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CdS PHOTOVOLTAIC FILM CELLS Microfiche (MF) .50

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By

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Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FINAL REPORT

RESEARCH AND DEVELOPMENT  
IN  
CdS PHOTOVOLTAIC FILM CELLS

by

T.A. Griffin, D.J. Krus, J.C. Schaefer

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

May 19, 1964 to May 19, 1965

Contract NAS 3-4177

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NASA Lewis Research Center  
Cleveland, Ohio  
Space Power Systems Division  
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## FOREWORD

This report was prepared by the Crystal-Solid State Division of the Harshaw Chemical Company. The work has been sponsored by the Space Power Systems Procurement Section of the NASA Lewis Research Center with Dr. A. E. Potter acting as Technical Advisor and Mr. Clifford Swartz acting as Project Manager .

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SUMMARY

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The report covers a one year development program to fabricate light weight, flexible, high efficiency, low cost thin film CdS solar cells capable of operating for long periods in space without appreciable degradation.

Cell weight reduction and increased power output has made possible initial power to weight ratios before cell degradation, of 77 watts per pound possible. This represents a gain factor of two over the previous contract period.

Increased space lifetime and cost reduction are a result of replacing electroformed grids with an electrodeposited type.

Cell design and material specifications are reported.

*Author*

## INTRODUCTION

This cadmium sulfide solar cell development program was a continuation of Contract NAS3-2493. The major objectives of this program were to fabricate light weight, flexible, high efficiency, low cost cells capable of operating for long periods in space without appreciable degradation.

Development efforts to reduce the overall weight has resulted in a cell with a power to weight ratio of 77 watts per pound. This value, substantially advanced over previous reportings, does not appear to be a limit. Increased cell efficiency and a reduction in substrate thickness by chemical milling made this improvement possible.

Cost reduction can be accomplished by mass production methods and by reduction of material cost. Since the electroformed gold mesh collector grid represents a large portion of the material costs, an effort toward replacement was made. Electrodeposition produced a cell design indicating a thermal cycle life five times greater than the electroformed grid types. In the early stages of this development the individual cells lost 85% to 100% of their indicated power output during the final electroding step. The power output loss was prohibitive. Subsequent efforts cut the loss figures to a range of 0% to 10%.

Cells provided with the electroplated grids also show a high loss during fabrication due to shorting. This result indicated the presence of holes in the barrier layer. Several such areas have been found and have been photographed. A microphotographic series is shown in this report. Film uniformity and surface texture could not be correlated with cell efficiency.

Experiments in the area of encapsulation by lamination were directed toward quick, repetitive, and reliable procedures. Impulse lamination appears to be a practical means of encapsulating one square foot panels unless additional supporting substrates are utilized. The rapid lamination often traps unwanted air.

Cells have been produced from sintered CdS layers, devoid of crystal orientation, and of low energy conversion efficiency.

Cell design and material specifications are reported.

## EVAPORATED FILM PROPERTIES

The maximum efficiency of the Cadmium Sulfide (CdS) evaporated film solar cell has steadily increased. Indications are that many of the high efficiency cells have an associated stability problem. Many cells fabricated in the same manner are also low in efficiency. An investigation was begun to determine the causes for the non-uniform behavior. It was suspected that the cause was non-uniformities in the CdS film.

### 1. Starting Charge

CdS thin films are produced by sublimation of CdS in a vacuum. Therefore, the CdS starting material was examined first. Previously the products of several manufacturers were examined but most were found unsatisfactory because of the range in particle size.<sup>(1)</sup> The General Electric powder met the particular physical requirement of no particles below one micron in diameter. Such a requirement is necessary for the fixtures used in the evaporators. Those powders with smaller particles (fines) caused excessive spatter on the evaporated films.

One of the powders compared with the General Electric CdS powder was a Sylvania CdS powder.<sup>(2)</sup> It contained many fines and could not be used without redesigning the filaments. Recently samples of a higher purity Sylvania CdS were obtained and tested. This material was found to have a more uniform particle distribution. Table I is a spectrographic comparison of samples of General Electric and Sylvania material. The two are very similar in impurity content. Films were made from both powders under normal conditions. The resulting films were very different. The films from the Sylvania material were powdery but without evidence of spattering. They also had a yellow layer next to the substrate. The General Electric powder produced the type of film normally expected.

Two approaches were followed to make usable films from the Sylvania powder. Films formed under the normal evaporation conditions were heated to 600°C in argon for one hour. Much of the powdery appearance disappeared but the molybdenum substrate was altered. It appeared that a molybdenum oxide or sulfide was being formed.

The second method employed the deposition of Sylvania material on the substrate at a temperature 100°C higher than normal. The films that were produced appeared similar to the films made with standard material at the standard substrate temperature.

The following is a comparison of the properties of typical films produced from the two types of materials.

	<u>Sample N94</u> (Sylvania)	<u>Sample N96</u> (G.E.)
Thickness	$1.2 \times 10^{-3}$ cm	$2.4 \times 10^{-3}$ cm
Hall Coefficient	7.47	2.76
Mobility	$16.3 \text{ cm}^2/\text{volt-second}$	$0.79 \text{ cm}^2/\text{volt-second}$
Carrier Conc.	$8.34 \times 10^{17} \text{ cm}^{-3}$	$2.26 \times 10^{18} \text{ cm}^{-3}$
Resistivity	0.46 ohm-cm	3.5 ohm-cm

The Sylvania films formed at the higher substrate temperature had a lower resistivity. Normally, a high substrate temperature will eliminate much of the free cadmium in the CdS film resulting in a resistivity increase. Neither film was purposely doped.

Cells were made from films of both materials. While the cells from the Sylvania material did not develop the same power as those from the G. E. material, it is possible that with certain adjustments equivalent cells could be made. The Sylvania cells were found to be about 75% as efficient as the G. E. cells. This might be attributed to the low resistivity in the Sylvania films as indicated by the poor shunt characteristics of the I-V curves.

## 2. Pressure Bursts

While the above tests were being conducted it was noted that large pressure bursts occurred at the initiation of filament heat. The magnitude of these bursts depended on the rate of filament heating. The question arose as to how much effect these pressure changes might have had on the properties of the films and the resultant cells.

A series of evaporations were made utilizing different rates of heating which resulted in bursts of varying magnitude. Hall samples were prepared from each evaporation. Cells were fabricated from the films. The films were examined by optical and x-ray techniques. Table II shows some typical results.

The pressure bursts ranged from as high as 44 microns to less than 1 micron. All the pressures were read on the same thermocouple. In general, the evaporation cycles were started in the  $10^{-5}$  mm pressure range.

The resistivities were found to be lower than the expected 1000 ohm-cm by a factor of ten. The mobilities were rather consistent, falling in the 0.07 to 0.14  $\text{cm}^2 \text{ volt-sec}^{-1}$  range. The film produced during the smallest pressure burst had the highest mobility. The carrier concentrations all were in the  $10^{17} \text{ cm}^{-3}$  range.

TABLE I  
 QUALITATIVE SPECTROGRAPHIC ANALYSIS  
 OF CdS POWDERS

	G.E. CdS Powder (Lot 185)	Sylvania CdS Powder (Lot T-32-1)
Aluminum	FT	FT <sup>-</sup>
Calcium	VFT	VFT
Copper	VFT	VFT <sup>+</sup>
Indium	---	---
Iron	VFT <sup>+</sup>	VFT <sup>+</sup>
Magnesium	VFT	VFT
Manganese	---	---
Nickel	---	---
Silicon	VFT	FT
Thallium	---	---

Key:     T = Trace .001-.01%  
           FT = Faint Trace  
           VFT = Very Faint Trace  
           --- = Not Detected

TABLE II

## Film and Cell Properties Vs. Pressure Bursts

Film No.	Fil Rise Time Sec.	Max. Pressure $\mu$	Duration of Burst Sec.	Film Thickness $\mu$	Resis-tivity ohm-cm	Carrier Cong. $\text{cm}^{-3}$	Mobility $\text{cm}^2 \text{-}^{-1} \text{ volt-sec}$	OCV Volts	Current Density $\text{ma/cm}^2$	Eff. %
N16	10	44	.75	22	130	___*	<0.1	0.44	10.0	2.6
N14	20	24	68	20	250	$3 \times 10^{17}$	0.7	0.45	6.85	1.8
N15	40	27	94	21	520	___*	<0.1	0.44	8.5	2.1
N17	60	28	60	27	95	$6 \times 10^{17}$	0.1	0.42	6.4	1.5
N18	90	4	75	26	140	$4 \times 10^{17}$	0.1	0.44	6.8	1.6
N19	120	3	75	23	230	___*	<0.1	0.44	6.7	1.8
N22	180	<1	200	20	190	$5 \times 10^{17}$	0.07	0.44	6.7	1.9
N24	300	<1	200	22	220	$2 \times 10^{17}$	0.14	0.45	9.8	2.3

\* Mobility was too low to measure

The best cells were produced from the largest and the smallest bursts.

Samples of these vapor deposited CdS thin films were examined by back reflection x-ray techniques. All samples were mounted without disturbing either the glass substrate or the CdS deposit. Since the depth of penetration of CuK x-rays in CdS is no more than about 25 microns, it may be seen that the results are more characteristic of the material in the last portion of the evaporation. The actual results showed that all lines in the patterns were from planes oriented randomly. The planes ordinarily observed in the back reflection pattern are (404) + (217), (315), and (306) + (321). A large fraction of (002) planes are nearly always parallel to the substrate. For samples N-18, N-22, and N-24, an increasing amount of preferred orientation was found in the back reflection region. This indicated that some form of biaxial orientation was occurring. Not only was the c-axis of crystallites perpendicular to the substrate, but the a-axis was also more frequent in particular directions in the plane of the film. It might be said that the films were more perfect in structure. Similar results have been found for CdS thin films epitaxially deposited on (001) faces of oriented CdS single crystals.

In order to check the portion of the CdS thin film which was deposited first (that closest to the substrate), films were removed from the glass substrate by dipping in liquid N<sub>2</sub>. Again, the back reflection x-ray patterns were taken and found to correspond to those of the randomly oriented type. This result may have been fortuitous because thermal shock can disturb the orientation somewhat.

A series of evaporations were made using both sintered and powder CdS as evaporants. The large pressure burst noted with powder charges were absent when sintered material was used.

The evaporation parameters, of filament temperature and substrate temperature, were varied with both materials. The resistivity of the films was varied from 10 to 10<sup>4</sup> ohm-cm. Mobilities ranged from less than 1 to 5 cm<sup>2</sup>/volt sec<sup>-1</sup>. These ranges were accomplished with both materials (sintered and powder).

The carrier concentration ranged from 10<sup>15</sup> to 10<sup>17</sup> e/cm<sup>3</sup> using sintered material. When powder was used it ranged from 10<sup>15</sup> to 10<sup>18</sup> e/cm<sup>3</sup>. The highest efficiency cells made from these films did not show a dependence on the starting material or resistivity. If anything those with high carrier concentration tended to be better.

### 3. Carrier Concentration

Several standard films made from powder evaporant had their bulk electrical properties measured. Below are three typical films and their properties.

<u>Film</u>	<u>Resistivity (ohm-cm)</u>	<u>Mobility (cm<sup>2</sup>/v-sec)</u>	<u>Carriers (cm<sup>-3</sup>)</u>
S161A	7.35	3.02	2.51 x 10 <sup>17</sup>
S165A	13.2	1.74	2.72 x 10 <sup>17</sup>
S185A	59	0.38	2.79 x 10 <sup>17</sup>

The resistivities reported are lower than usual. Previous films fell in the 100 to 1000 ohm-cm range. This change could not be related to any changes in the evaporation parameters or materials. Further tests are being run in which the evaporation conditions are being widely varied. A closer control on resistivity seemed indicated. Control of carrier concentration by doping rather than by cadmium excess was attempted. Therefore CdS powder was doped with indium for use as the evaporant. The calculated range was 10<sup>19</sup> cm<sup>-3</sup>. The data below obtained from the films show that the doping range was attained in the films.

<u>Film</u>	<u>Resistivity (ohm-cm)</u>	<u>Mobility (cm<sup>2</sup>/v-sec)</u>	<u>Carriers (cm<sup>-3</sup>)</u>
S169A	5.8 x 10 <sup>-3</sup>	80.9	1.34 x 10 <sup>19</sup>
S173A	2.2 x 10 <sup>-2</sup>	30.2	9.53 x 10 <sup>18</sup>

These films did not produce the expected gain in efficiency or in stability. However, they did demonstrate that the film properties can be reliably controlled by an added dopant.

### 4. Conclusions

More experiments are necessary to establish the combination of electrical properties necessary for the CdS films in order to produce the most stable, uniform, high efficiency photovoltaic cells. The fact that there does not seem to be any correlation to measurable properties would lead one to believe that the bulk conditions are not the only important ones. Perhaps it is the surface condition or the layer of CdS near the surface that is more important. Since some of the test cells to date have been made by preparing the surface of the CdS by etching, the final answer may be a surface treatment. It is possible that the best cells will require not only definite bulk properties but also a layer of completely different properties near the junction. This could explain the variation in efficiency, and uniformity as well as in stability of cells produced from CdS films with similar bulk properties.



## SINTERED CdS FILMS

The purpose of this study was to develop a sintered CdS film with photovoltaic properties. A suspension of CdS was applied to a metallic substrate with subsequent sintering in an inert atmosphere. This approach could eliminate the need for expensive vacuum deposition equipment. Substrates used for the study were cleaned by washing and etching prior to storage in methyl alcohol. The cleaned substrates were sprayed with a suspension of CdS in water to which cadmium chloride was added to aid in maintaining the suspension. The substrates were maintained at 100°C during spraying. The resulting films were sintered in an argon atmosphere. Presumably, this heat treatment volatilizes the CdCl<sub>2</sub> leaving a CdS film. The films found free of cracks and flaking were chemiplated.

Variables investigated were 1) substrates, (molybdenum and tin-coated stainless steel; 2) spraying technique, (time of each spray: 1 to 2 sec.; interval between sprays: 10 to 30 seconds; number of sprays: 24) and 3) suspension composition, (Gafac dispersant additive; methyl alcohol instead of water). The results of 23 runs (53 substrates) are presented in Table III. Films made initially were mud-cracked and coarse textured. Indium probes showed that these films did not make ohmic contact to the substrate. Films numbered 10 through 15, 17, 19 and 21 were barrier chemiplated. Number 12 exhibited a slight photovoltaic effect; the other cells were not rectifiers and showed no photoeffect. An attempt to obtain better contact to the substrate was made by using two mil tin-coated stainless steel. However, the film flaked and cracked on these substrates. Cells made from films 26 and 27 showed no photovoltaic effect.

Attention was again turned to using molybdenum substrates, while varying the concentration of cadmium chloride. First efforts with 1 part CdCl<sub>2</sub> to 2 parts CdS led to films which cracked and flaked when sprayed onto the substrate. A concentration of 1 part CdCl<sub>2</sub> to 5 parts CdS was finally used. Cells were made from films numbered 38, 40, 45 and 59. Films numbered 38, 45, and 49 gave photovoltaic effects with number 38 having the greatest output: 0.26 volts, V<sub>oc</sub>; 9.8 ma, I<sub>sc</sub>; 0.23% efficient; area: 3 cm<sup>2</sup>. Surprisingly, an x-ray diffraction pattern of the surface of film number 41 (produced under the same conditions as film number 38) showed no preferred orientation.

The results of this study show that a CdS film formed by sintering of sprayed material produces a photovoltaic effect. The characteristics of such films at present are 1) no preferred orientation, 2) poor ohmic contact to the substrate, and 3) numerous pinholes and cracks.

### FILM AND BARRIER UNIFORMITY

It has been noted in the past that cell geometry appears to be related to conversion efficiency. Nominal 3" x 3" cells have displayed a tendency to have higher efficiency than 1" x 3" cells. On large area cells, it has been possible to locate small areas with efficiencies higher or lower than

## SINTERED CdS FILMS

Run No.	Cell Nos.	Suspension Mix*	Substrate Mat'l and Size	Sintering Temperature (°C)	Sintering Time (min)	Film Appearance
1	1,2	A	Pyrex 1" x 3"	600	30	Brown in center, yellow edges, mud cracked
1A	1,2			600	30	No improvement after additional heat
2,3	3-7	A	Molybdenum 3/4" x 1 1/2"	700	30	Dark brown, mud cracked
4	8,9	A	Molybdenum 3/4" x 1"	650	30	Less mud cracks
5	10,11	A	Molybdenum 3/4" x 1"	600	30	Same as Run 4
+6	12,13	A	Molybdenum 3/4" x 1"	700	30	Same as Run 4
7	14,15	A	Molybdenum 3/4" x 1"	600	30	Same as Run 4
8	16,17	A	Molybdenum 3/4" x 1"	500	30	Reddish-yellow, coarse texture
9	18,19	A	Molybdenum 3/4" x 1"	300 600	15 30	No improvement
10,11	20-23	B	Molybdenum 3/4" x 1"	600	30	Smoother
12	24,25	C	Tin-coated SS 3/4" x 1"	300 700	15 30	Flaked film, dark yellow
13,14	26-29	C	Tin-coated SS 3/4" x 1"	700	30	Same as Run 12
15	30,31	C	Tin-coated SS 3/4" x 1"	800	30	Same as Run 12
16	32,33	D	Molybdenum 3/4" x 1"	No Sinter		Smoother films but chipped on spraying
17,18	34-37	D	Molybdenum 3/4" x 1"	No Sinter		Same as 16
+19,20	38-41	E	Molybdenum	700	30	Fairly smooth
+21	42-45	E	Molybdenum 3/4" x 1"	650	30	Fairly smooth but dark spots
+22,23	46-53	E	Molybdenum 3/4" x 1"	650	40	Same as 21

+ Cell from run showed photovoltaic effect

\* Suspension A: 5 gms. CdS, 1/2 gms. CdCl<sub>2</sub>·2 1/2 H<sub>2</sub>O, 50 mls. H<sub>2</sub>O  
 B: Gafac dispersing agent added to A  
 C: CH<sub>3</sub>OH instead of H<sub>2</sub>O  
 D: 10 gms. CdS, 5 gms. CdCl<sub>2</sub>·2 1/2 H<sub>2</sub>O, 50 mls. H<sub>2</sub>O  
 E: 10 gms. CdS, 2 gms. CdCl<sub>2</sub>·2 1/2 H<sub>2</sub>O, 50 mls. H<sub>2</sub>O

that of the cell. A theoretical explanation of these observations has not been found. In analyzing the problem, it is necessary to determine the uniformity of the CdS film and the barrier layer. Better uniformity should provide higher cell efficiencies.

### 1. Film Uniformity

CdS evaporated films exhibit certain evident non-uniformities while probably possessing others not as yet identified. Non-uniformities already observed are of a visual nature. Films differ in appearance from one evaporation to another and even different parts of individual cells may not appear uniform. One difference is in color. Skilled technicians have reported this difference and have predicted fairly accurately on this basis which films will produce good cells. These films are produced with slightly different substrate temperatures. These indications of difference have not been confirmed spectrophotometrically.

Another non-uniformity observed in the CdS evaporated films is the texture. Some areas show an imperfect specular appearance. Other areas have a velvety reflectance, perhaps due to crystal growth facets of approximately the same orientation.

Under microscopic examination, five types of surface formations have been observed. The first type can be characterized by a nearly flat surface. When this surface covers a large enough area, it appears somewhat specular to the unaided eye. The second type is a pit with the suggestion of geometrical regularity in its form. When the population density of such pits is high, the area has a velvety appearance. The third type is a formation caused by a particle of CdS loosely bound to the film. A sprinkling of these particles on the film is referred to as "spatter". Frequently, an amorphous pit is found beneath the particle, suggesting that the particle was deposited before the full thickness of the film was built up. The fourth type appears as a shapeless bump or protrusion in the surface of the film. This type of bump may be an adherent particle of CdS which has been deposited as spatter at an early stage of the film formation and has been subsequently covered as the film continues to develop. Under high magnification, positive discrimination between such a bump and the pit mentioned above is difficult. The fifth type of formation is referred to as a "pinhole". It is a narrow perforation which usually extends through the film to the substrate. Sometimes the form of the pinhole suggests that it is in the same family as the regularly shaped pit mentioned above. Another instance may look like the pit remaining when a CdS particle has broken away from the film. Certain pinholes cannot be identified as belonging to either class. Pinholes have been found in cells which were "shorted".

In films where surface texture appears the same to the unaided eye, a difference in color seems to be related to a microscopic difference in texture, and not of type. The surfaces in both cases are flat with a sprinkling of microscopic pits.

Both film color and texture are probably influenced by variations in evaporation rate and substrate temperature, from film to film and from area to area on an individual film.

## 2. Barrier Uniformity

Various methods of testing cells for barrier uniformity have been investigated briefly. Some non-uniformities have been noted which seem to affect the electrical properties of the cells. The methods and observations are outlined below.

Some cells with low-short-circuit currents show a sprinkling of spots where the "barrier" was not formed. These spots have been observed under a microscope with polarized light at normal incidence. This suggests the use of polarized light in other types of inspection such as Brewster angle observations.

Thermoelectric probing was tried but without useful results. For the CdS cells, special equipment and techniques probably would need to be developed for this method. It would require a heated probe made of a material with a Seebeck coefficient approximately the same as the barrier.

Occasionally, a cell with an electroplated barrier will show very noticeable variations in visual appearance across the surface of the cell. That is not always an indication of the cell's efficiency. A few of the low efficiency ones were examined. Some of the cells with low short circuit currents displayed a sprinkling of clear spots apparently devoid of a barrier. These spots were discovered by means of a microscope with polarized light directed toward the sample at normal incidence. Photographs have been made of the electroplated barrier showing the voids or holes in the barrier. These areas have been found to be as large as twenty microns across. Figure 1 illustrates one of these voids, right of center, at a magnification of 750X without a filter. Figure 2 is the same area viewed under red light, while Figure 3 utilized green light. These colored filters emphasize the missing barrier area on black and white panchromatic film. Under white light this vacant area looked red-orange indicating CdS, while the surrounding area appeared blue-gray.

Other cells show no voids in the barrier when viewed under high magnification but do not produce high currents.

To develop a concept of the uniformity and stability of the chemi-plated barrier layer the following tests were conducted.

A copper sulfide layer was formed by chemiplating CdS single crystals having resistivities ranging from  $10^4$  ohm-cm in the light, to greater than  $10^9$  ohm-cm in the dark. Such values should prevent the CdS from having an effect on the Hall measurements made on the barrier layer. The barriers were put on lapped crystals, etched crystals, and crystal surfaces that were one-half lapped and one-half etched.

All of the copper sulfide layers were measured and found to be p-type. The layer thicknesses were estimated to be about 2 microns. This estimation is an upper limit for the thickness.

After the film properties were measured, the contacts were removed and the films were heated in vacuum for 12 minutes at  $200^\circ\text{C}$ . After heating, the samples were fitted with new contacts and the properties of the film were measured again. Table IV shows the results of the measurements before and after heating.

From this data it is evident that the copper sulfide film is rather insensitive to the condition of the surface on which it is placed, and is not affected by being contiguous to the high resistivity CdS. A temperature of  $200^\circ\text{C}$  does not affect the results.

From these tests it appears that an important role in the formation of high efficiency cells is played by the portion of the CdS film involved in the barrier formation process. This was discussed under the section on film properties.

#### ELECTROPLATED GRIDS

An early method for current collection of the CdS cell involved hand ruling the p-type surface with a silver paste or ink. Much of the active surface was covered and the conductivity of the silver conductors was low.

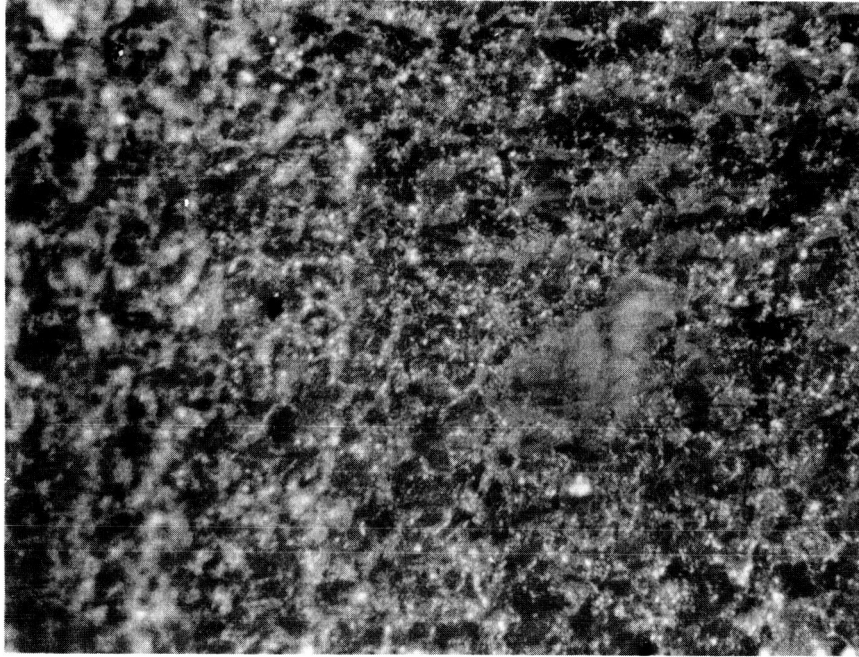


Figure 1. Barrier Layer Under Polarized Light with No Filter

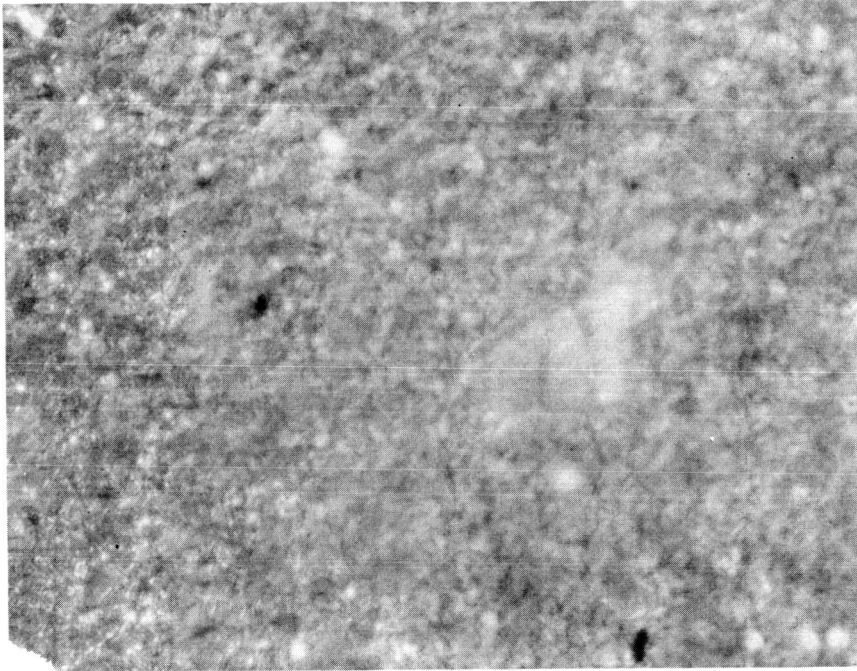


Figure 2. Barrier Layer Under Polarized Light and Filter Passing Red Light

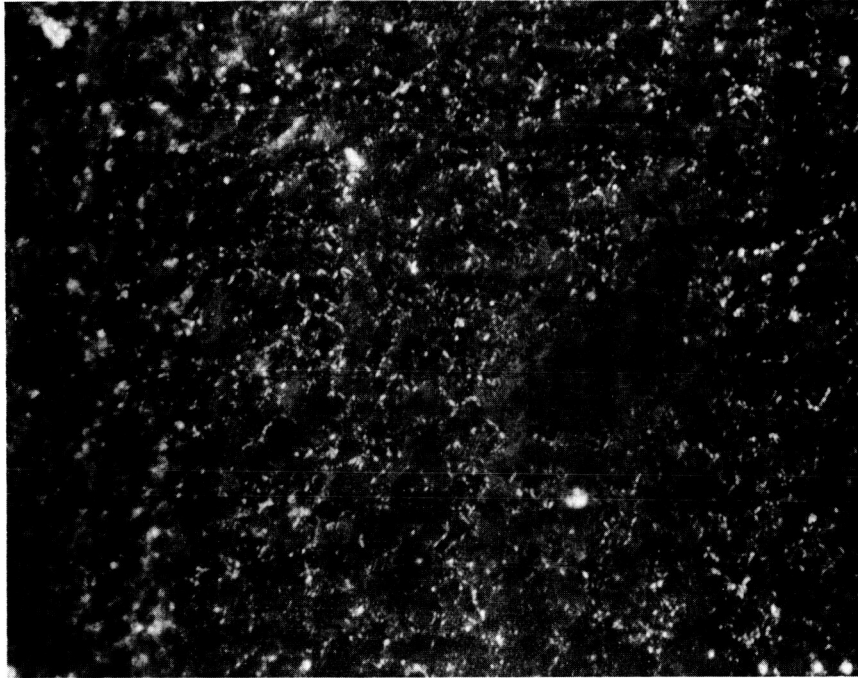


Figure 3. Barrier Layer Under Polarized Light and Filter Passing Green Light



TABLE IV

## HALL DATA ON BARRIER LAYER

<u>Sample</u>	<u>Treatment</u>	<u>Resistivity</u> (ohm-cm)	<u>Mobility</u> (cm <sup>2</sup> /v-sec)	<u>Carriers</u> (cm <sup>-3</sup> )
1	Lapped (unheated)	$5.62 \times 10^{-3}$	3.94	$2.81 \times 10^{20}$
	Lapped (heated)	$4.16 \times 10^{-3}$	4.45	$3.38 \times 10^{20}$
2	$\frac{1}{2}$ Lapped $\frac{1}{2}$ Etched (unheated)	$5.97 \times 10^{-3}$	6.13	$1.7 \times 10^{20}$
	$\frac{1}{2}$ Lapped $\frac{1}{2}$ Etched (heated)	$3.5 \times 10^{-3}$	10.6	$1.68 \times 10^{20}$
3	Etched (unheated)	$9.07 \times 10^{-3}$	2.53	$2.72 \times 10^{20}$
	Etched (heated)	$5.12 \times 10^{-3}$	3.61	$3.38 \times 10^{20}$
4	Etched (unheated)	$1.46 \times 10^{-2}$	3.43	$1.25 \times 10^{20}$
	Etched (heated)	$3.71 \times 10^{-3}$	4.99	$3.38 \times 10^{20}$

The introduction of a high purity gold metal electroformed collector with a light transmission range of 83% to 87% was a milestone in the collection of the power generated by a given cell. The gain in collector efficiency was at an increase in cost. The gold electroformed grids are very expensive.

In order to evaluate a cell with the electroformed grid, the cell had to be laminated. This required considerable time until a test fixture was designed that permitted quick and economical cell evaluation. This device allowed intimate contact between cell and collector during the test period before actual lamination. This fixture has been adopted as standard equipment. (3)

Such a procedure was satisfactory at this stage of development. Two hundred and sixty cells were delivered to NASA, Lewis Research Center, Cleveland, Ohio, for an in-house testing program. One of the tests required repeated thermal cycling to simulate orbital flight. The early cells delivered for this purpose were constructed with the electroformed gold collector electrode. Many cell units survived 400 cycles and then became erratic in behavior. Four hundred cycles were considerably less than the desired one year orbital equivalent. These tests indicate that the heavy gold mesh may be a source of shorting caused by the movements of the mesh and other cell materials during the heating and cooling cycles. At NASA some indication was found that gold contacts rubbed against the p-type layer tend to become non-ohmic.

A change in collector electrode design was indicated. Experimental investigation resulted in a procedure for the electrodeposition of a gold grid on the p-type layer by use of a photoresist mask. In addition to intimate contact, this method is economically advantageous. The operating cells of over 2.3% conversion efficiency were tested and found to be capable of exceeding 1200 thermal cycles. Initially, however, very low yields and relatively low power cells resulted. One of the causes of the low efficiencies obtained by electroplating was a lack of sufficient conductor cross section resulting in high series resistances. Increased plating time and current density increased the grid thickness. However, water degradation of the cell due to long immersions in the aqueous plating bath was suspected as the major cause of power loss and low yields. The goal of the research in this area was clearly defined: a compatible metallic grid which has sufficient cross-sectional area to insure carrier collection without significant IR losses and which is applied in a manner non-injurious to the cell.

#### 1. Photoresist Process

The photoresist mask through which the grid is electroplated can be applied to the p-layer by standard techniques.

The application of a negative-photoresist layer requires exposing the resist-coated cell to light through a photographic mask which is a positive of the grid. Spraying the cell with developer, alcohol, and air causes a photoresist mask to form on the cell. The developer removes the unexposed portions of the photoresist. The cell is ready for plating. After plating, the remaining resist must be removed. The prescribed method for removal requires scrubbing the surface with a developer-soaked tissue and rinsing with alcohol. The above steps are repeated until removal is accomplished. This abrasive action may loosen or dislodge parts of the grid or the barrier. The disadvantages of this latter procedure are readily apparent.

A new positive-working photoresist provides higher resolution, requires less heat during processing, has a lower frequency of pinholes, and can be

more easily removed after the plating operation. To remove the resist mask after plating, the cell is briefly dipped in one of many organic solvents. Thus, resist removal requires no abrasion and only brief contact of the cell with foreign solutions.

A study involving twenty-four  $1\frac{1}{2}$ " x  $1\frac{1}{2}$ " sample cells was made to compare the performance of cells fabricated by the two photoresist procedures. Twelve cells were masked with negative-working photoresist and plated in the gold solution using the fifteen minute plating as described below. (See Grid Electroplating.) Twelve cells were also masked with positive-working photoresist and were plated in the same manner. All twenty-four cells were laminated. Comparison of physical appearance of the grid and IV characteristics of the cells before and after plating rendered both processes equal. Because of the ease of operation, the positive-working resist was adopted as standard.

Some difficulty has been experienced in obtaining precisely defined grids because of non-uniform photoresist coating. This problem was solved by using two coats of resist: a thin initial layer and a heavy subsequent layer. The thin coating wets the surface of the p-layer sufficiently so that the second coat spins on the cell uniformly.

## 2. Grid Electroplating

Results of thermal cycling tests indicate that electrodeposited grids adhere to the p-type layer more tenaciously than pressure-contacted electroformed mesh. Development of a grid of this type renders lamination unnecessary for affixing the current collector grids to the p-layer.

### a. Plating Solutions

In addition to the commercially available gold plating solutions discussed below, other solutions and metals were investigated.

Cells gridded by the electrodeposition of copper and nickel from aqueous solution appeared to be short circuited on oscilloscope IV curves.

Electroless depositions of nickel were made on several cells. Two different solutions were used with both solutions depositing nickel in the grid lines and on the photoresist. Cell degradation and difficulty experienced with the removal of unwanted nickel covering the photoresist resulted in a rejection of this approach.

Solutions were made in which alcohol rather than water was utilized as the solvent. Experiments were conducted with two low-water content electrolytic solutions: (1) copper sulfate in methyl alcohol and sulfuric acid, and (2) silver nitrate in methyl alcohol and nitric acid. The copper solution gave good, heavy uniform deposits, but resulted in shorted cells. The silver solution was not useable since the silver nitrate would not remain in solution.

An immersion process consisting of a solution of gold chloride and methyl alcohol was studied. The mechanism involved a reaction which continued only until the surface was lightly plated. These tests also produced degraded cells.

Many plating techniques were found in the literature but initial considerations eliminated these as incompatible with the CdS-Cu<sub>x</sub>S<sub>y</sub> system.

#### b. Gold Plating Process

Because attempts to find a suitable non-aqueous electrolyte or a suitable non-gold solution were negative, efforts were directed toward developing a non-injurious plating technique using standard acid gold solutions. Acid electrolytes were necessary because of the obvious cyanide attack on the p-layer.

The gold plating process initially required 0.45 ma/cm<sup>2</sup> current density, 21°C bath temperature, and a plating time of two hours to obtain a gold thickness of 1.2 microns. Later, bus bars were plated on the p-layer along with the grid pattern in an attempt to increase conductivity. Since the total current flowing through the bath was not increased, the current density dropped to 0.3 ma/cm<sup>2</sup>. The lower current density produced an average conductor thickness of 0.8 microns.

At this point it was obvious that the information obtainable from the handbooks and manufacturers literature on these baths was not adequate to solve the plating problem. A study program was needed that would produce data concerning all parameters in a relatively short period of time.

A standard test cell used by electroplaters to determine plating conditions is known as the Hull Cell<sup>(4)</sup>. This device has proven to be of immense value for research. In use the cell is filled to an exact level with the particular plating solution and an anode is placed at the rear of the cell. The cathode is inserted opposite to the anode at a prescribed angle. A specified current is caused to flow. The net effect of the angle is the non-uniform distribution of current across the face of the cathode. The end nearest the anode has the highest current density while the other end has the lowest current density. This gradient permits the selection of the desired deposit. Repeated tests at various currents, temperatures and current density ranges provide data rapidly.

Both nickel-coated brass cathodes and solar cell cathodes were used in the Hull cell in order to evaluate plating current densities and temperatures. The results, which were obtained by visually comparing the cathodes, indicated that a temperature range of 21°C to 66°C and a current density range of 0 to 2 ma/cm<sup>2</sup> would yield a uniform, non-pitted deposit.

Grids were electrodeposited on solar cells at four current densities (0.3, 0.6, 1.0 and 1.5 ma/cm<sup>2</sup>) and at three temperatures (21, 49 and 66°C). The time in the solution for each set of variables were adjusted so as to give grid thickness of about two microns. Optimum plating conditions were determined on the basis of three cell characteristics; differences in I<sub>sc</sub>, V<sub>oc</sub> and the I-V curve shape before and after grid electroplating. The plating conditions which resulted in the smallest changes in the cell were found to be 1.0 ma/cm<sup>2</sup> current density at 49°C and a plating time of 45 minutes. These conditions produced a grid thickness of two microns. Under these conditions, cell degradation caused by plating was still observed although the loss of efficiency was considerably decreased.

At 49°C a large reduction in the plating time from 45 to 15 minutes has been effected by plating at a low current density of 1 ma/cm<sup>2</sup> for 5 minutes and then at a higher current density of 5 ma/cm<sup>2</sup> for 10 minutes. This method enables the use of a relatively high current density and results in an increase in the thickness of the gold deposit from 2.0 to 2.5 microns. Cells with power losses of 10% or less have resulted. It is possible that a linear increase of current density from a low value up to 5 ma/cm<sup>2</sup> may result in further improvement.

It has been found that a cell lowered into the plating solution with no voltage applied, becomes coated with gold, probably due to a chemical replacement reaction. Since the commercial gold plating solution is a proprietary formula, the specific reaction can only be speculated. Such replacement reactions have been previously noted as damaging to the barrier. In order to eliminate the possibility of such electroless or immersion plating, cathodic protection is provided by applying the voltage to the cell prior to immersion.

Solution filtering has also been found to be of importance in preventing cell degradation during electroplating. After a few cells have been plated, a yellow powder of unknown chemical composition appears suspended in the solution, making the solution appear cloudy. This material can be removed between platings by filtration but continuous filtration is recommended in the solution operating specifications.

The yellow substance found in the standard gold plating solution has been analyzed by emission spectrograph and x-ray diffraction. The spectrographic analysis showed a high gold and sodium content. The compound could not be identified by the diffraction pattern although the compound possesses a good crystalline structure.

A high speed gold plating solution obtained from a commercial supplier has been investigated and found unsuitable. Low open circuit voltages invariably resulted.

Two other plating solutions were investigated: a gold alloy solution and a gold strike (pre-plate) solution. The chemically neutral alloy bath is capable of high plating rates. The alloy plate produced uniform grids which were more than twice as conductive as those obtained using only the standard gold plating solution. Less degradation has been observed. The gold strike solution failed to give better results in conjunction with either the standard gold or the gold alloy. Heavy fogging resulted when the strike solution was used.

### 3. Auxiliary Bus Bars

The most serious problem remaining for electroplated grids is the development of a suitable bus bar network. The bus bars are necessary to reduce the series resistance associated with the relatively thin grids. Reduction of the series resistance by means of thicker grids requires prohibitively long plating times which frequently results in badly shorted cells and reduced grid transmission. The most efficient bus bars used to date have been silver foil strips laminated against the electroplated grid. Attempts to solder the foil to the gridded foil revealed that there is a problem involving the amount of solder. An excess amount of solder invariably attacks the barrier. It has been demonstrated that these silver strips can be successfully spot welded to the gold grid without any harm to the cells. (5)

Ruled silver print and sprayed-on conductive epoxy were investigated for use as bus bars and were found to be unsatisfactory.

A photoresist mask was designed which enable gold bus bars to be plated simultaneously with the grid. The thinness of the gold bus bars, and its resultant resistance, necessitated spot welding silver foil leads on top of the gold.

With an auxiliary anode configuration, it was possible to increase the bus bar thickness to five microns. However, it was discovered that when cells are electroplated without the bus bar network, the degradation is less. A non-deliterious method of bus bar plating is being sought.

A peripheral bus bar configuration was investigated and compared with the "extended-H" network now employed. Theoretical considerations show that for a fixed bus bar network surface area and thickness, the square design should be more efficient. Preliminary investigations have shown that the two configurations are comparable.

#### 4. Other Work

##### a. Unheated Cells

There is some evidence that unheated, chemiplated-barrier cells do not degrade as rapidly in the presence of water vapor as heated cells. For this reason unheated, chemiplated-barrier cells were grid electroplated and then heated to maximum efficiency. In general, the open circuit voltages were low (.38 volts). However, there is some doubt as to whether representative samples were obtained because of the low efficiency of the standard from the same 6 in. x 6 in. substrate. Cells with unheated, extra-thick p-type layers also showed a similar effect: low open circuit voltages (.20 volts).

As a check, six  $1\frac{1}{2}$ " x  $1\frac{1}{2}$ " unheated-barrier cells were plated using the alloy procedure. Cells were subsequently heated to obtain maximum efficiency. None of the cells were as efficient as the pre-heated cells.

##### b. Effects of Light During Plating

Light could conceivably influence the cell during the plating process since the bulk CdS is photoconductive in nature and the barrier degradation is believed to be caused by a photochemical process. Experiments conducted to evaluate the effect of light on the cell during grid electroplating have shown no observable effects.

##### c. Pre-cleaning Solution

A commercially available, neutral, cleaning solution primarily intended for cleaning copper printed circuits prior to plating was investigated. Improved contact and better adherence of electrodeposited gold was expected. Results of these tests show that, although the open circuit voltage remained about the same after gold electroplating, the short circuit current decreased to about one half of its original value.

#### d. Less Dense Grids

Prior work on pressure test results has indicated that a 25 lpi grid network could be used instead of the present 70 lines per inch grid without loss of efficiency. With the 25 lpi grid more active cell area **would be obtained**. A test of eight 3 in. x 3 in. cells demonstrated that, using the present technology, 25 lpi electroplated grids are not sufficient to collect the carriers without a loss in efficiency.

#### 5. Summary

The best plating method to date to obtain less than 10% degradation at 75% yields (provided films with few pinholes can be selected) is as follows. The p-layer of the cell is coated with the positive-working photoresist by the two-spin method as above. This coating is then exposed to ultraviolet light through a photographic mask which is a negative of the 70 lpi gold grid. A dip in developer and a distilled water wash produces the desired mask. The cell is then mounted on a plating board. A small brush dipped in photoresist is used to mask any pinholes observable under a microscope. Grid electroplating is done in two steps: (1) 1 ma/cm<sup>2</sup> at 25°C for 5 minutes in the acid gold solution and (2) 5 ma/cm<sup>2</sup> at 55°C for 10 minutes in the neutral gold alloy solution. Following a rinse in running distilled water, the cell is dried with tissues and placed in an oven at 200°C for 30 seconds to remove remaining water. The photoresist mask is removed with acetone and the cell is tested in a special pressure test unit which has a bus bar arrangement similar to the laminated bus bars.

### CHEMICAL MILLING SUBSTRATES

One of the purposes of this development program was to produce more flexible and lighter weight cells. The most obvious component to concentrate on was the substrate. Thinner or less dense metal might be employed. It was found previously that thinner molybdenum (one mil) presented a handling problem.<sup>(6)</sup> Other less dense metals also presented problems such as poor thermal match and poor adherence due to surface conditions<sup>(7)</sup>.

Since two mil molybdenum was easy to handle, a process was developed whereby the thicker molybdenum was retained throughout the entire cell fabrication procedure. Then immediately before, or after lamination, the back of the cell (the molybdenum) was chemically milled to the desired thinness.<sup>(8)</sup> This effectively reduced the weight of the cell, and avoided the difficulties of working with extremely thin metal foils during fabrication. Although a fine control has not been established for this process, cells have been made that demonstrate over forty watts per pound. One 3" x 3" cell of 5.2% efficiency was found to be seventy-seven (77) watts per pound. This cell did degrade later to a value of 42 watts per pound. Milled cells (3" x 3") generally weigh about two grams.

#### 1. Process

The milling solution is composed of 50% HNO<sub>3</sub> and 50% H<sub>2</sub>O by volume. Stronger nitric acid baths are too fast for proper control and yield pitted surfaces. Although the acid action is satisfactory at this concentration there are indications that excessive heat is being generated during milling.

At present, the best procedure requires the lamination of one mil H-film and one-half mil nylon on the face of the cell only. A narrow picture frame of plastic is used on the back to ensure a seal on the edges of the substrate. The cell is then dipped into the etching solution for thirty seconds, rinsed in water, dipped into HCl, and then rinsed again in water. This is repeated until the substrate is at the desired thickness. One method used to control the thickness entails the etching of a piece of molybdenum that is somewhat thinner than the cell substrate. The cell and the molybdenum piece are given identical treatment. When the Mo piece disappears, then the cell substrate thickness is approximately equal to the original difference between the cell substrate and the piece of molybdenum.

## 2. Problems

When the two mil molybdenum substrate is milled to the range of three tenths to seven-tenths of a mil, it has a tendency to curl. Reducing the thickness to less than three-tenths of a mill alleviates the curling problem. If the molybdenum is milled much thinner than three-tenths of a mil, the CdS film tends to separate from the substrate. This may be connected with the heat generated during etching.

Another problem is that the etching solution slowly attacks the nylon. For this reason, the nylon must cover only the front of the cell and not be allowed to overlap. It is sufficient to seal the edges with a plastic picture frame that overlaps the back of the molybdenum.

In summary, it might be noted that while this milling process still has problems, it is inherently simple. It reduces the handling problems and produces the results expected with thin foils. It opens new possibilities in power-to-weight ratios, and even in cell construction. It has been reported that a rear wall cell was fabricated by this method utilizing photoresist masking techniques.<sup>(9)</sup> There are several rear wall and front wall combination cells that can conveniently be constructed when this milling process is included in the fabrication procedure.

## ALTERNATE SUBSTRATE MATERIALS

Since the discovery of the chemical milling process the use of thinner molybdenum foils has not been pursued.

Investigation of other substrates that appear more desirable than molybdenum because of cost, density, conductivity, thermal expansion or ability to form a good contact to n-type CdS has been made in the past as a means of achieving weight reduction. At times, the results have been promising, but none have yielded the reproducibility achieved with molybdenum.

### 1. Conductive Paper

Films were successfully evaporated on conductive paper.<sup>(10)</sup> These CdS films had a close even texture. Very little problem was experienced with thermal expansion match. There were, however, two problem areas. The first was the insufficient conductivity of the paper. To overcome this the paper was coated with a layer of silver. This was applied by spraying and by evaporation. The second problem was the embrittlement of the paper during the barrier formation process. This made the handling after plating rather difficult.



Some cells were made with silver interface layers of sprayed silver. All of these cells shorted during test. This was due to the uneven silver which caused the CdS to be uneven, and therefore caused localized shorts through the thin areas.

A cell  $2 \text{ cm}^2$  was made on a paper coated with several hundred angstroms of evaporated silver. This cell was 1.3% efficient. It was very brittle after barrier formation. The feasibility of using such paper was demonstrated. However, because of the necessity of using an interface conductor on the paper and with the advantages of the chemical milling process it does not now offer any advantage over the molybdenum substrate. It is possible that in a production process the paper could be used as a supporting substrate and then discarded in the final cell packaging.

## 2. Invar

Cells made on Invar have been found to be very good or very poor with none of intermediate quality. In many cases a yellow powdery layer has formed immediately adjacent to the substrate. It was discovered that by evaporating on Invar substrates held at high substrate temperatures (about  $300^\circ\text{C}$ ) the yellow layer is eliminated and that the adherence of the CdS is improved. However all of the cells made from these films are rather low in efficiency.

## 3. Other Materials

Tin clad steel was one of the new materials investigated. Adhesion of the CdS was poor and curling was severe. These difficulties were caused by substrate surface conditions and mismatch of thermal expansion coefficients.

Cells made on titanium degraded about 50% and could not be recovered. In an attempt to determine the cause of the degradation, the films were removed revealing a dark gray titanium surface. Identification of the gray interface was difficult. Pieces of polished titanium were packed in sulfur and in CdS powder. These samples were heated to  $150^\circ\text{C}$  in argon and then allowed to remain in the closed container for two days. In both cases, the titanium surface turned gray.

# CELL PACKAGING

## 1. Lamination

The film cell package at present consists of the CdS film and barrier layer on the substrate, and a collector mesh laminated between sheets of plastic. The plastic serves several purposes. It holds the collector mesh to the barrier (unless electroplated collectors are used), it serves as a protection from physical damage and gross amounts of water. It is a barrier to low energy protons and even some electrons, and it serves as a light weight mounting structure.

Previously the laminating procedure required that the cell package be placed in platens and heated in a press for more than one-half hour. Since the plastics and the cells have properties that change due to heat, it was desirable to minimize this heating period. To accomplish this an impulse

type laminator has been installed that can complete the encapsulation cycle in a few minutes. This laminator is capable of handling up to one foot square arrays. Instead of utilizing heated platens the heat is supplied directly to the cell package through a thin metal diaphragm-type resistance heater.

This sealer is now operational. The optimum heating cycle is 45 seconds. If a shorter heat is used there is considerable shrinkage due to the orientation of the thermoplastic film. Comparative tests were made of the two lamination procedures. Cells were tested on the pressure test unit, the laminated, some in the impulse sealer, some in the heated platens. The results are in the following table.

<u>Cell No.</u>	<u>Type of Lamination</u>	<u>Cell Efficiency Before Lamination</u>	<u>Cell Efficiency After Lamination</u>
S103-A	Impulse Sealed	2.45%	2.72%
S103-C	Impulse Sealed	2.25%	2.41%
S103-B	Heated Platens	2.08%	2.38%
A103-D	Heated Platens	2.33%	2.69%

The results show that the impulse sealed cells are essentially equivalent just after lamination.

It is recognized that the impulse sealer does not allow for a long vacuum pump-out which may prove harmful to the cell over an extended period. If long outgassing is necessary it can be provided for in a vacuum bake-out oven prior to impulse sealing. A decay problem that is not associated with lamination makes it difficult to evaluate the effects of the types of lamination on lifetime. More will be said on this decay problem later in this report.

## 2. Encapsulants

The best encapsulant for space is H-film. Both one mil and one-half mil sheets have been used successfully.<sup>(11)</sup>

Pyre ML varnish <sup>(11)</sup> which seems to be uncured H-film has been used as an encapsulant. The transmission of the Pyre ML varnish was checked and compared with that of H-film. As can be seen from Figure 4, the varnish transmits further into the blue to about 425 millimicrons while the H-film cuts off at about 480 millimicrons. It was reported that the yellow color of the H-film results from impurities and appears during curing. For this reason, some Pyre ML film was used to coat the cells since the possibility exists that all of the properties of the fully cured H-film are not necessary for protection of the cells. These pyre ML coatings were much lighter in color than the H-film and their absorption edge was shifted toward the blue.

Three 3" x 3" cells with electroplated grids were preheated to 175°C for one hour. Cell "A" was coated with a 100% mixture of Pyre ML, and Cell "B" was coated with a 75% mixture of Pyre ML and 25% Dimethylformamide. Cell "C" was coated with 50% Pyre ML and 50% DMF. All three coatings were spun

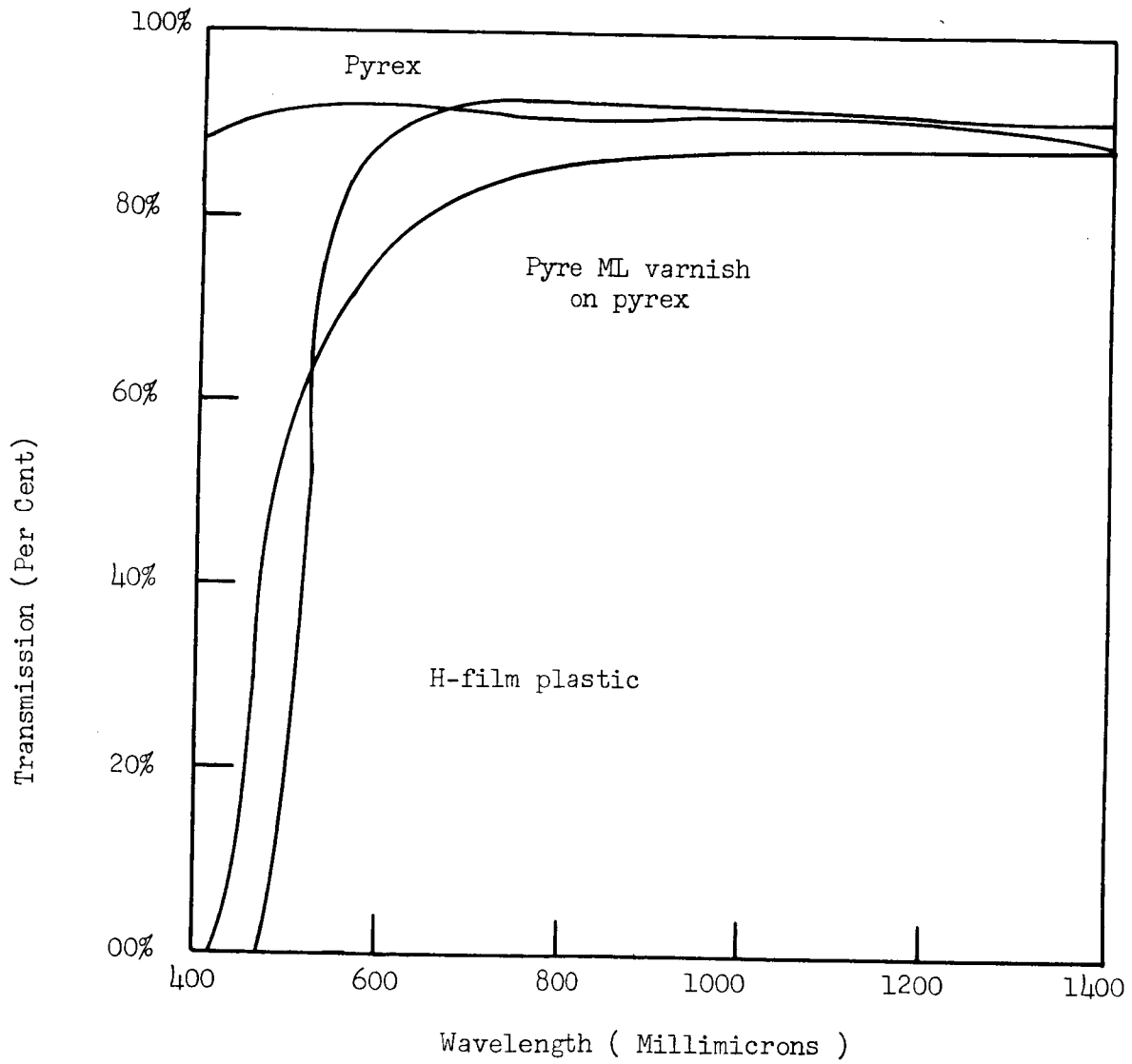


Figure 4. Transmission of H-film and Pyre ML Varnish

on the cells to a thickness of less than 0.2 mil. All cells were then cured at 200°C for three hours. The electrical response showed some degradation due to the solvents.

The three cells were then immersed in H<sub>2</sub>O for 48 hours. Data taken at the end of the test showed a significant degradation. It appears that the varnish can not be applied as a liquid.

Some cells were coated with films made from Pyre ML varnish. These films cracked and dark spots appeared on the surface upon lamination. The films also became very brittle. When films made from the Pyre ML varnish were cured in an oven at 100°C for several hours they also became very brittle and changed to a darker yellow.

Since the varnish could not be used by itself or laminated as a partially cured film, it was applied over cells laminated in nylon only and with nylon-mylar. More of the blue light could reach the barrier region. Some success has been realized with the Pyre ML mylar-nylon combination. However, since the H-film causes about a ten percent loss and is more convenient to use, no further effort was expended on the varnish.

A film of polydimethylphenol ether was obtained from NASA, Lewis Research Center as an encapsulating material. This material has been reported to have many of the properties of H-film with the disadvantage of being colored. Upon lamination, it became very brittle, similar to the results obtained with polystyrene.

### 3. Lead Attachment

For a period of time solder containing indium was used to hold the silver lead to the gold mesh. Within a few weeks the barriers were found to be damaged. Darkened areas appeared in the barrier type cells. Upon testing it was determined that the amount of solder present in the contact was important. To reduce the degree of degradation the amount of solder to be used was kept to a minimum. Any excess would invariably attack the barrier.

When the electroformed mesh was replaced by the thinner (two micron thick) electroplated grid, the solder problem became more severe. It was nearly impossible to apply sufficient solder to attach the auxiliary silver bus bars and leads to the collector while at the same time using a minimal amount to prevent attack. A thicker grid could alleviate the problem. An earlier section of this report discusses progress in this area.

Successful cells have been fabricated by initially depositing gold bus bars as previously described with an auxiliary silver bus bar and lead spot welded to the top of the gold stripe. A micro-gap welder<sup>(5)</sup> has been obtained for this purpose. A unit of this type prevents damage to the cell barrier. An initial improvement in efficiency was noted for cells with welded connections compared to those with pressure connections. An improvement in the cell package with regard to thermal cycling also resulted. The indications from tests run at Harshaw and those in progress at Lewis Laboratory, NASA, are that the welded connection greatly improves the reliability and life of the cells during repeated thermal cycling in high vacuum. It appears that this type of collector arrangement is more satisfactory than any previous type.

## PILOT LINE

During this contract two significant changes were made in the pilot line. The first major change was a switch from the electroplated barrier to the chemiplated barrier. This change resulted in higher cell efficiencies.

The second was an improvement in the pressure test unit design.<sup>(12)</sup> Figure 5 is a picture of this new fixture. These improvements include a better diaphragm arrangement, elimination of the hand clamps, and improved electrical contacts.

Approximately five hundred cells were fabricated on the pilot line during this contract. Many were over 4% with a few over 5% efficient based on grid area. The highest efficiency reported was 5.2%. The average efficiency for the contract period was slightly less than three per cent. This low average reflects the problems experienced with the transistor washer. This problem was caused by a fungus contained in the filter cartridges as obtained from the manufacturer. The electroplated cells included in this average were also lower in efficiency than the chemiplated cells.

During this contract 12 each 6" x 6" arrays and 16 each 3" x 3" cells were delivered to the Contract Monitor. They demonstrated chemical milling, electroplated collectors, spot welded leads and various encapsulants.

The watts per pound ratio calculated for cell 1849HN was 77 watts per pound at the initial 5.2% efficiency. It degraded to only 42 watts per pound at delivery time. Most of the cells delivered were in the twenty to forty watts per pound category.

## CELL DEGRADATION

Many of the most efficient cells have displayed the most instability. Contrary to the type of degradation previously seen this could not be traced to moisture. Cells placed in a vacuum did not improve but degraded significantly. It was found on examination that the vacuum chamber was contaminated with sulfur.

Bare cells placed in this sulfur contaminated vacuum overnight degraded more than 30%. Even encapsulated cells degraded 20% after three days in the sulfur contaminated vacuum. Cells placed in clean vacuum do not degrade, in fact, they improve with time.

It does not seem that an ordinary desiccator is adequate storage for the cells. Those placed in a regular desiccator degraded 30% in two days and 50% in one week. Those placed in freshly dried desiccant sealed in plastic and placed in the normal desiccating cabinet dropped only 1% to 4% in thirty days. Cells placed in freshly dried desiccant, sealed in plastic, and refrigerated at less than -18°C showed no degradation after thirty days.

From the above tests it is evident that the present cells, especially the highly efficient, must be protected from both small amounts of moisture and from sulfur. More work must be done to determine the sources of sulfur that are responsible for degradation. Some may be in the cell package itself.

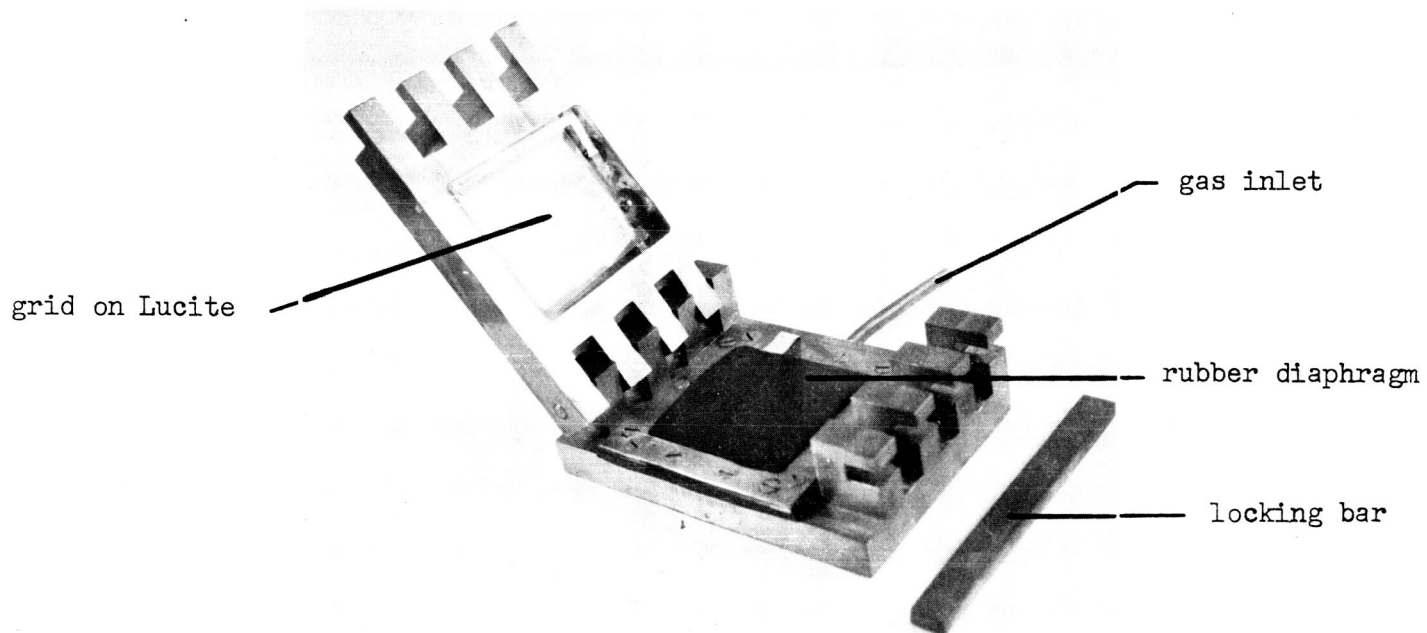


Figure 5. Pressurized Solar Cell Test Apparatus

## CELL DESIGN RECOMMENDATIONS

The following section contains the recommendations for the cadmium sulfide solar cell design most suitable for a thin-film solar cell space power system according to the present state of the art. It consists of material specifications, a drawing of the cell (Figure 6), and typical cell electrical characteristics (Figure 7).

### 1. Material Specification

#### (a) Material: Cadmium Sulfide

Grade: Cadmium sulfide powder for solar cell use shall be of electronic grade only.

Impurities: Impurities in CdS powder for solar cell use shall not exceed the following limits as determined by spectrographic analysis.

<u>Element</u>	<u>Parts per million</u>
Aluminum	2.0
Calcium	1.7
Copper	1.0
Indium	1.0
Iron	2.0
Magnesium	1.0
Manganese	0.0
Nickel	0.0
Silicon	2.0
Thallium	0.0

Source: Cadmium sulfide is available from the General Electric Company, or the Sylvania Electric Company.

#### (b) Cuprous Chloride

Grade: AR grade cuprous chloride shall be used.

Impurities: Cuprous chloride shall meet ACS specification. Impurities shall not exceed the following maximum limits.

Arsenic (As)	0.001%
Insoluble in Acid	0.020%
Iron (Fe)	0.005%
Substances not precipitated by H <sub>2</sub> S as sulfates	0.20%
Sulfate (SO <sub>4</sub> )	0.10%
ASSAY (CuCl)	Min 90%

Preparation: Cuprous chloride shall not be used "as is". Preparation of cuprous chloride shall be accomplished by rinsing it in water with a pH of 1, filtering out the powder and drying it.

Storage: After preparation the cuprous chloride should be stored in dark bottles in a dry atmosphere.

Source: Cuprous chloride is available from the Mallinckrodt Chemical Works.

(c) Molybdenum Foil

Thickness: 0.002"  $\pm$  .005"

Size: Sheets 6 $\frac{1}{2}$ " x 6 $\frac{3}{8}$ "

Special Requirements: 1. Stress relieve after rolling.  
2. Surface to be smooth and free of pits, scratches  
3. Molybdenum must be prepared by the powder metallurgy process.  
4. Purity 99.9% required.

(d) Material: Gold Mesh

Lines Per Inch: 70

Line: 0.00153"

Space: 0.01286"

Maximum Transmission: 0.85%

Size of Sheet: 9.5" x 11.5"

Note: This material is available only through the Buckbee Mears Co., 245 East 6th Street, St. Paul, Minnesota under ruling Number 1144.

(e) Material: Mylar Plastic Film

Type: Type A Mylar film

Thickness: Both  $\frac{1}{2}$  mil (0.0005") and 1 mil (0.001") are required.

Source: This material is available from the DuPont Chemical Company.

(f) Material: Polyimide Plastic Film

Type: Type H plastic film (H-film)

Thickness: Both  $\frac{1}{2}$  mil (0.0005") and 1 mil (0.001") are required.

Source: This material is available from the DuPont Chemical Company.

(g) Material: Nylon Plastic Film

Type: 77C

Thickness:  $\frac{1}{2}$  mil (0.0005")

Source: This material is available from the Allied Chemical Company.

(h) Material: Silver Foil (High purity)

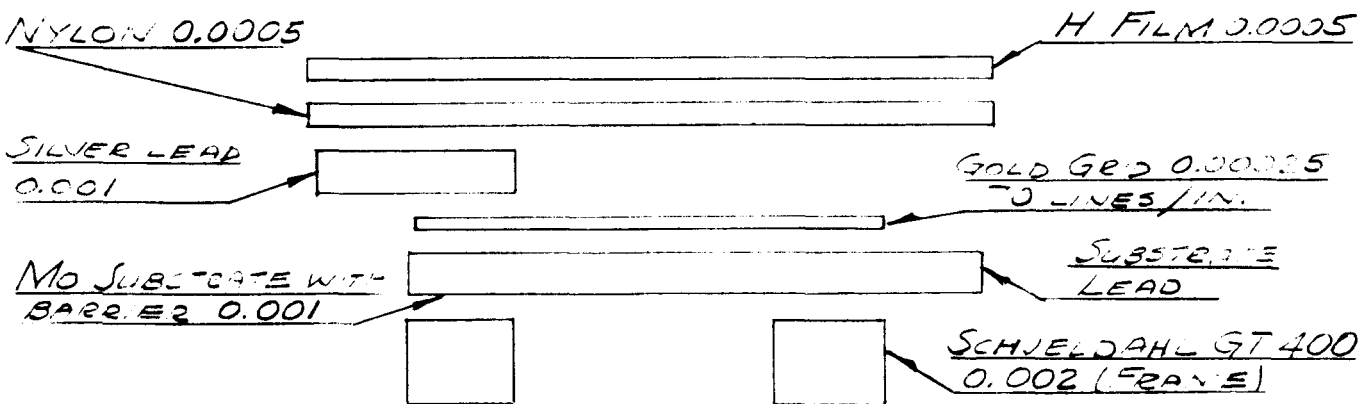
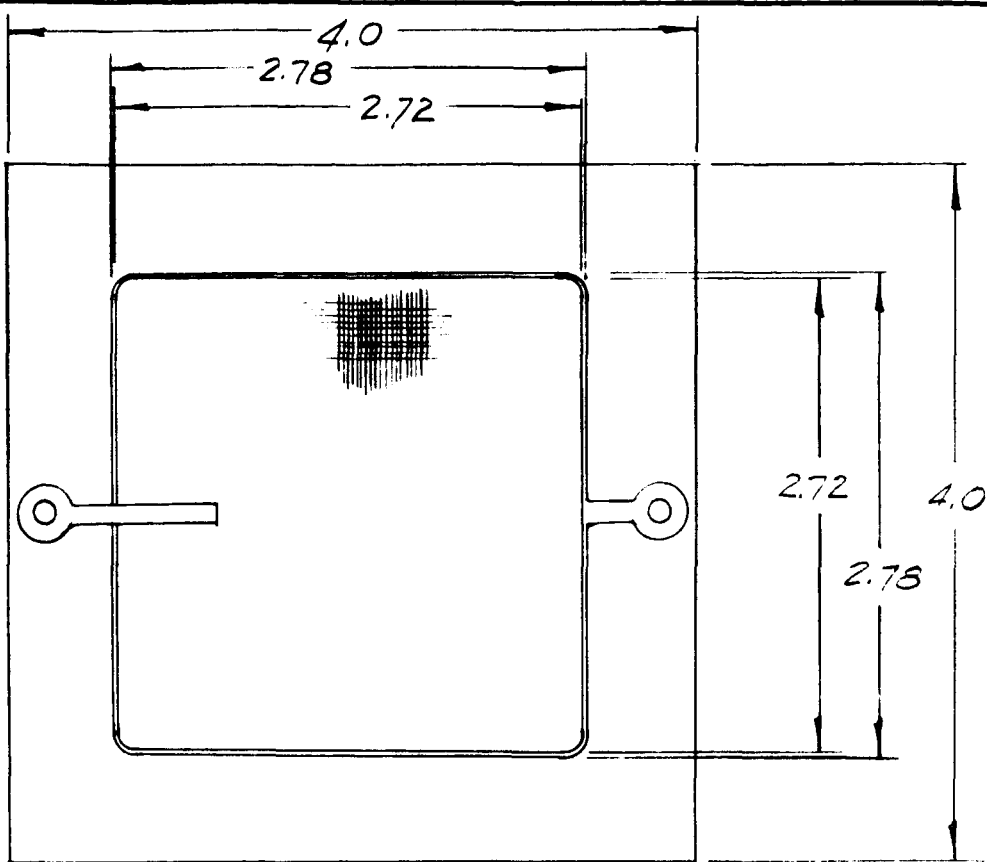
Thickness: 1 mil (0.001")



Width: 0.125"

Source: This material is available from the Handy and Harmon Company.

Note: Dimensions are not critical.



SECTIONAL VIEW  
SHOWING RELATIVE THICKNESSES  
FIGURE 6

SCALE Full & NOTED	MATERIAL	REV.	NO.	CHANGE		DATE	DR.	APP.
		THE HARSHAW CHEMICAL CO. 1945 EAST 97TH ST. CLEVELAND, OHIO 44106 CRYSTAL-SOLID STATE DIVISION						REF.
TOLERANCES UNLESS OTHERWISE SPECIFIED	DR.			TITLE  CdS SOLAR CELL		TYPE		
	CH.					DWG. NO.		
	APP.					A		

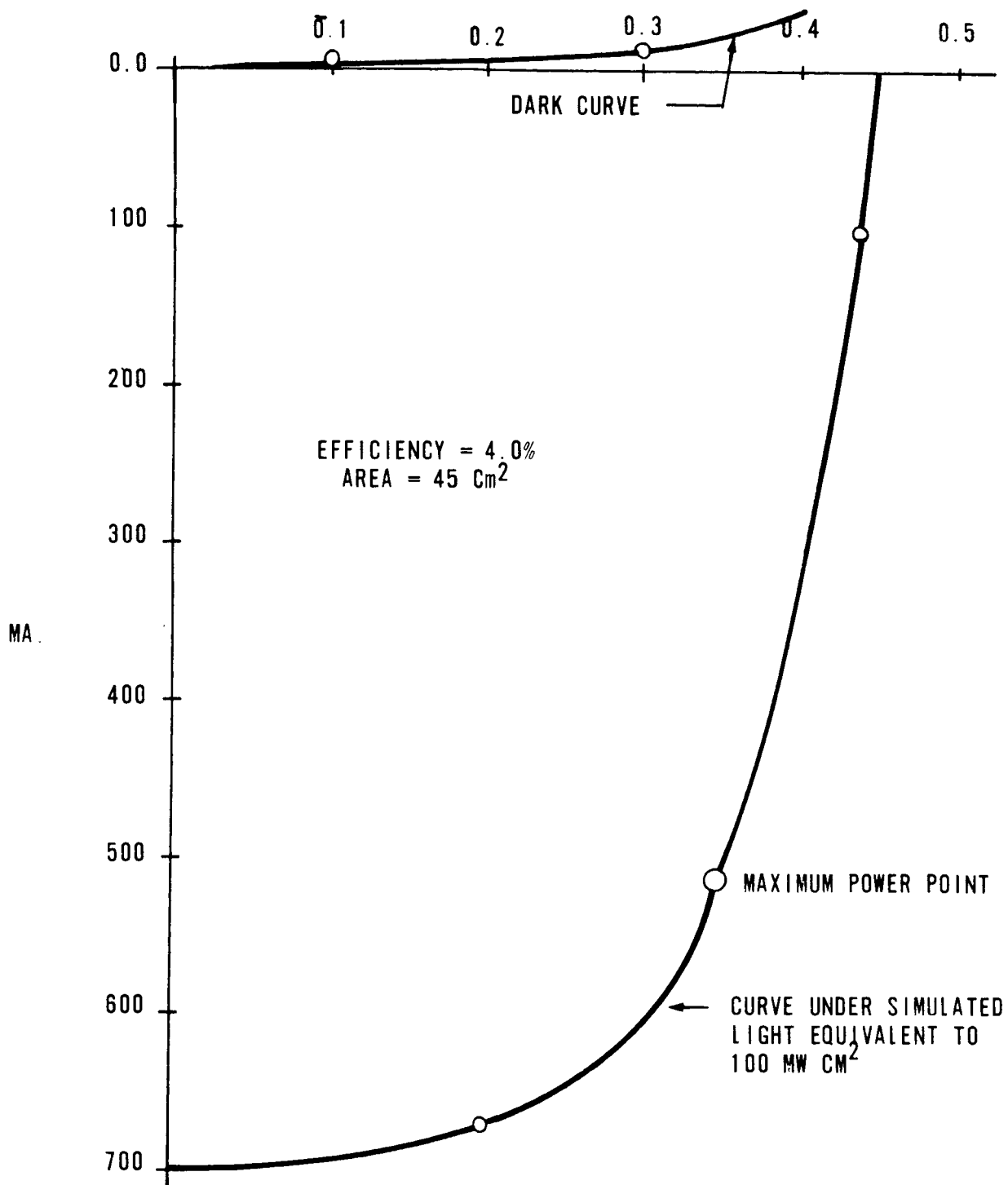


FIGURE 7  
TYPICAL I-V CURVE

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