-V Curve for CdSe Film on Transparent Conducting Substrate

		S, m							
		2.5	2.0	1.5	1.0	0.5	0.1	0.01	0
Na ₂ S, m	2.5	-0.784	-0.788	-0.792	-0.802	-0.814	-0.832	-0.851	-0.880
	2.0	-0.787							
	1.5	-0.760				-0.790			
	1.0	-0.716			-0.760			-0.840	
	0.5								
	0.1						-0.730		
	0.01				-0.675			-0.710	

Fig. 10 Variation of Rest Potential with Electrolyte Composition and Concentration (vs SCE)

		S, m							
		2.5	2.0	1.5	1.0	0.5	0.1	0.01	0
Na ₂ S, m	2.5	<div>17% 20%</div>	30%	34%	41%	67%	91%	96%	96%
	2.0	24%							
	1.5	<div>40% 42%</div>							
	1.0	55%			63%			96%	
	0.5								
	0.1				86%		95%		
	0.01							98%	

ALL IN 1 m KOH

PATH LENGTH 1 mm

Fig. 11 Transmission at 500 nm of Various Polysulfide Electrolytes

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Fig. 12 Effect of S Concentration on I-V Performance of a Thin Film Electrode

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The following conclusions are drawn from the research conducted this quarter:

- o The chemistry and microstructure of the "as deposited" films depends on the Se to Cd ratios used during deposition
- o The standard heat treatment (400°C, 15m, air) has a slight effect on films deposited with $x < 1$ and imparts more radical changes to the films as the x value increases from 1.15 to 3 or greater
- o In all cases the heat treated films exhibit a strong 0001 growth texture
- o For the standard heat treatment, "as deposited" films with $x = 3$ yield the best I-V performance
- o The performance of CdSe electrodes evaluated to date is probably limited by the small crystallite size and defect structure of the films
- o The electrolyte composition has a significant effect on the I-V performance of a given electrode. This is due to the variation in optical transmission of the solutions as well as their I-V characteristics.

RECOMMENDATIONS

Recent experiments indicate the critical step in achieving higher conversion will be post deposition processing. In order to enhance the crystallite size in the thin film and improve the defect structure, heat treatment schedule variation will be undertaken. In addition, the analysis of electrolyte concentration and composition effects will be continued.

PLANNED FUTURE WORK

Continued activities are projected as follows:

- o Selection of two or three x values and determination of deposition reproducibility by I-V evaluation
- o Post deposition heat treatment variation, on films with two or three x values
- o Chemical and microstructural determinations on selected processed films
- o Optical and electronic measurements on selected films
- o Further analysis of electrolyte composition and concentration effects.

PROGRAM STATUS

Current versions of the Program Plan, Program Labor Summary, and Program Cost Summary are presented in Figs. 13-15.

Fig. 13 Program Plan

Fig. 14 Program Manpower Summary

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Fig. 15 Program Cost Summary

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