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THIRD QUARTERLY TECHNICAL PROGRESS REPORT

on

LARGE AREA THIN FILM CADMIUM SULFIDE
SOLAR CELL ARRAY INVESTIGATION

J. C. Schaefer
R.J. Humrick
E. R. Hill

Solid State Research Laboratory
Crystal-Solid State Division
The Harshaw Chemical Company
1945 E. 97th Street
Cleveland 15, Ohio

Period of 15 March 1963 to 15 June 1963

21 June 1963

Contract No. AF 33(657)-9975
Project No. 8173, Task No. 817301

Flight Accessories Laboratory
Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by The Harshaw Chemical Company, Solid State Laboratory covering the work accomplished during the period from March 15, 1963, to June 15, 1964 under Contract AF 33(657)-9975. This report is being published and distributed prior to Air Force review. Its publication is for the exchange and stimulation of ideas and does not constitute approval by the Air Force of the finding or conclusions contained therein.

The work of this project deals with certain specific problem areas of the cadmium sulfide thin film front wall solar cell. Related contracts sponsored by the Air Force by other Defense Agencies, and by NASA at Harshaw are concerned with other aspects of cadmium sulfide solar cells, other photovoltaic conversion systems and with the investigation of the properties of various semiconductor materials with photovoltaic possibilities.

This contract is being monitored by Mr. L. D. Massie, ASRPP-20, Project Engineer AF Aero-Propulsion Laboratory of the Aeronautical Systems Division, WPAFB, Ohio. The detailed work of the project had been divided into three major sections with a principal investigator in charge of each. Cell Development efforts have been under the supervision of R. J. Humrick including work on orbital evaluation, cell contactin cell stability, cell and array construction, and other methods of film formation. Mr. Humrick has been assisted by W. W. Baldauf, T. A. Griffin, and R. W. Olmsted. Materials Research has been conducted by G. A. Wolff supported by R. F. Belt, E. L. Lind, D. D. Bell and J. R. Hietanen. Cell Research efforts on basic barrier studies has been conducted by E. R. Hill, as the principal investigator, and assisted by D. H. Dickey. Technical and administrative direction of the project has been carried out by J. C. Schaefer.

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INTRODUCTION AND SUMMARY

During this quarter a 5.1% thin film cell has been produced on a 1" x 1" substrate. This result compares favorably with the maximum efficiency of 5.4% reported for a single crystal CdS cell. A procedure for up-grading low efficiency cells to the average efficiency level has also been developed.

A non-destructive x-ray technique has been used successfully to photograph dislocations in single crystal CdS. This procedure promises to yield a fund of information.

Efforts to produce an ultra-pure CdS by distillation of the elements and subsequent reaction is underway.

Work has been carried on in the analysis of the I-V data and spectral response in an effort to catalog this data in the form of a model. The present data can be made to fit a p-n junction with photoconductive series and shunt resistances. Some reject "shorted" cells have been studied at low temperatures where the I-V curve begins to resemble a backward diode. Injection luminescence with very low conversion efficiency has been observed with the radiation lying in the band between 1 and 1.5 ev.

PART I - CELL DEVELOPMENT

Orbital Evaluation

Temperature Cycling

A 6" x 6" array (358MN) similar in construction to the panels submitted to the Air Force for orbital evaluation was subjected to an additional temperature cycling test of ten cycles covering a much larger temperature range of -200 C to +50 C. Each cycle was of 50 minutes duration. The efficiency at the beginning of the test was found to be 2.11%, while at the end of ten cycles the efficiency was approximately the same, 2.08 percent. Figure 1 is a plot of efficiency vs. temperature for the ninth cycle.

A report has been received from the Air Force regarding the previously submitted flight panels with a copy of the data taken at Table Mountain. The data received was in close agreement with the measurements taken in the Harshaw Laboratory.⁽¹⁾ Figure 2 is a photograph of the four flight panels as submitted to the Air Force. The center array of each panel contains the silicon heat sensors (thermistors). The one on the top is shown at left, and one for the bottom as shown on the right.

Barrier Formation

Cell Up-grading

It is believed that the barrier and its formation holds the key to any large improvement in cell solar energy conversion efficiency. This approach has resulted in modest gains in efficiency which has continued to stimulate interest in this area. The collection of current from the barrier or p-layer by means of the gold grids has doubled the output of the cells, therefore, any gain in the basic quality of the cells is doubled.

Various plating times, variations in current densities, drying and oxidation times, and variations in humidity, continue to be studied to determine their effect on the formation of the barrier and their ultimate effect on the cell efficiency. Some of these studies have been part of previous reports. One of the studies being reported at this time is a study of the effect of the total plating time on cell performance. Experiments designed to study this effect yielded a rather unexpected result. Cells of low efficiency can be improved markedly, but the same procedure will not improve a good cell.

The reclamation, or up-grading procedure, may simply be a matter of replating over the previous barrier by the normal procedures, or it may consist of removal of the previous barrier and then plating a completely new barrier on the cell.

Initial observations have shown quite satisfactory results. Eighteen cells were replated ranging from poor (less than 1% efficient) to good (greater than 2.5%). The general type of cell replated was one of essentially low output but with a fairly good I-V characteristic curve.

From Table I, it can be seen that poor cells have made a large improvement, while good cells have shown no noticeable improvement. In all cases the current densities were increased regardless of the change in other parameters. In the table, the cells were separated into groups according to their original values. The first figure listed

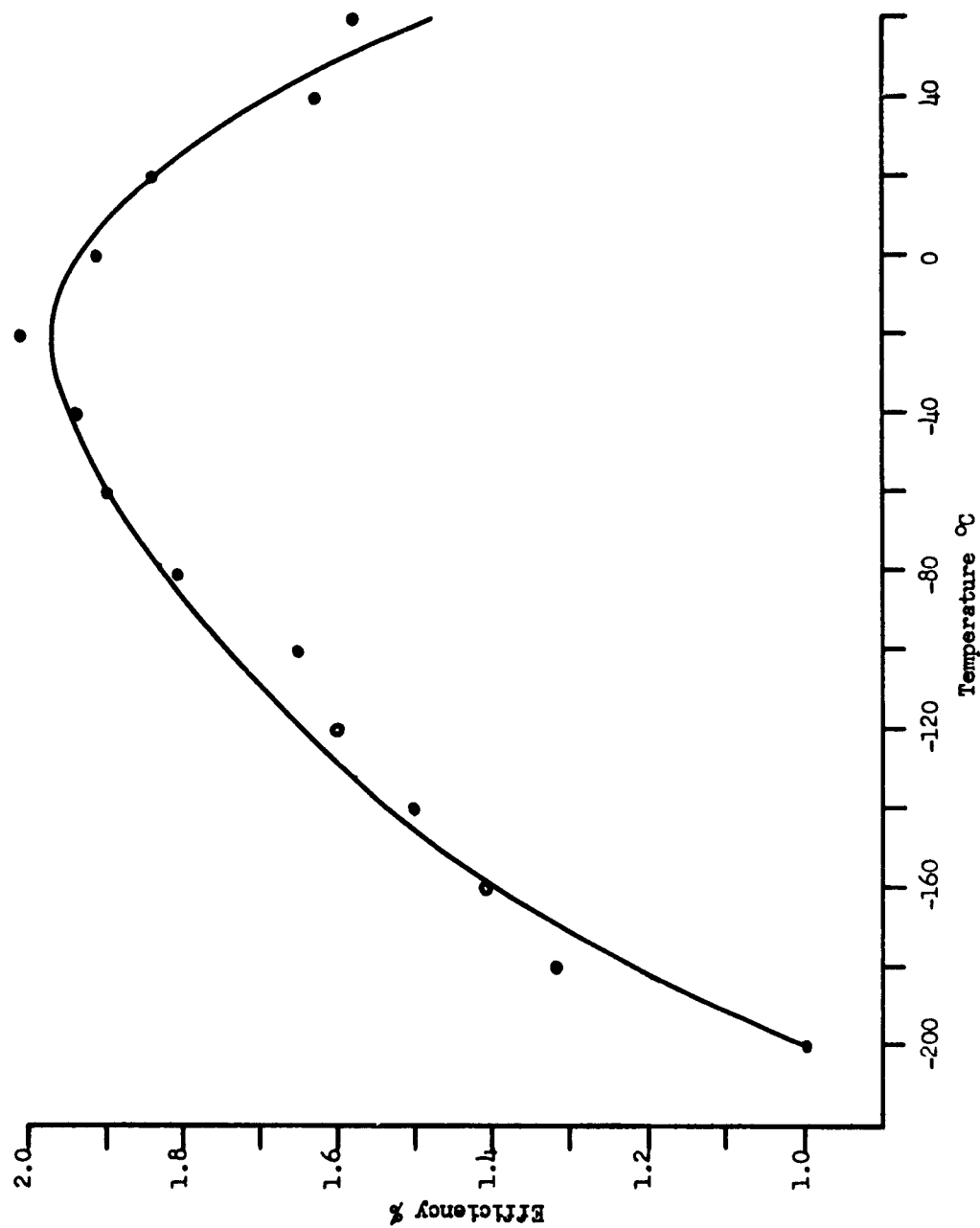


Figure 1: Efficiency vs. Temperature for laminated CdS Thin Film Solar Cell

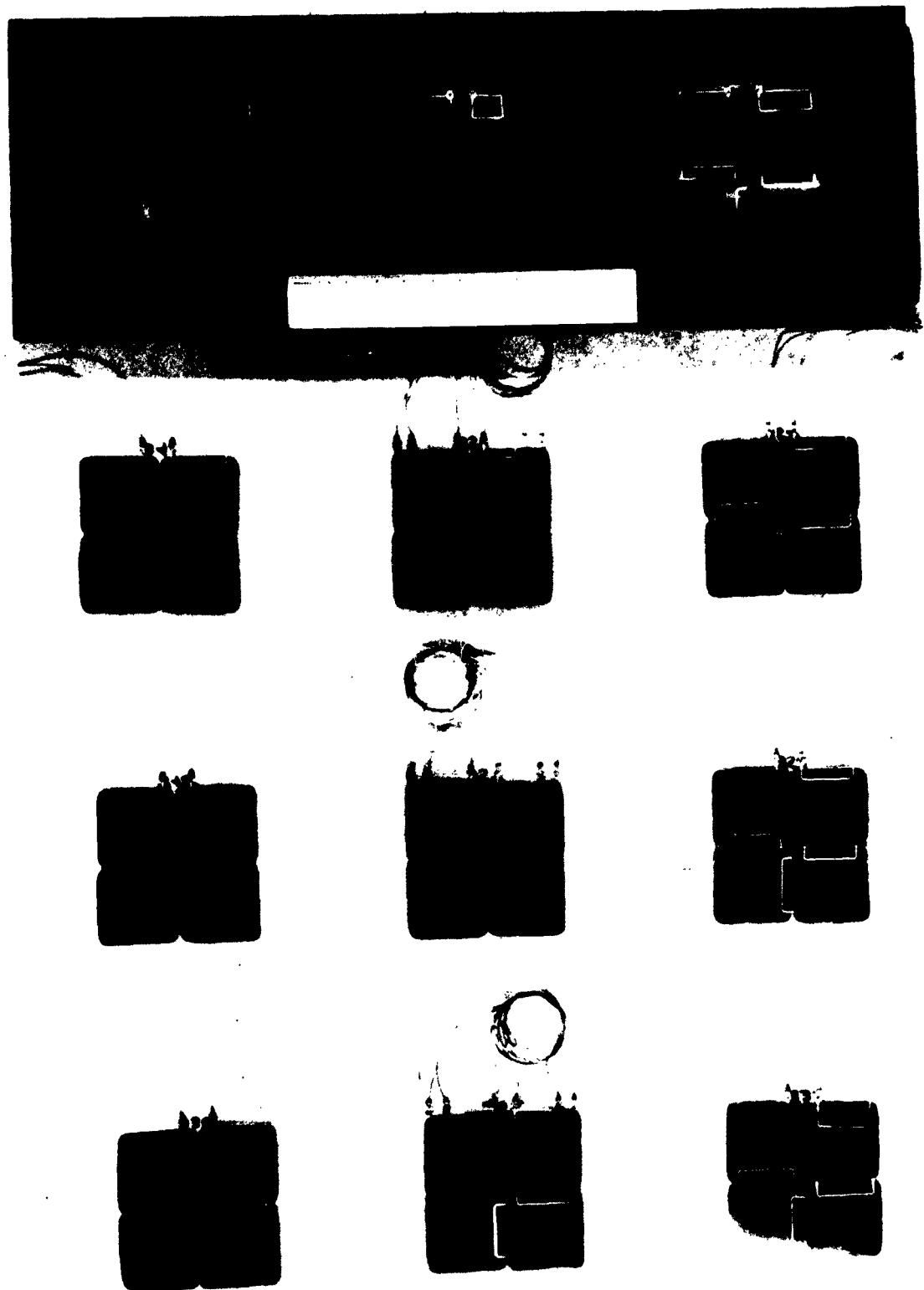


Figure 2: Photograph of Flight Panel

is the initial average and the last figure the average obtained after replating:

TABLE I
CELL IMPROVEMENT DATA

	V_{oc}		I_{sc}/cm^2 (ma)		Efficiency %	
	(before)	(after)	(before)	(after)	(before)	(after)
POOR	.42	.48	1.3	7.1	.3	1.9
FAIR	.47	.48	5.1	7.6	1.7	2.5
GOOD	.50	.48	8.1	9.9	2.8	2.8

In general it seems as though poor cells can be improved, while the good ones are not noticeably changed. This indicates a variation in the quality of the barrier formation.

Oxidation

An apparent correlation between the humidity and average cell efficiency has prompted experiments involving the use of very dry air for the purpose of the simultaneous drying and oxidation of the copper electrodeposited on the CdS. For this purpose, an air drying unit was obtained that could continuously supply -60°C dew point air to the forced convection drying and oxidation oven used on the pilot line.

The initial experiment was to determine the effect on the performance of the cells by varying the period of time in the oxidising oven. Quantities observed were the open circuit voltage, short circuit current density, efficiency, and a parameter, the quality factor "Q". The quality factor is a measure of the squareness of the I-V characteristic.⁽²⁾ A total of 87 cells were evaluated in the experiment of which 73 were 1" x 3" in size. Table II tabulates the results as of the present time.

It appears as though the OCV, the SCC and efficiency can be increased with longer residence times in the oven using very dry air for the oxidation of the barrier. The drop in the "Q" factor with increasing time in the oven is not understood. Work in this area is being continued.

Figure 3 shows the installation of the air dryer on the wall with the transistor washer on the left and the forced convection oven on the right.

Cell Contacting

Eight 3" x 3" test cells were fabricated using 70 lines/in. Gold, Silver, Copper and Nickel grids. The Gold proved superior in all eight test cells followed by the Copper, Silver, and Nickel. An expanded metal grid was also tried but poor results were obtained. Expanded grids of a finer mesh will be tried along with woven metal grids.

Cell Stability

More cells were constructed and put on life test. A life test vacuum unit was

TABLE II
DATA ON OXIDATION EXPERIMENTS

<u>Cell Size</u>	<u>Time (hr)</u>	<u>V_{oc} (volts)</u>	<u>I_{sc} (ma/cm²)</u>	<u>"Q" Factor</u>	<u>Efficiency (%)</u>
3" x 3"	.25	0.46	9.2	0.53	2.2
3" x 3"	1.5	.49	11.2	.50	2.8
1" x 3"	.25	.46	6.8	.56	1.9
1" x 3"	1.0	.47	6.9	.56	1.8
1" x 3"	1.5	.48	7.9	.55	2.1
1" x 3"	2.0	.49	8.4	.52	2.1

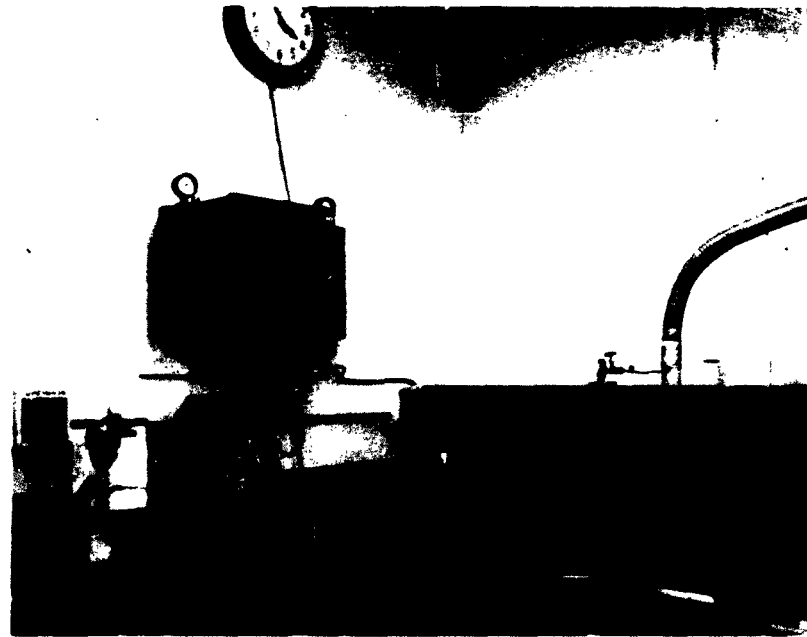


Figure 3: Photograph of Transistor Washer, Air Dryer, and Oven.

constructed using Aluminum stock and O-ring seals.

A water life test unit was also put into operation.

Radiation samples (1cm x 1cm) were tested and returned to Harshaw from NRL for examination. Figure 4 shows the very slight degradation due to electron bombardment with regard to power output.

Cell and Array Construction

Encapsulating Materials

Work is still being done with various new plastics in an effort to determine the best materials for encapsulation of solar cells with emphasis on clarity, physical characteristics of the seal, resistance to outer space environment and water vapor permeability. Experiments were conducted with KEL-F, Mylar (Type M) and Teflon (FEP) films.

Difficulty was encountered in heat sealing the Teflon FEP in that it sealed, but its optical properties were reduced. The Mylar (Type M) turned brown when sealed. Both of these effects were problems due to the one-half hour cooling cycle, during which time the films convert to crystalline form and become hazy. This effect is characteristic of many thermoplastic thin films.

Experiments with KEL-F proceeded satisfactorily, obtaining excellent seals, using 2 mil, 5 mil, and 10 mil samples.

Lamination experiments are still being carried out with Schjeldahl Adhesive GT-300 which is a 1/2 mil resin coating on 1 mil Mylar. Poor results were obtained with the 1 mil resin on the 1 mil Mylar due to the fact that the resin flowed under sections of gold collector grid, causing poor contact between the grid and cell.

Design has begun on the square foot array and one-half square foot array for delivery to the Air Force. Some unique methods shall be used for this purpose.

Pilot Line

The production of cells on the pilot line has continued to be an important part of our program. It contributes cells for experimentation while serving as a continual check on the processes and the effect of any changes made in the process.

The total number produced in this period was 393 cells, consisting of 1" x 3" and 3" x 3". In general, the cells produced have averaged higher in efficiency and slightly less in open circuit voltage.

The highest efficiency cell measured during this period was 5.12%.

Plans are being made for re-tooling of the Kinney evaporator to produce 6" x 6" films. These films would be trimmed to various sizes for use in experimentation as well as continuing to complement our pilot line production. Experiments performed using portions of a given 6" x 6" film that had been cut into small sizes would be more indicative of the effect of experimentation performed simply by the elimination

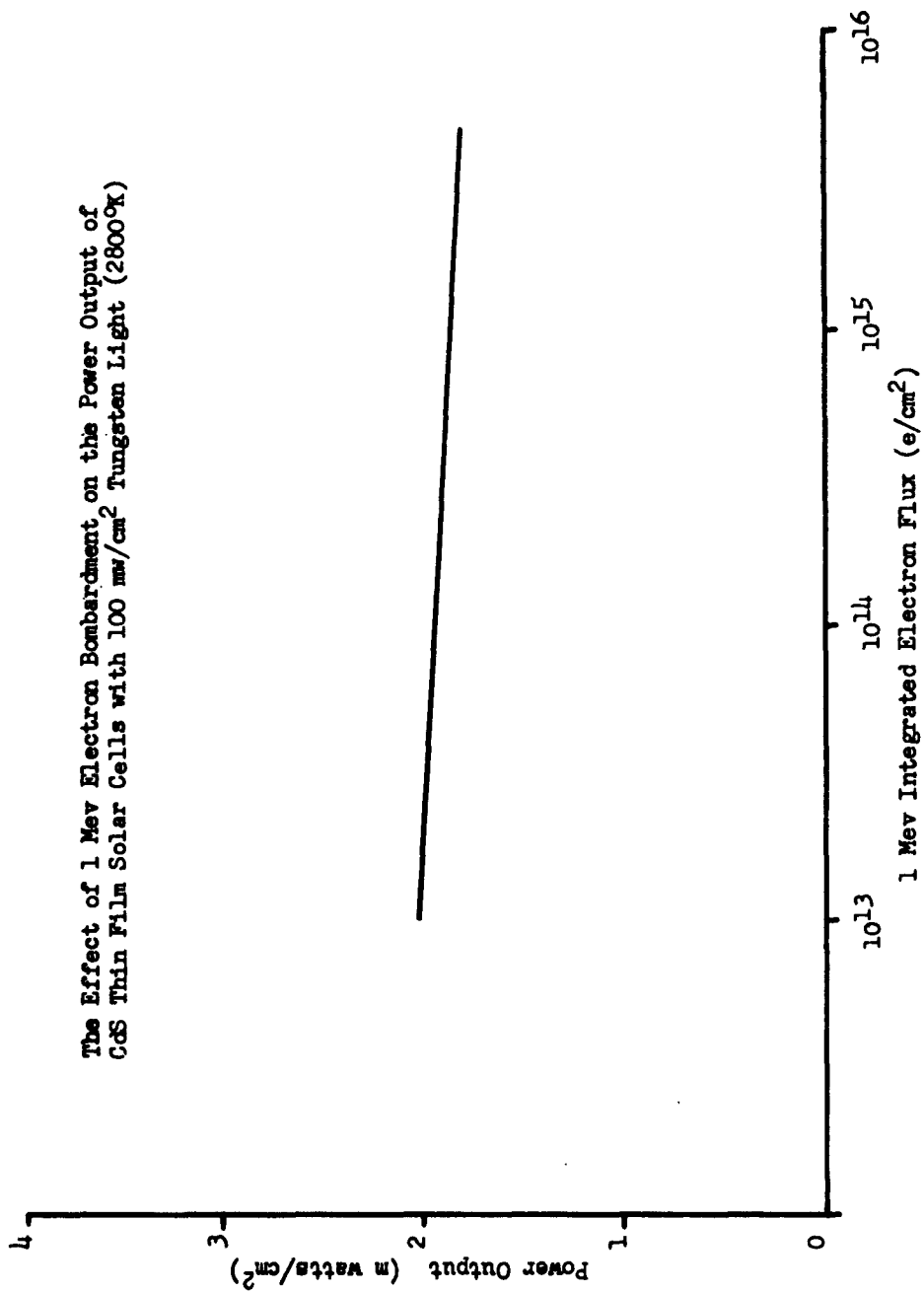


Figure 4: Effect of Electron Radiation on CdS Cells

TABLE III

ARRAY DATA

<u>No. of Arrays</u>	<u>Size</u>	<u>Description</u>	<u>Efficiency %</u>		
			<u>Min.</u>	<u>Max.</u>	<u>Avg.</u>
13	1 cm x 1 cm	Radiation Samples	--	--	--
15	1 cm x 2 cm	Radiation Samples	2.6	3.8	3.1
5	1" x 1"	Experimental Cells	MECHANICAL SAMPLES		
14	1" x 1"	Test Cells	0.9	*5.12	2.2
14	1" x 3"	Experimental Cells	MECHANICAL SAMPLES		
11	1" x 3"	Test Cells	0.7	3.7	2.4
8	3" x 3"	Grid Test Cells	--	--	--
10	3" x 3"	Test Cells	1.2	2.9	2.5
12	6" x 6"	Test Cells	1.6	2.7	2.2

*Based on the substrate area minus the area covered by the electrodes and the collector grid.

of evaporation variables from one run to the next. In addition, a greater number of small cells can be produced in the same length of time.

TABLE IV
PILOT LINE DATA

<u>Cell</u> <u>No</u>	<u>Size</u>	<u>Ocv.</u>	<u>Efficiency %</u>			<u>Scrap</u>
			<u>Min.</u>	<u>Max.</u>	<u>Avg.</u>	
347	1" x 3"	.47	1.0	3.6	2.1	61
46	3" x 3"	.47	1.2	3.4	2.4	6

Light Intensity Variation Effects

Variations in light intensity have been found to have little effect on cell efficiency until the intensity has been increased to about 200 mw/cm² or greater. This is equivalent to two suns as measured terrestrially.

For the purpose of this experiment, a small section (1.3 cm²) of a laminated cell was measured using collimated light from an RFL-2 Tungsten lamp, operated at 140 VAC. Intensity of illumination was measured by both a G. E. Radiation Meter [G-Cal/(cm²)(min)] and an Eppley thermopile (mv). This also served as a check on the calibration of one meter to the other. The upper limit of light intensity available due to physical limitations was about 325 mw/cm².

From the graph of light intensity versus efficiency and intensity versus short circuit current (Figure 5), it can be seen that the efficiency shows very little change until the higher intensities were employed. Another test will be run to verify the findings and also note effects of still higher intensities.

Other Methods of Film Formation

Electrophoretic deposition of CdS on Molybdenum substrates can be controlled quite readily with regard to obtaining a smooth, dense film, however, difficulty occurs in the sintering process necessary for formation of a usable film. If the temperature within the quartz tube chamber is allowed to rise very high, the CdS leaves the substrate and deposits on cooler portions of the chamber, along with the formation of Molybdenum Sulfide on the substrate. When a lower temperature is used, the adherence of the CdS to the substrate is improved, but the film still is not useful as a photovoltaic cell.

A change in deposition methods using a mixture of CdS and CdCl₂ sprayed onto a substrate is now in the process of being evaluated. Glass substrates are being used initially to determine the proper percentages of CdCl₂ and CdS as well as the desired temperatures at which the film should be sintered. Initial attempts using this method has shown some promise in that a hard recrystallized film of CdS has been formed on the glass after the CdCl₂ has been evaporated. The film is slightly photoconductive, but is discontinuous probably due to incomplete dissolving of the CdS by CdCl₂. Work is continuing in an effort to form a continuous crystalline film on the glass before changing to a Molybdenum substrate.

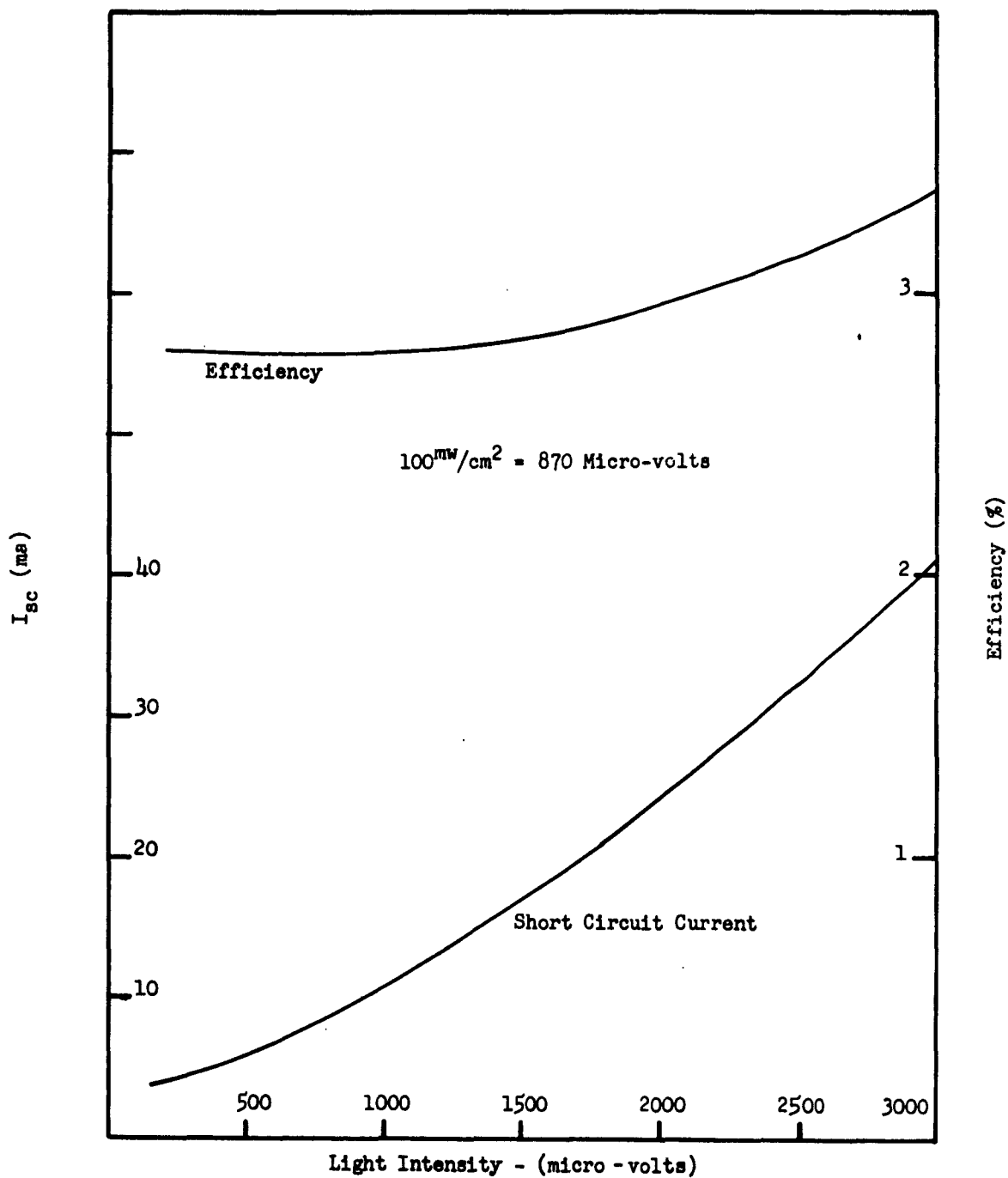


Figure 5: Light Intesity vs. Efficiency & Short Circuit Current

PART II - MATERIALS RESEARCH

Cadmium Sulfide Preparation and Purification

The previous quarterly report discussed the work which has been started on the purification of cadmium metal. This is the first step in the overall plan of preparing pure cadmium and pure sulfur for the purpose of reacting the elements together to form very pure cadmium sulfide.

An all quartz unit for purification of cadmium by distillation under vacuum has been described in the previous report and is shown in Figure 6, of this report. This unit is enclosed in an insulated metal case equipped with glass inspection ports in order to maintain the entire quartz still above the melting point of cadmium metal. The unit was tested during the present report period and found to have insufficient resistance heaters in the metal case to maintain the entire unit at the desired temperature of 340°C . More heaters are being installed and the unit will again be tested.

Zone refining of cadmium is also being pursued as an independent purification technique to remove those impurities which are difficult to remove by distillation. The marked tendency for cadmium to oxidize in the molten state is causing difficulty. In the present report period, ultra pure hydrogen has been used as the ambient atmosphere, but oxide formation is evident here just as was previously reported for an argon-atmosphere. A deoxo unit followed by a phosphorous pentoxide tower inserted in the line gives a noticeable reduction in oxide formation, but does not entirely remove it. A Serfass hydrogen purifier has been obtained and will be used in further zone refining experiments. Removal of oxide from the molten zone in cadmium zone refining is considered to be important since impurities may accumulate in the oxide film and not be affected by zone refining.

Table V presents the spectrographic analysis of cadmium metal obtained from three different sources. The Cominco and United Mineral and Chemical Corporation sources are reported to be 99.9999% pure, but do not seem to be very much better than reagent grade cadmium in terms of a number of different impurities.

Table V also gives the results of the spectrographic analysis for the two sources of high purity sulfur which we are considering. These samples were concentrated ten times before analysis. The American Smelting and Refining sample is seen to be significantly better than the Johnson Matthey sample.

A simple sulfur distillation unit (Figure 7) has been built to effect gross separations of sulfur from impurities such as glass chips, carbon etc. which seems to be present in commercially available pure sulfur. Results will be given in the next report.

Dislocations and X-ray Diffraction Microscopy of CdS

In previous reports under this contract, etch pit studies were extensively applied towards fundamental problems of CdS single crystal growth, polycrystalline grain growth, and the general effects of dislocations. For continuation of these studies a complementary technique for dislocation viewing has been developed. This technique utilizes x-ray procedures and is therefore non-destructive. Furthermore,

TABLE V
ANALYSES OF CADMIUM AND SULFUR

Element	Cominco Cadmium	UM & CC Cadmium	Reagent Cadmium	Asarco Sulfur*	Johnson-Matthey Sulfur*
Aluminum	FT	FT	VFT+	VFT+	FT-
Bismuth	FT	VFT	VFT	--	--
Boron	--	--	--	--	VFT-
Cadmium	VS	VS	VS	--	--
Calcium	T-	FT+	FT-	VFT	VFT
Chromium	--	FT-	--	--	--
Copper	FT-	FT-	FT	FT	FT
Gallium	FT	VFT	VFT-	--	--
Iron	FT+	T-	FT-	FT-	FT
Lead	VFT	VFT	T	--	--
Magnesium	T-	T-	FT+	VFT+	FT
Manganese	VFT	VFT+	VFT-	--	EFT
Nickel	VFT	FT-	VFT-	--	VFT+
Silicon	T	T-	FT+	FT-	FT+
Silver	VFT	VFT-	EFT	--	--
Sodium	T	T	T	--	--
Tin	VFT+	VFT	VFT	--	--
Titanium	VFT	VFT+	VFT-	--	--

KEY: T = Trace, FT = Faint Trace, VFT = Very Faint Trace
EFT = Extremely Faint Trace, -- not detected.

* The sulfur samples were concentrated 10 times before analysis.

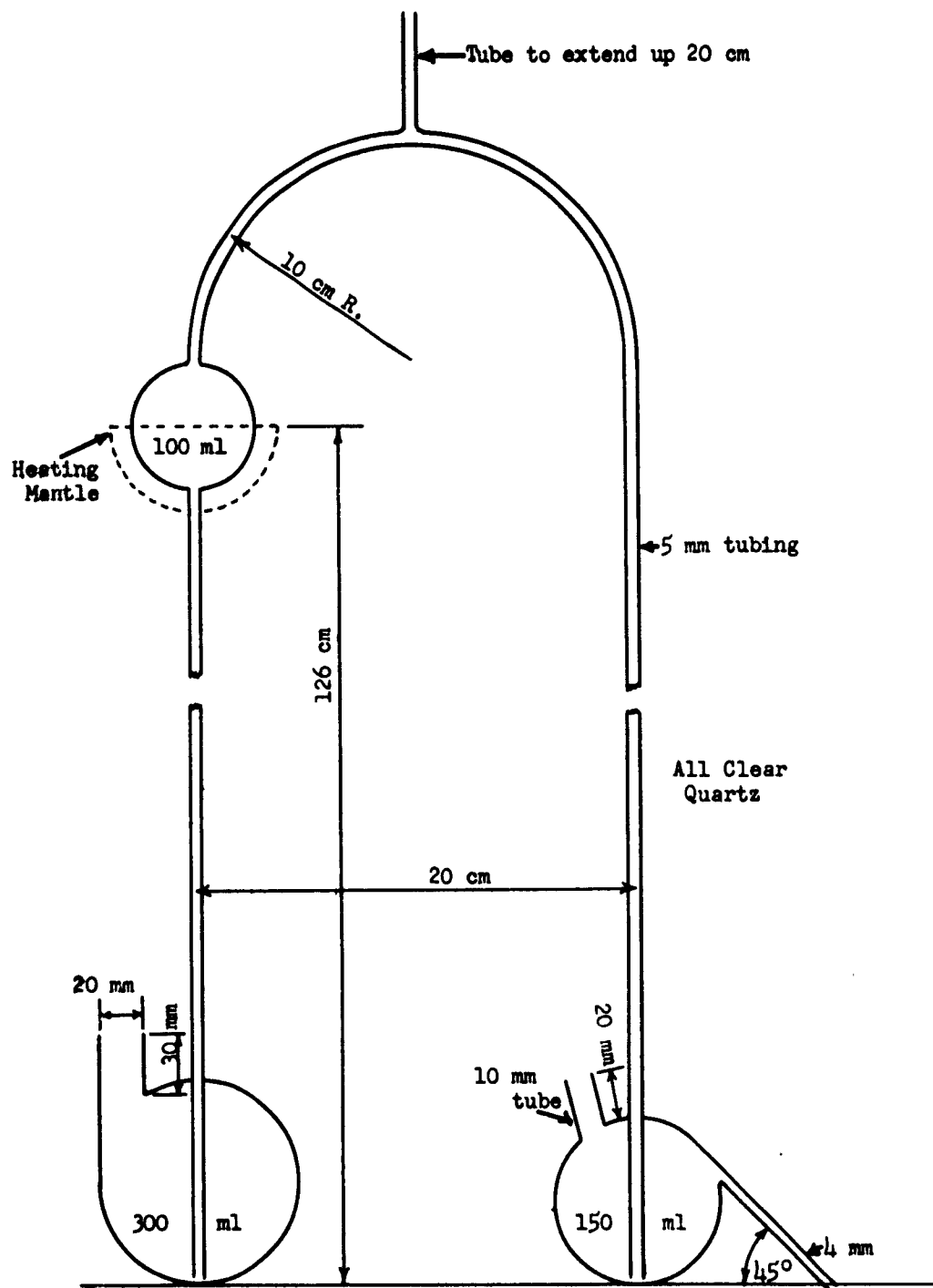
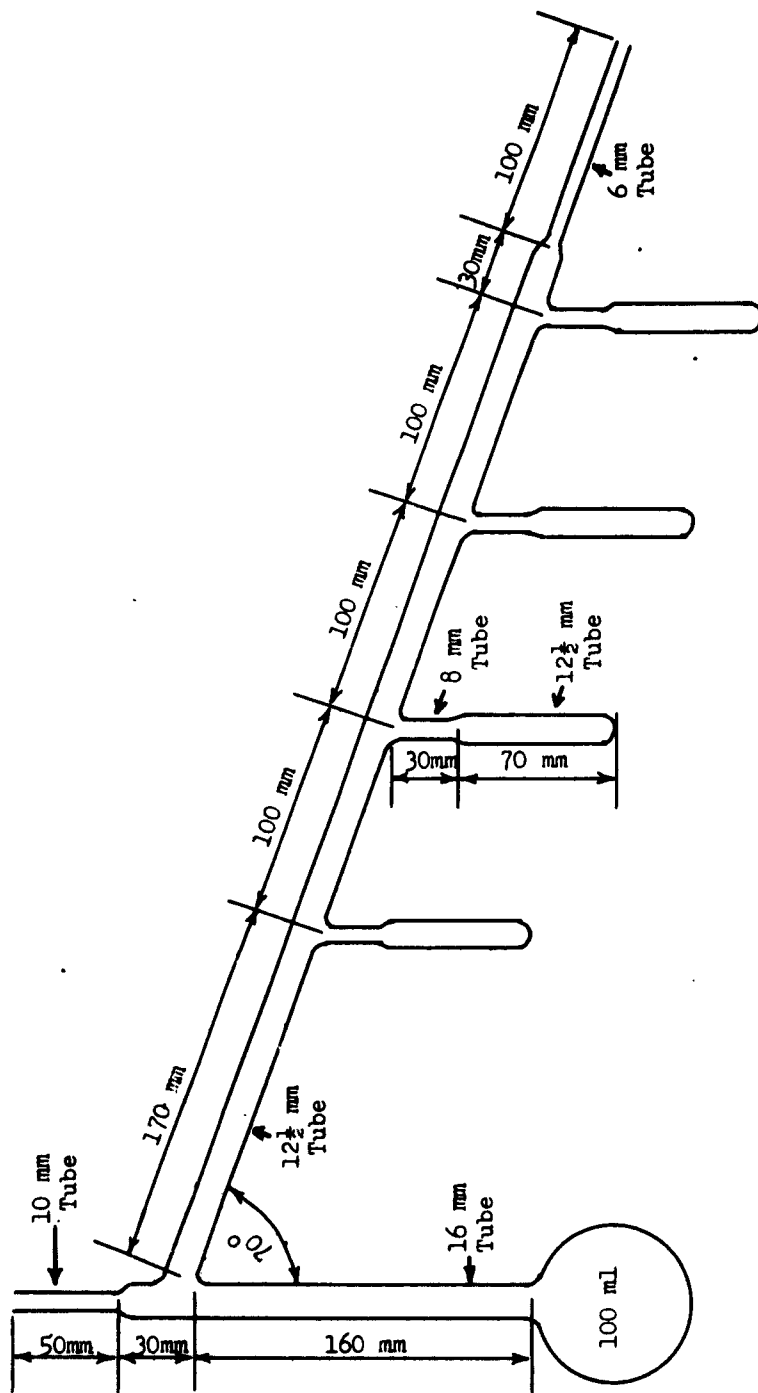


Figure 6: Cadmium Distillation Unit



All Pyrex 4 Receivers Are Identical

Figure 7: Sulphur Distillation Unit

the course of dislocation lines within the crystal interior can be determined. The proper material for study must necessarily be a single crystal of fairly high perfection. The construction of the x-ray apparatus is such that it can be adapted to either Bragg or Laue type geometry. Thus, the examination of thin films is possible and grain orientations are theoretically derivable. Initial work has, however, been confined to the single crystals.

Needle like growth of CdS single crystals has been obtained in modifications of the Reynolds-Cyzak method. Frequently these small needle crystals have extensive face development in a direction perpendicular to the needle axis (the [0001] direction) and take on the appearance of blades. Several of these crystals were examined under the microscope by ordinary and polarized light. One was selected which was truly single crystal. This blade was then examined by the Lang technique of x-ray diffraction microscopy.

After mounting on the diffractometer, the crystal was oriented to obtain diffraction from the (10 $\bar{1}$ 0) planes. AgK α_1 radiation was utilized by passage through a narrow slit system which limited the horizontal divergence to 100 seconds of arc. The scanned width of the crystal in front of the x-ray beam was .35 mm. The size of the x-ray beam was approximately .1 mm. wide and 15 mm. high. Figure 8 is a photograph of the original blade taken under transmitted light. The difference in shading along the width were due to reflection losses and were not visible under polarized light. There were no apparent defects on the surface of the crystal. Small particles of dust and other fragments of CdS were removed by means of a soft camel's hair brush. Figure 9 is the x-ray diffraction micrograph of the crystal blade. The original photograph was recorded on a Type A Autoradiographic Plate. This plate does not have the ultimate resolution of a nuclear plate but is faster and adequate for most survey work. On the plate, dislocation lines are clearly evident over most of the crystal area. Two portions of the crystal show nodes with four or five dislocation line segments emanating from them. The width and intensity of dislocations vary with their direction through the blade in accordance with the respective orientation of Burgers Vector and the diffracting planes. This information can be fruitfully utilized to obtain data on dislocation type, orientation of Burgers Vector, and dislocation reactions.

Further work is currently being performed on CdS single crystals of larger area and prescribed orientations. These are generally cut from the seedplate ingot or large feedpile crystals. While the dislocation contents of these crystals may be much higher than the needles or blades, thin sections are giving good results. It is planned to study a few of these crystals as a function of orientation and also to continue some additional work on the blades or platelets. The problem of grain orientation in polycrystalline thin films is also under investigation.

PART III - BASIC BARRIER STUDIES

Spectral Response

Spectral response data has been extended to cover more samples of front and rear wall cells providing confirmation of the previous data. During these tests, two particularly interesting samples were found. These were normally processed front wall cells which showed normal performance up thru the pressure test unit phase.



Figure 8: Cadmium Sulfide Single Crystal of Blade Type Growth, Transmitted Light, 21X.

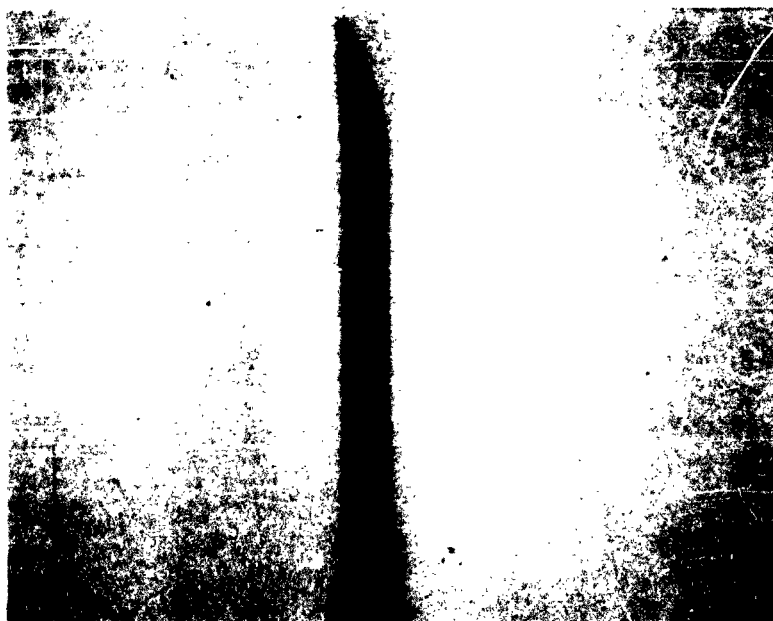


Figure 9: Transmission X-ray Diffraction Micrograph of Blade Section Showing Dislocation Lines, 21X.

After the lamination process, however, short circuits seemed to appear resulting in the delivery of very little power. The cells were then immersed in liquid nitrogen and the I-V curve examined. The results are shown in Figure 10. The room temperature dark I-V curve shows a parabolic dependence of current on voltage in both forward and reverse modes, indicating the current to be limited by sheet resistance. Under simulated sunlight, the generated current density was about 8 ma/cm² with an open circuit voltage of 0.14 volts. At liquid nitrogen temperature, the dark I-V curve is very unusual, and in fact, resembles the data for so-called backward diodes. Denoting the direction of generated current as being negative, the analyses of the I-V curves shows unusual results. The forward curve bears no resemblance to the diode at 77°K and if the diode equation is used to fit the data in the forward direction the following expression can be used:

$$I = 0.1 \left[\exp \frac{2V}{150 \text{ } ^\circ\text{K}} - 1 \right] \text{ ma/cm}^2$$

The saturation current and correction term in the exponent are both incredibly high, making no sense at all. In the reverse direction, the situation improves only slightly in that the data fits:

$$I = 0.06 \left[\exp \frac{2V}{17 \text{ } ^\circ\text{K}} - 1 \right] \text{ ma/cm}^2$$

The generated short circuit current shown for 77°K is not that for simulated sunlight and in fact the current at 77 K is slightly below that at room temperature. The exact value has not been determined as yet. As of this date, the I-V data is confusing and requires further data and analysis.

The spectral response for this cell is shown in Figure 11. This data is somewhat surprising in that a relatively high quantum yield of about 0.5 is indicated over almost the entire region of response. No enhancement effect was found at any photon energy. This high quantum yield is unusual in light of the measured simulated sunlight short circuit current, since one would expect about 20 ma/cm² rather than the observed value of 8 ma/cm². Sheet resistance does not account for the discrepancy since the difference between the light and dark curves at room temperature is constant from zero out to at least 0.5 volts reverse bias. Further study of these samples seems to be in order.

Cells have been operated at high forward current densities to study any injection luminescence which may occur. The samples were pulsed with a square current pulse of 50 millisecond duration at a repetition rate of 1 pulse each 5 seconds. Single crystal cells were operated up to 1 amp/cm² and a weak luminescence was observed. By use of filters, the luminescence was seen to lie between 1 and 1.5 e.v. so the flux was measured with a silicon cell. A ratio of 1 collected photon per 10⁵ injected electrons was observed. Higher current levels or cooling of these cells in general causes them to crack away from their mountings. Front wall film cells were immersed in liquid nitrogen and operated. Radiation was again observed in about the same band but at much lower conversion ratios. These cells were operated up to 25 amp/cm² and the conversion ratio was slightly less than 1 photon per 10⁶ injected electrons. The emitted light levels in all cases were much too low to allow spectral analysis by a monochromator. The next step is to remove part of the front wall barrier layer by abrasion or etching to determine the effect of self-absorption on the emission. Thus, the data at this time is preliminary but provides evidence that the effect is present and will offer another

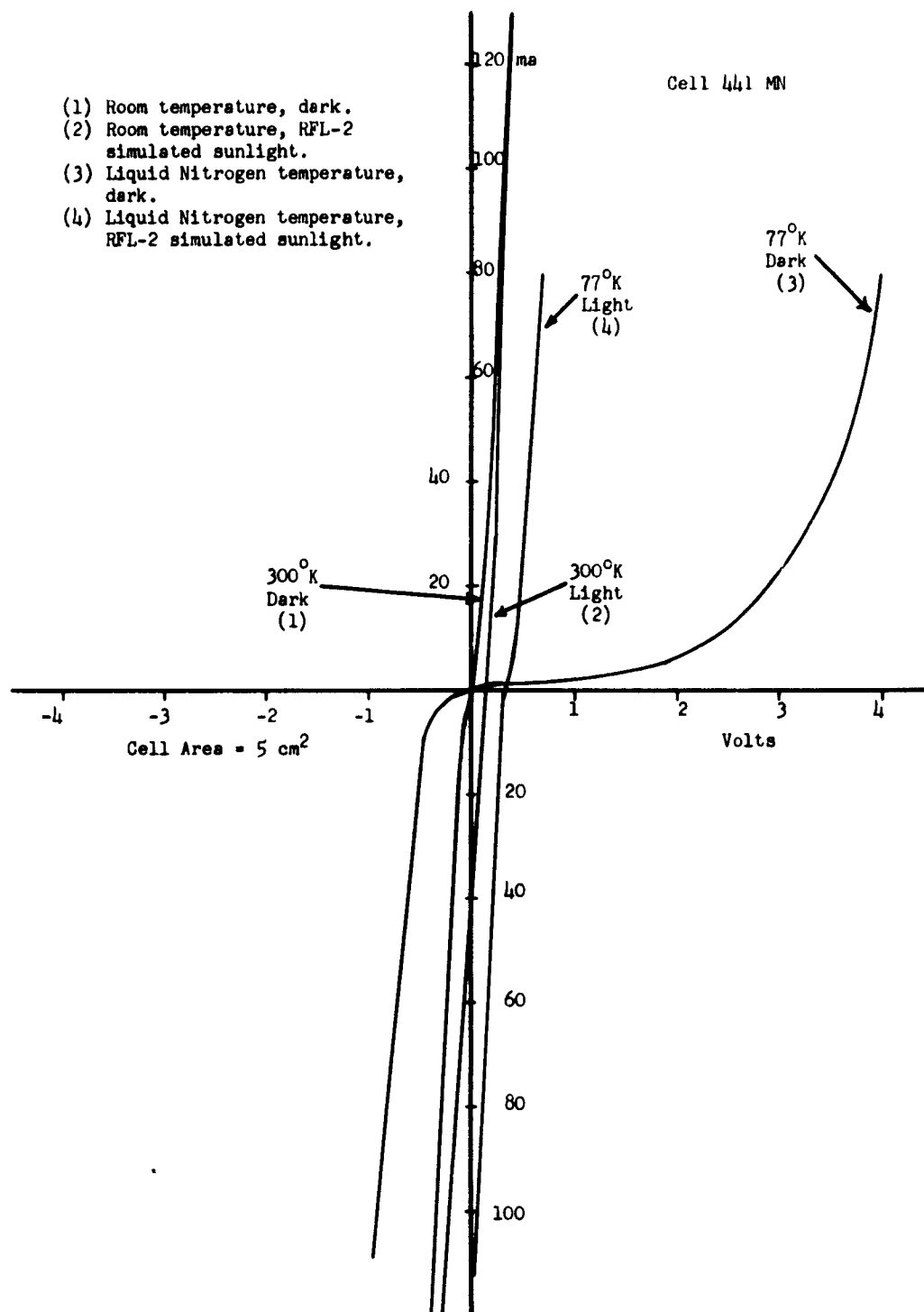


Figure 10: I-V Curves at Room Temperature and Liquid Nitrogen Temperature

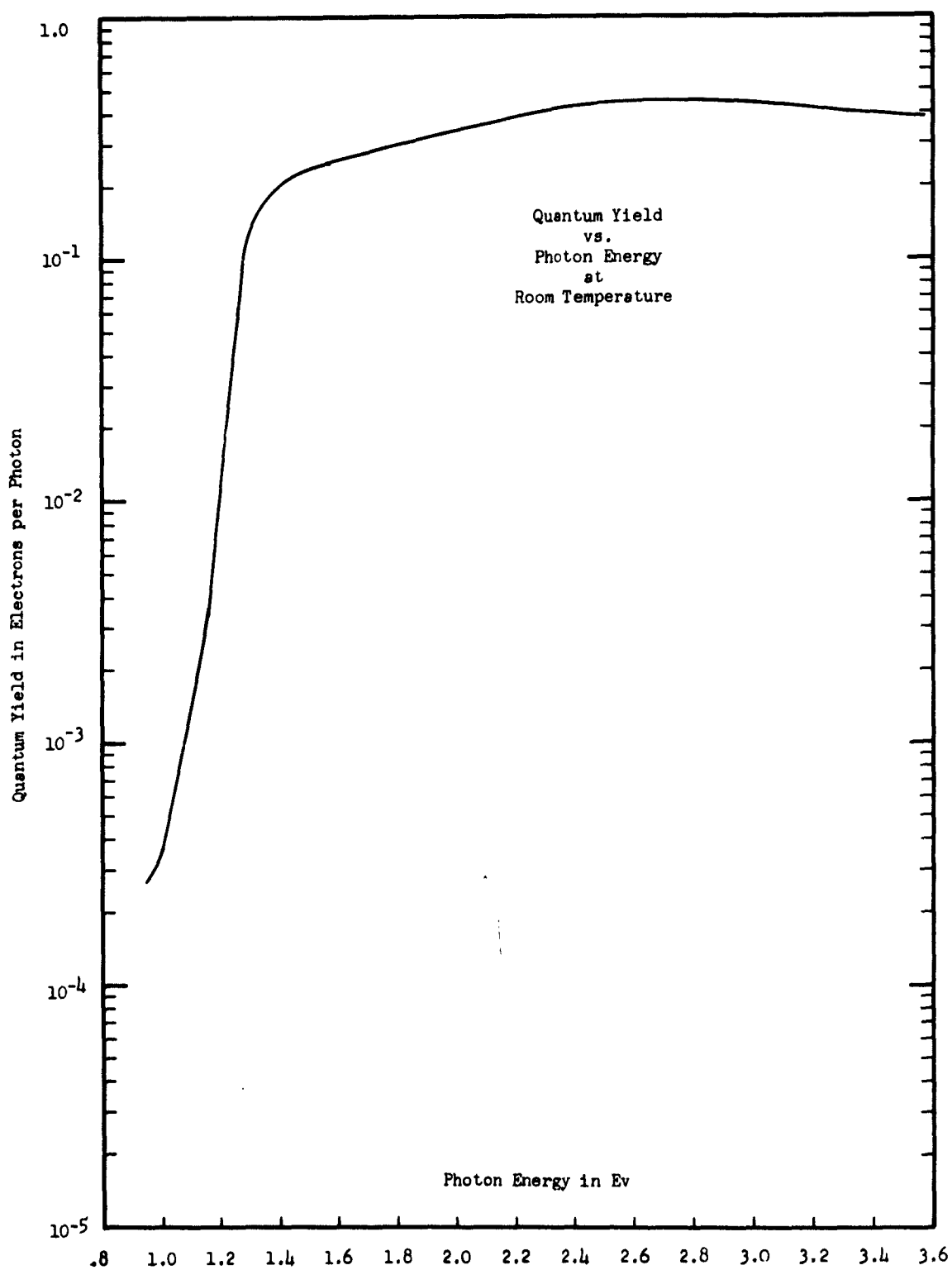


Figure 11: Monochromatic Spectral Response-Cell No. 441MN

tool for cell study.

I-V Characteristic Analysis

The CdS photovoltaic cell can be analyzed in terms of an equivalent circuit containing a series resistance, a parallel resistance, a diode and a constant current source. To completely describe a given cell under different illuminated conditions, it is necessary to assume that all four elements have properties which depend on the light intensity and photon energy.

The I-V characteristics of a single crystal rear wall cell were measured under various conditions of illumination. Two of the curves are shown in Figure 12, for no illumination and for monochromatic radiation of energy 2.3 e.v. The equivalent circuit characteristics were computed and plotted on the same graph. To obtain a fit with experimental points, it was necessary to describe the diode with $I = I_0 \exp(qV/nkt)$, where n was 2.9 for the dark curve, and 1.35 for the illuminated curve. It was also necessary to assume different values for the series resistance: 57 ohms in the dark and 16 ohms under illumination. For monochromatic radiation with a photon energy less than 1.4 e.v., the I-V curve is similar to the dark curve, except a shunt conductance appears which is proportional to the radiation intensity.

The I-V measurements on this cell have lead to a number of conclusions:

- 1) series resistance is photoconductive
- 2) recombination occurs in barrier region (see section on enhanced quantum yield)
- 3) shunt resistance is photoconductive with spectral sensitivity different from that of series resistance
- 4) device can be characterized in terms of a p-n junction-like barrier, but with saturation current typical of a 1.1 e.v. semiconductor.

Enhanced Quantum Yield

As mentioned in earlier reports, the response of a CdS photovoltaic cell to white light cannot be predicted from an integration of the cells monochromatic response. The short circuit current produced by two superimposed monochromatic light beams is in general greater than the sum of the currents produced by the individual beams. A tentative explanation for this anomaly has been deduced from an analysis of a cell's I-V characteristics in the dark and under illumination, and from some experiments using chopped light.

The most important feature of the CdS photovoltaic cell is that it responds to light with photon energy as low as 1.1 - 1.2 e.v. Another feature is that the shape of the I-V curve for most cells changes radically (compared to the dark curve) when the cell is illuminated with photons of energy greater than about 1.6 e.v. (see Figure 12) the dark forward current varies exponentially with voltage with a slope q/nkt , where n is typically greater than two. When the cell is illuminated with the high energy photons, n usually decreases to some value less than two. According to p-n junction theory, (3) n should be unity for a device whose forward characteristic is dominated by diffusion currents, but may increase to values near two if there is appreciable generation and recombination in the space-charge region. Although the Sah-Noyce-Shockley theory does not account for values of n greater than two, we feel it is safe to assume that a decrease in n corresponds to a reduction in recombination rate in the

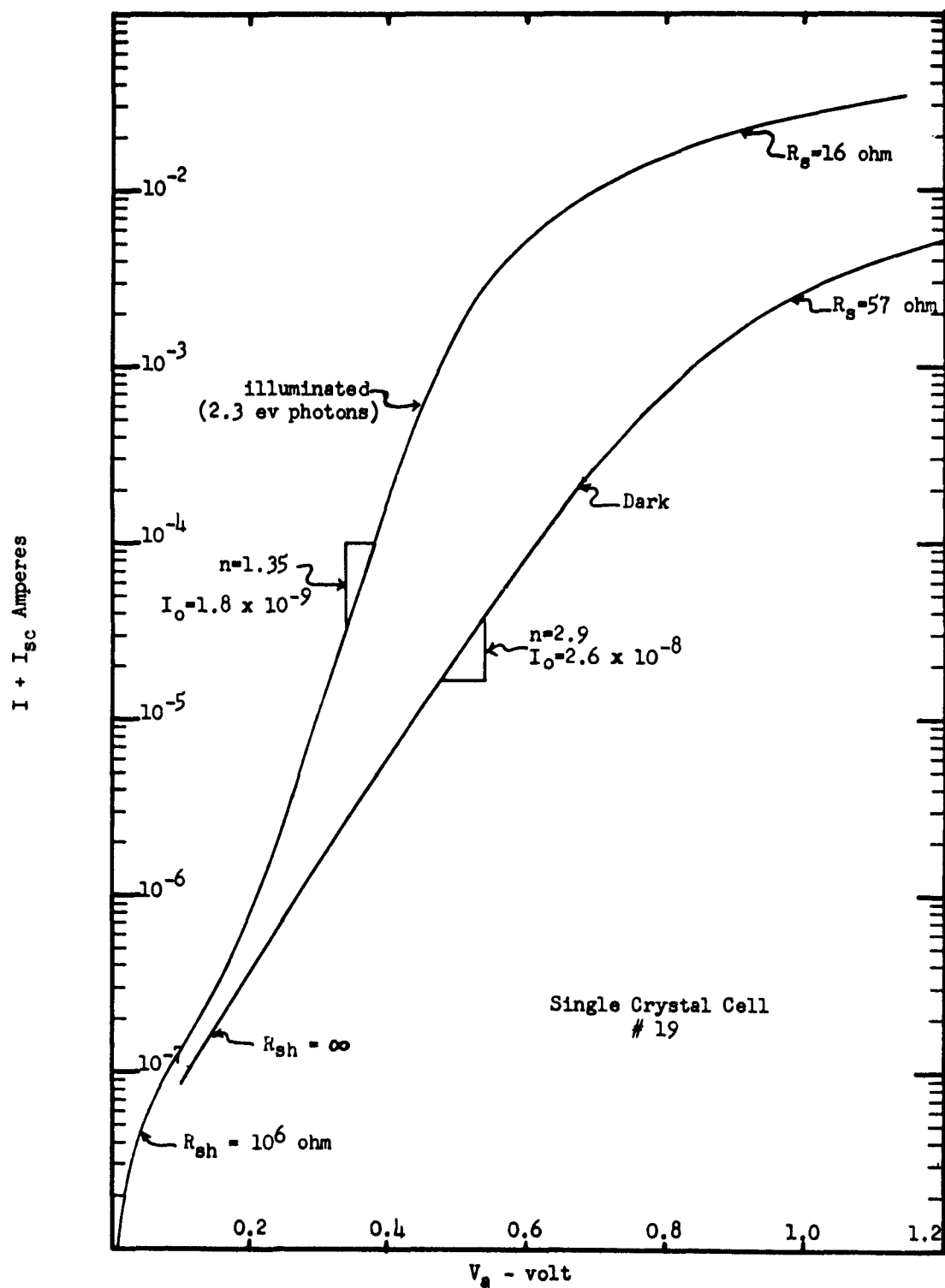


Figure 12: I-V Curve - Rear Wall

barrier region. This implies that for a CdS cell illuminated with photons of energy less than 1.6 e.v. appreciable recombination takes place in the barrier region, and that this recombination is reduced when the cell is illuminated with high energy photons.

If a cell is illuminated with 1.3 e.v. photons, most of the current carriers produced by the radiation will be removed by these postulated recombination centers in the barrier region. If high energy photons are now applied, these centers may become de-activated, if the photon energy is greater than the centers' ionization energy. The carriers produced by the 1.3 e.v. illumination could then find their way to the external circuit and be observed as short circuit current. Thus the addition of high energy photons can greatly enhance the overall quantum yield of low energy photons. Experimentally, it is seen that photon energies in the range 1.4 to 1.8 e.v. are sufficient to de-activate the recombination centers. A complete description of the behavior of these centers is not available, but there are certainly a number of possible processes which could explain the observed characteristics.

WORK PLANNED FOR NEXT QUARTER

The barrier oxidation experiments will be continued to determine the optimum time and temperature. The reclaiming and up-grading experiments will also be continued in order to establish a standard procedure, and to determine whether the initial barrier should remain or be removed.

Construction of the one square foot array and the one-half square foot array will be accomplished. It is believed that a new method of assembly will prove to be superior to previous methods.

One evaporator will be retooled to enable the evaporation of 6" x 6" films on molybdenum.

X-ray investigation of dislocations will be continued. Attempts will be made to obtain better resolution to facilitate this study. The X-ray study will be extended to polycrystalline thin films.

Spectral response studies are to be continued, in particular to determine the change occurring when a cell deteriorates in the atmosphere. Work will begin on treatment of plated cells in oxygen at various temperatures and times with subsequent angle lapping and probing of the barrier region. Work will start on the incorporation of impurities such as copper and silver in the evaporated CdS film to determine their effects. Work will be continued on the I-V and spectral response determination and analysis on present samples. Theoretical studies of the statistics of recombination and trapping will be carried out in an effort to find a model to fit the data already gathered.

REFERENCES

- 1) T. A. Griffin and J. C. Schaefer Fourth Quarterly Progress Report, Contract No. NAS 3-2493, Page 11.
- 2) Schaefer, Wolff, and Hill, Second Quarterly Progress Report, Contract No. AF 33(657)-9975, Page 3.
- 3) Sah, Noyce, and Shockley, Pros. IRE, page 1228 (Sept. 1957).

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