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FINAL REPORT

STUDY OF THIN FILM LARGE AREA PHOTOVOLTAIC SOLAR ENERGY CONVERTER

BY

W. J. DESHOTELS and F. AUGUSTINE

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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CONTRACTOR REPORT

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By W. J. Deshotels and F. Augustine

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STUDY OF THIN FILM LARGE AREA PHOTOVOLTAIC SOLAR ENERGY CONVERTER

by

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SUMMARY

A process for fabricating thin film CdS backwall solar cells on polyimide plastic foil substrates has been developed. This process consists of vacuum evaporating approximately 50 microns of indium-doped CdS onto a lapped surface of 0. 002" thick DuPont H-Film at 200°C, processing a barrier on the CdS by applying a water slurry of Cu_2O and heating, contacting the barrier with conductive silver paint, and then laminating the cell to an 0. 001" thick film of Mylar using a nylon plastic adhesive.

Other transparent insulating substrate materials have been evaluated as substrates for backwall film cells. Factors affecting the vacuum evaporation of CdS films have been studied and a trade-off made between low film resistance yielding low open circuit voltages and higher film resistance causing appreciable series resistance effects.

The plastic substrate cell has reached the 1. 5 to 2. 0% efficiency level. Further improvements are anticipated since efficiencies greater than 4% have been obtained with insulating glass substrate cells.

author

1. 0 INTRODUCTION

Thin film solar cells are still in the early developmental stages. However, these cells show promise of realizing large area low cost arrays which are very light in weight, and capable of extreme compaction during launch and ascent into orbit, Thin film, large area, cadmium sulfide photovoltaic cells have been fabricated as large as thirty-six square inches with conversion efficiencies of about 3 percent.(1) These films have been flexible substrates and are presumed to be highly resistant to radiation damage since they do not depend on high crystalline perfection.

The work described herein is based on the backwall cell arrangement in which sunlight is incident on a highly conducting transparent cadmium sulfide layer and is absorbed in an opaque modified cadmium sulfide layer below the transparent layer. Compared to the frontwall cell, the backwall cell has two principal advantages: 1) The high conductance of the top, transparent, CdS layer minimizes the area of metal grids or bus bars that have to be placed in the path of the incident radiation. 2) The light sensitive layer is protected from the ambient by the relatively thick transparent CdS layer on one side and may be protected by metal foil or another impervious coating on the other.

The principal purpose of this study is the development of a CdS photovoltaic solar energy converter consisting of a large area transparent plastic substrate on which is an array of closely spaced, small (nominally one-inch square), backwall, CdS photocells connected in series or in parallel, depending upon the desired voltage-current output.

This report covers work performed under Contract NAS3-2795, and in the period October 1, 1963 through September 30, 1964. It is a continuation of the investigation begun under the auspices of NASA Western Operations Office, Contract NAS7-203 for the period October 1, 1962 through September 30, 1963.

2.0 EVAPORATED FILMS

Thick CdS films have been formed by vacuum evaporation of indium-doped sintered CdS powder onto heated glass and H-Film plastic substrates at vacua of about 10^{-6} Torr.

2.1 Equipment

An Optical Film Engineering Co. vacuum system with a 12 inch diameter bell jar, and a Vacuum Electronics Co. system with an 18 inch diameter bell jar were employed for the CdS evaporations performed under this contract. Both systems were provided with tungsten coil substrate heaters positioned above the substrate, and with inner pyrex glass chambers to contain the evaporation proper.

Figure 1 illustrates the evaporation set-up for the smaller system. The substrate holder was designed to hold a 4" x 4" substrate of either glass or H-Film clamped in a frame. The substrates were mounted so that they formed the lower surface of an aluminum box-like chamber. Several different evaporation sources were evaluated, but a quartz crucible as shown in Fig. 2 was evolved which gave best all around results and was used for most of the evaporations of this contract. The advantage of this design is that the crucibles can be readily removed and cleaned and replaced, and they are independent of the heater coils. Also, the design permits insertion of a thermocouple in the center well where the couple does not come into direct contact with highly corrosive sulfur vapors.

The hot wall chamber technique was employed for these evaporations using an inner pyrex glass cylinder to contain the CdS vapors, and an adjacent outer pyrex glass cylinder wound with a tungsten filament as a source of heat.

The evaporation set-up for the larger Veeco system was similar except that the substrate holder was 9" x 9" in size designed to hold four 4" x 4" glass or plastic substrates, and with proportionately larger cylinder wall and source to substrate dimensions, etc.

2.2 Substrates

Various insulating substrates have been tried with some degree of success for vacuum evaporated CdS film solar cells.

2.2.1 Glass

A heat resistant borosilicate glass supplied by the Cincinnati Gasket Packing and Mfg. Co. was used for most of the earlier work of this contract. This glass was 1/16 inch in thickness and was used in 4" x 4" plates. To obtain smaller specimens for experimental evaluations, the glass was scored into eighths prior to CdS evaporation and broken into 1" x 2" pieces after film formation.

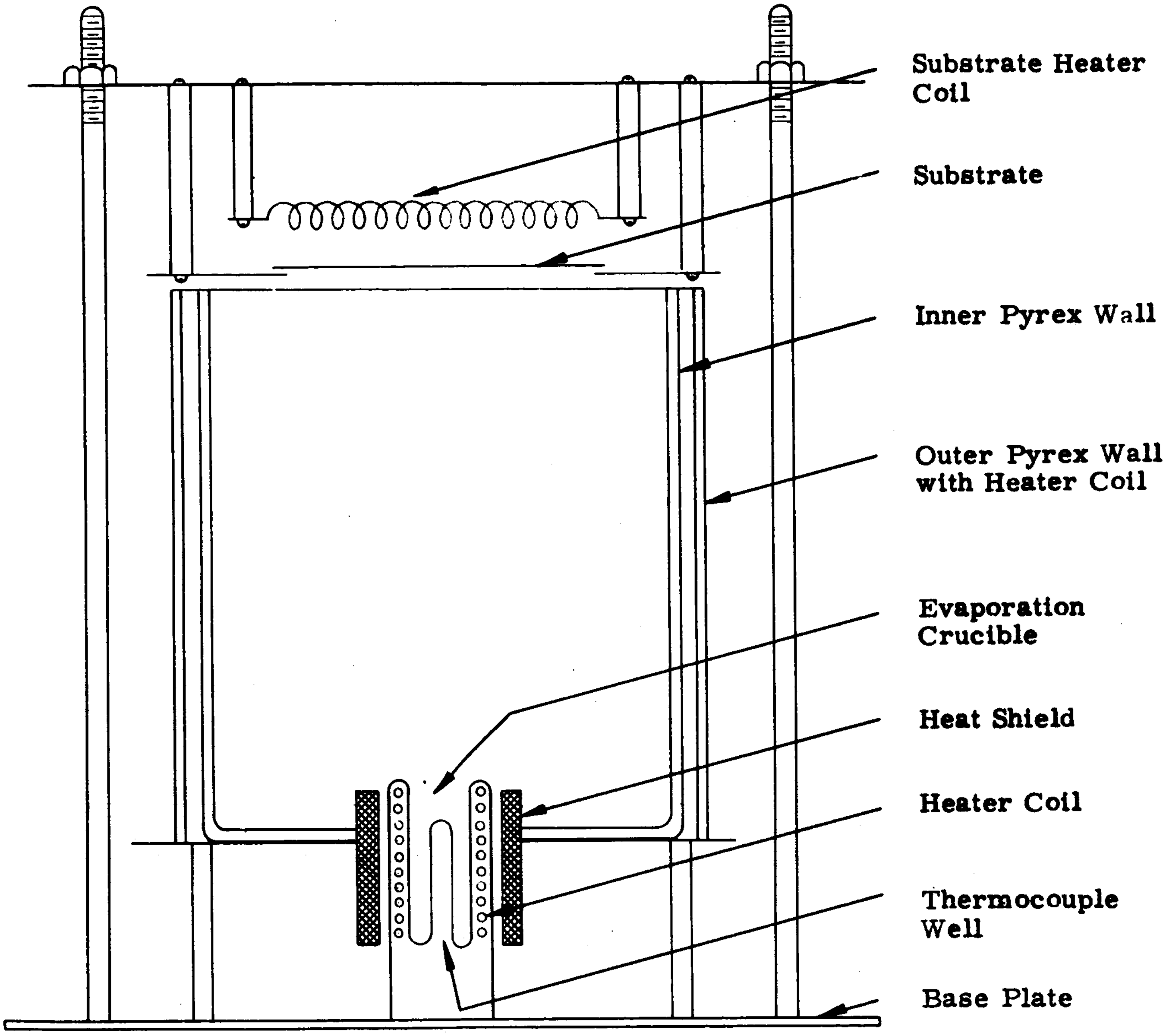
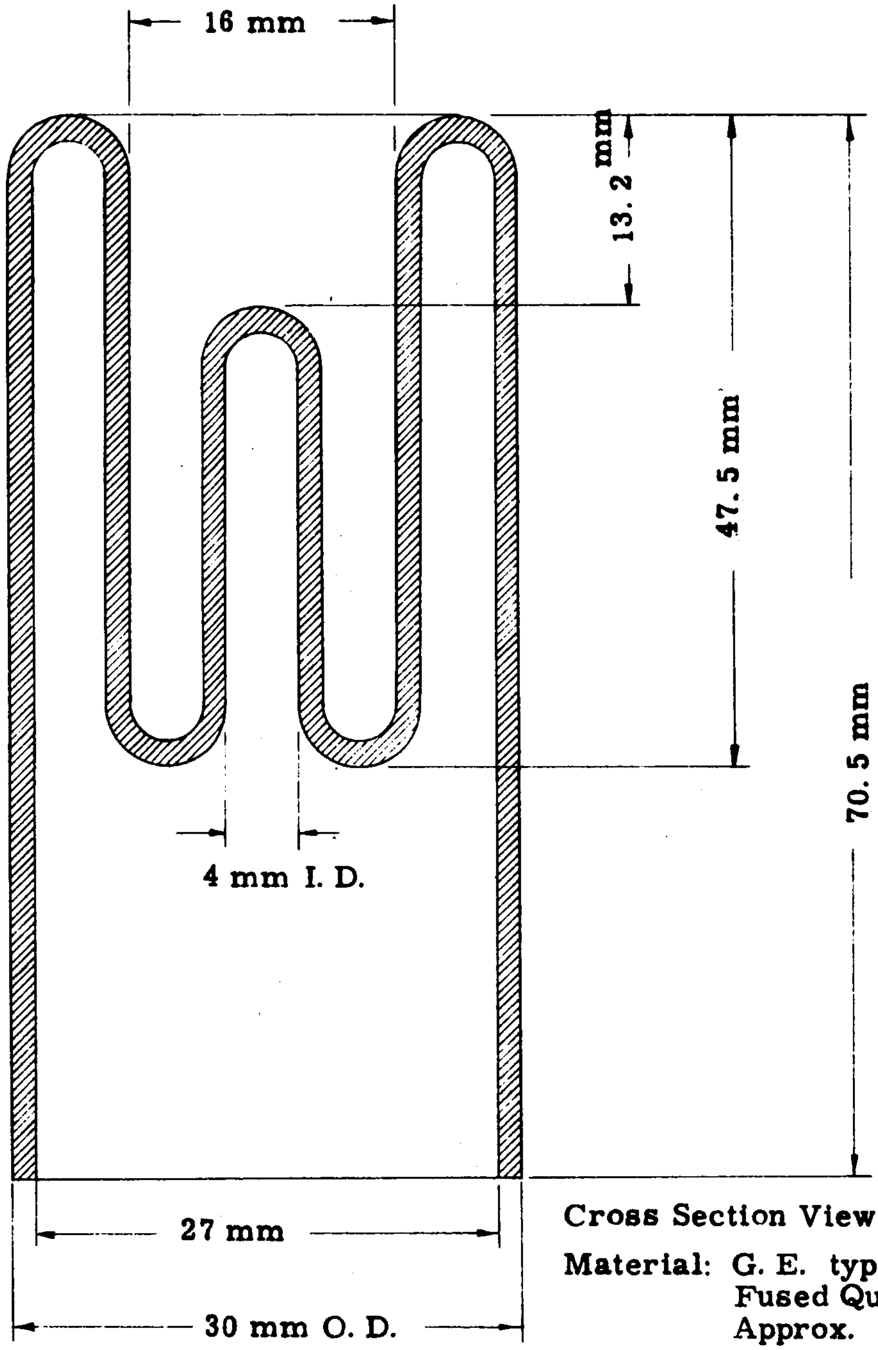


FIG. 1 CdS EVAPORATION SET-UP, 12" Vacuum System



Cross Section View

Material: G. E. type 204 Clear
Fused Quartz Tubing
Approx. 1 mm wall

FIG. 2 QUARTZ CRUCIBLE FOR CdS EVAPORATION

To improve the adherence of the thick CdS deposited layer, the glass was lapped on one surface with 1000 grit silicon carbide abrasive, cleaned with detergent, alkali, and several boiling distilled water rinses prior to evaporation.

2. 2. 2 H-Film

After reasonably reproducible results were obtained on glass substrates, a thin polyimide plastic foil, trade-marked "H-Film", was secured from the duPont Co. and used as a flexible lightweight substrate for CdS film cells. This material is characterized as a high temperature dielectric with outstanding mechanical properties from liquid helium temperature up to 500 to 600°C. It is optically compatible with CdS for rearwall cell operation as it transmits light well for wavelengths greater than 0. 5 microns. It is available in various width rolls in thicknesses of 0. 001 and 0. 002", suitable for the present application.

Due to the extreme flexibility of this H-Film plastic it had to be held clamped in metal frames for evaporation of CdS and subsequent cell processing. Reasonable adherence of CdS was secured only when the H-Film was lapped with 1000 grit silicon carbide abrasive to yield a roughened surface for the CdS. Also careful cleaning in alkali, detergent, and acid solutions followed by distilled water rinses was necessary. A stannous chloride sensitizing dip was found to be beneficial in securing adherent well-structured CdS films.

2. 2. 3 Textolite

A silicone glass laminate, trade-marked "Textolite", as supplied by the General Electric Company was tried as a substrate in one series of experiments. This material was secured in thicknesses down to 0. 008", and is a translucent (approximately 75% transmission) plastic with much greater stiffness than the thinner H-Film, making it easier to handle. It is able to withstand temperatures up to 250°C continuously without altering its mechanical and optical properties.

This material was also lapped and cleaned prior to CdS film evaporation. However, film adhesion was generally poor, though there were indications of good adherence on some smaller areas. Thus, it is possible that improved cleaning or surface sensitizing might yield a satisfactorily adherent CdS film suitable for thin film solar cells.

2. 3 CdS Material

The charge used for evaporating CdS films is a mixture of doped and undoped sintered material made from luminescent grade cadmium sulfide secured from the General Electric Company. The cadmium sulfide is sintered in quartz tubes on the following schedule:

1 hour under vacuum at 825°C.
1 hour under argon (790 mm Hg) at 1225°C.
Cooled naturally to room temperature.

The resulting hard boules are ground in mortar and pestle and stored until use.

The doped material (0. 1 mol% indium as sulfide) is blended with undoped material in the approximate ratio of 1:2. The exact proportion is adjusted with each lot of material to yield the desired CdS film conductivity. In a typical evaporation 16 grams of the mixture are charged into the crucible and about 13 grams are actually evaporated to give a film of several mils thickness.

2. 4 Evaporation Process

2. 4. 1 Optimum Film Parameters

Whenever possible, film resistivity, carrier concentration and thickness were measured on at least one film sample from each evaporation. From the resistivity and carrier concentration the Hall mobility is calculated. These film characteristics have been compared with the open circuit voltage, short circuit current and conversion efficiency of the cells fabricated from the films.

The result is a set of specifications such that a film, meeting these specifications, might reasonably be expected to yield good quality cells. These are:

Film Resistivity	0.025 ohm-cm - 0.035 ohm-cm
Carrier Concentration	8×10^{18} cm^{-3} - 10×10^{18} cm^{-3}
Hall Mobility	20 cm^{2}-volt^{-1}-sec^{-1}-27 cm^{2}-volt^{-1}-sec^{-1}
Thickness	50 microns - 60 microns

2.4.2 Evaporation Rate, Cell Efficiency and Film Thickness

The data taken on cells from sixty evaporations were examined in various ways. One interesting result was obtained when the efficiency of the best cell from an evaporation was plotted against the deposition rate for that evaporation. These data are shown in Fig. 3, and it appears that the best cells are obtained for the highest deposition rates. Indeed, with but one exception, no cells with efficiency greater than two percent were obtained at an evaporation rate less than about 0.19 micron per second. When open circuit voltage and short circuit current were plotted in the same manner, it was observed that the maximum attainable current also increased with deposition rate, while no such trend was observed for the open circuit voltage.

In Fig. 4 the variation in cell open circuit voltage and short circuit current are plotted against the thickness of the CdS film. In general both increase with increasing film thickness.

3.0 CELL PROCESSING

3.1 Collector Electrode

It was suspected that the indium peripheral electrode contacting the n-type CdS might be responsible for at least part of the deterioration observed. Indeed, this seemed to be borne out by the behavior of cell 102-7 which had an electroplated rhodium electrode in place of the indium. A number of metals were investigated as possible candidates for the role of contact to n-type CdS. Some were electroplated and some were vacuum evaporated. In a few instances, both

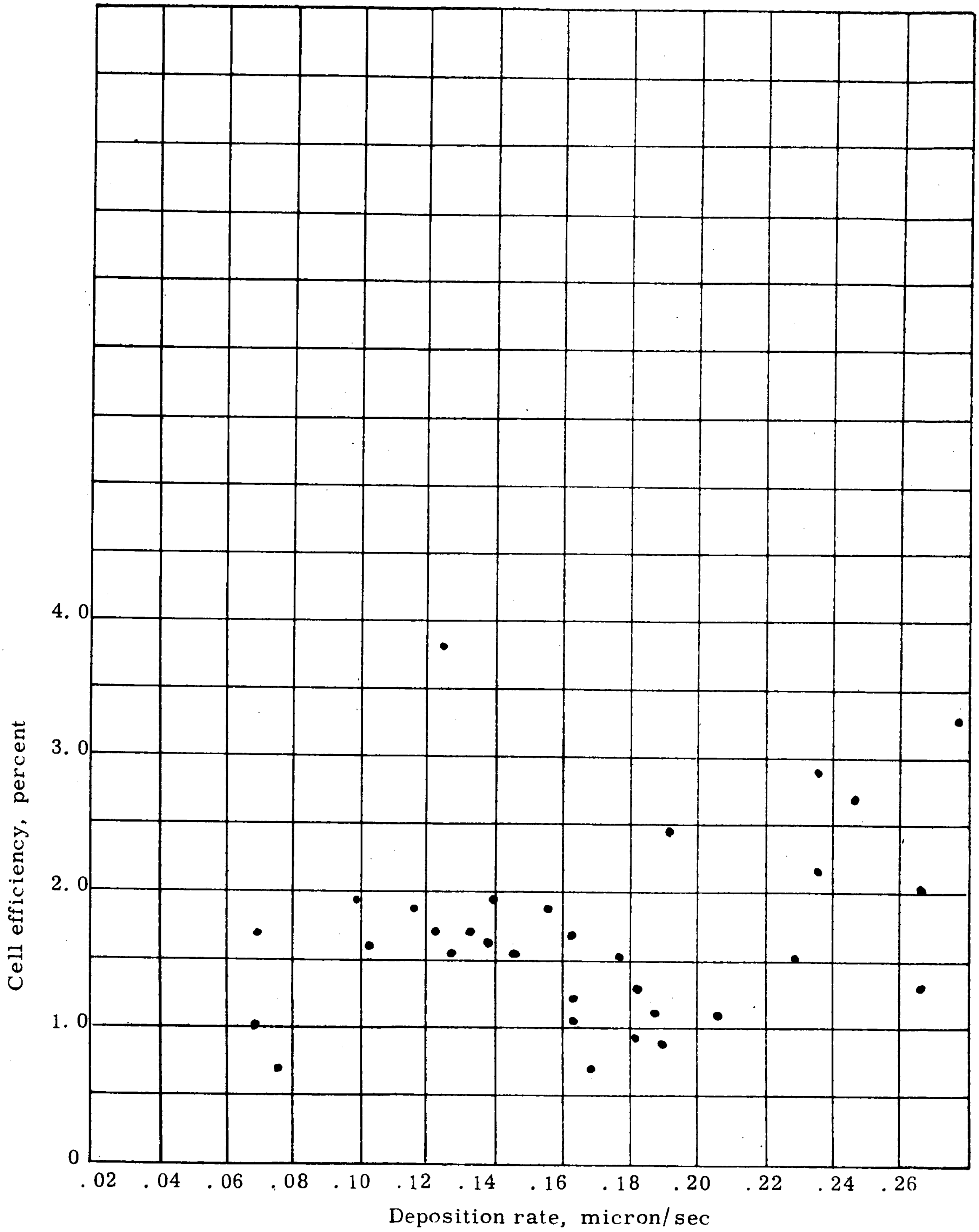


FIG. 3 EFFECT OF DEPOSITION RATE ON CELL EFFICIENCY

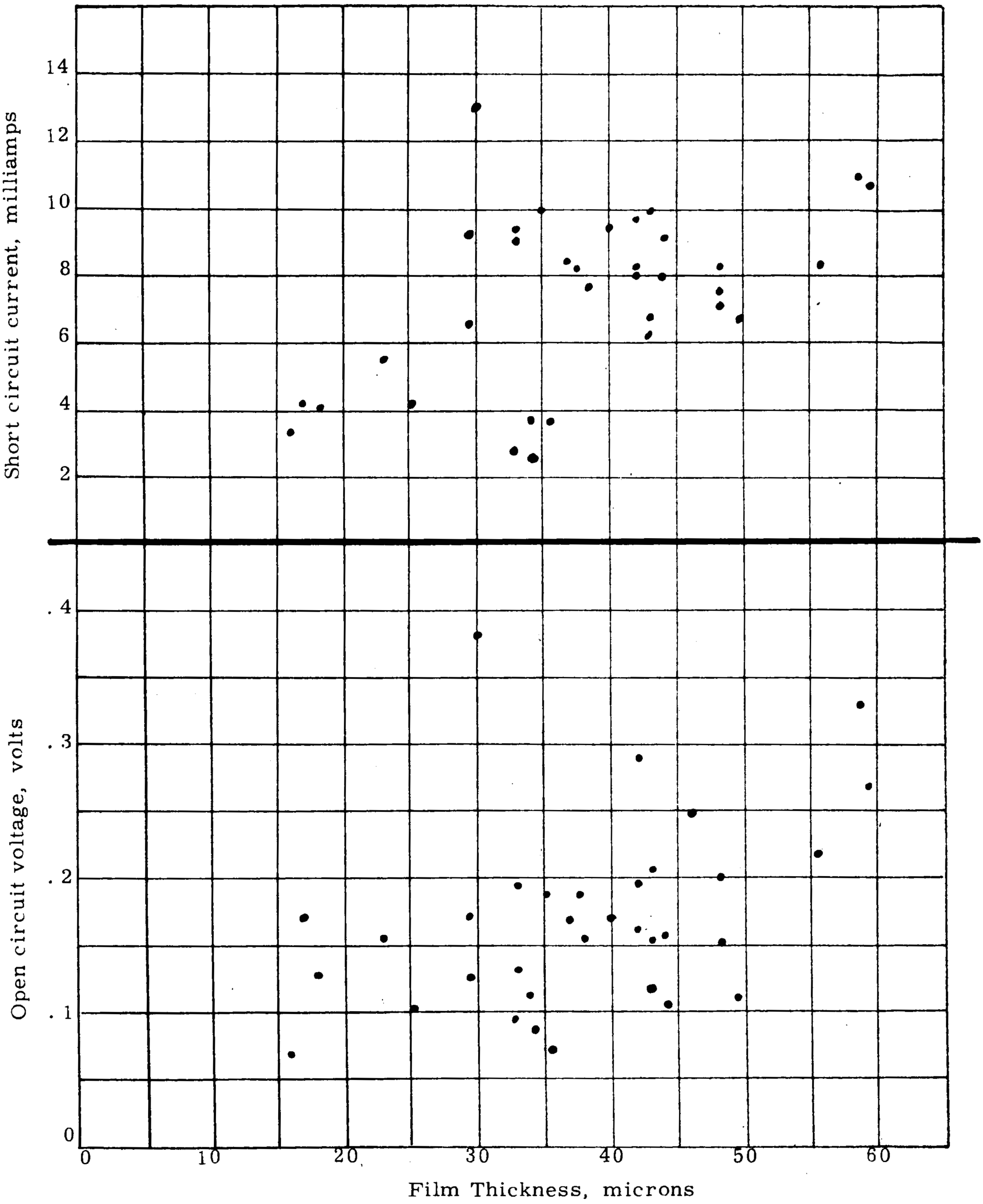


FIG. 4 EFFECT OF FILM THICKNESS ON OCV AND SCC

methods were tried with the same metal. Successfully electroplated contacts were obtained with Ni, Rh, and Pt. Electroplated rhodium was quickly discarded because of its strongly acid plating bath. Any pinhole in the film was quickly attacked with subsequent lifting of the film around the hole. Rhodium would quickly plate out on both sides of the film. A similar result was observed at the edge of the film where lifting would occur rather often. Nickel, plated from a Watts type bath worked very well. Platinum also gave good electrodes.

The resistance between two nickel stripes electroplated on a CdS film was compared with the resistance measured between two mercury-indium amalgam stripes of similar geometry. There was no significant difference between the two. An i-V plot obtained from one of the nickel stripes (compared with an amalgam stripe for reference) was a straight line through the origin even for quite high current densities of several amperes per square centimeter. Although nickel may be easily and quickly plated, it is considered undesirable to wet the CdS film with the plating solution.

Vacuum evaporated electrodes were considered next. Stripes of Ni, Al, Ag, Au, Cu, Mn, Mg, Cr, Sn, Pb, Fe, and Pt, were evaporated on CdS. In order to compare these various electrodes, a mercury-indium alloy stripe was placed on the CdS a short distance away from each. The i-V curve tracer using the 4-probe method was used to plot an i-V characteristic for current flowing into one contact, through the CdS film and out the other contact. Both voltage polarities were used. Whenever a straight line through the origin was obtained, the resistance of the contact-CdS combination was obtained from the slope of the i-V characteristic. This measurement was made for each electrode except platinum which was excluded simply because it was too difficult to evaporate a sufficiently thick layer.

The measurements were repeated after the film, with electrodes, had been heated on a 300°C hot plate in air. The data are summarized in Table I.

TABLE I. Resistance Between Evaporated Metal Electrodes and In-Hg Amalgam Electrode
(Resistance in ohms)

Heating Time Minutes	Al	Ag	Au	Cu	Mn	Mg	Cr	Ni	Sn	Pb	Fe
0	Non-ohmic	0. 05	0. 21	0. 32	0. 11	0. 03	0. 21	0. 06	Non-ohmic	0. 03	0. 01
4	Non-ohmic	0. 36	0. 20	Non-ohmic					0. 002	0. 03	0. 01
10	Non-ohmic	0. 45	0. 17	Non-ohmic	0. 03	0. 20	0. 26	0. 20	0. 004	0. 01	
20	Non-ohmic	0. 11	0. 16	Non-ohmic							

These resistances are remarkably low. There is doubt about the validity of the last silver measurement because the silver stripe had been noticeably reduced in thickness and area and had turned quite black. For this same reason, manganese, magnesium, tin, lead and iron were eliminated. These metals are too easily oxidized and possibly sulfodized to be considered for reliable contacts. Thus, only gold, chromium, and nickel, are left after eliminating the non-ohmic contacts aluminum and copper. The principal objection to chromium and nickel is the difficulty of soldering to these metals. Gold on the other hand is inert, easily solderable and easy to evaporate. Therefore, several additional gold stripes were vacuum evaporated onto various CdS films and a careful examination of the Au-CdS contact was undertaken. Figure 5 shows the voltage current relationship for CdS film 147-2 between evaporated gold electrodes. These curves were obtained immediately after the gold evaporation. The gold electrodes are stripes one-inch long and 1/8-inch wide. The stripes were 11/16-inch apart. In Fig. 5, curve 1 shows the linearity for a maximum current of 0. 93 mA at 4 mV corresponding to a resistance of 4. 3 ohm. The maximum current density was 1. 15 mA-cm^{-2}, the area of the gold electrodes was 0. 806 cm^{2}. Curve 2 shows the linearity for a maximum current of 112 mA at 400 mV, corresponding to a resistance of 3. 58 ohms. The maximum current density in this case was 139 mA-cm^{-2}. The fact that the slopes of the curves are different show that gold electrodes are not truly ohmic. On the other hand, the fact that the slope changed only about 20 percent while the current density increased by a factor of more than 100 shows the departure from Ohm's law is quite small. It should be pointed out here that the resistivity of the cadmium sulfide film was 0. 026 ohm-cm before heating.

After these measurements, the film was heated for one hour at 250°C in the oven used for processing photovoltaic cells. The measurements described above were repeated and the data are shown in Fig. 6. The heating decreased the resistance measured between the gold stripes. The slope of curve 1, Fig. 6 shows a resistance of 3. 26 ohms

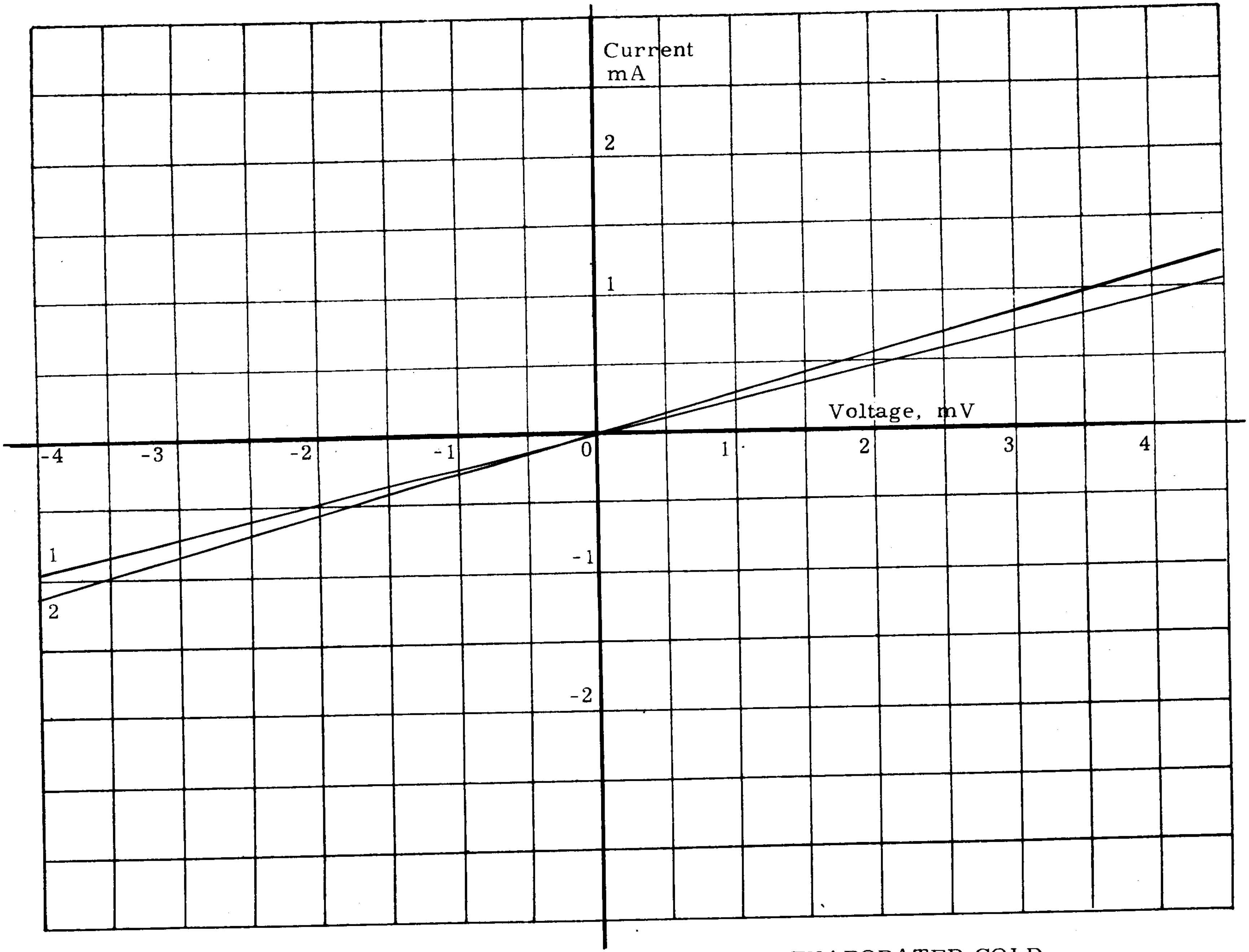


FIG. 5 I-V CURVE OF CdS FILM BETWEEN EVAPORATED GOLD ELECTRODES, BEFORE HEATING (Film 147-2)
(Curve 2, Multiply scales by 100)

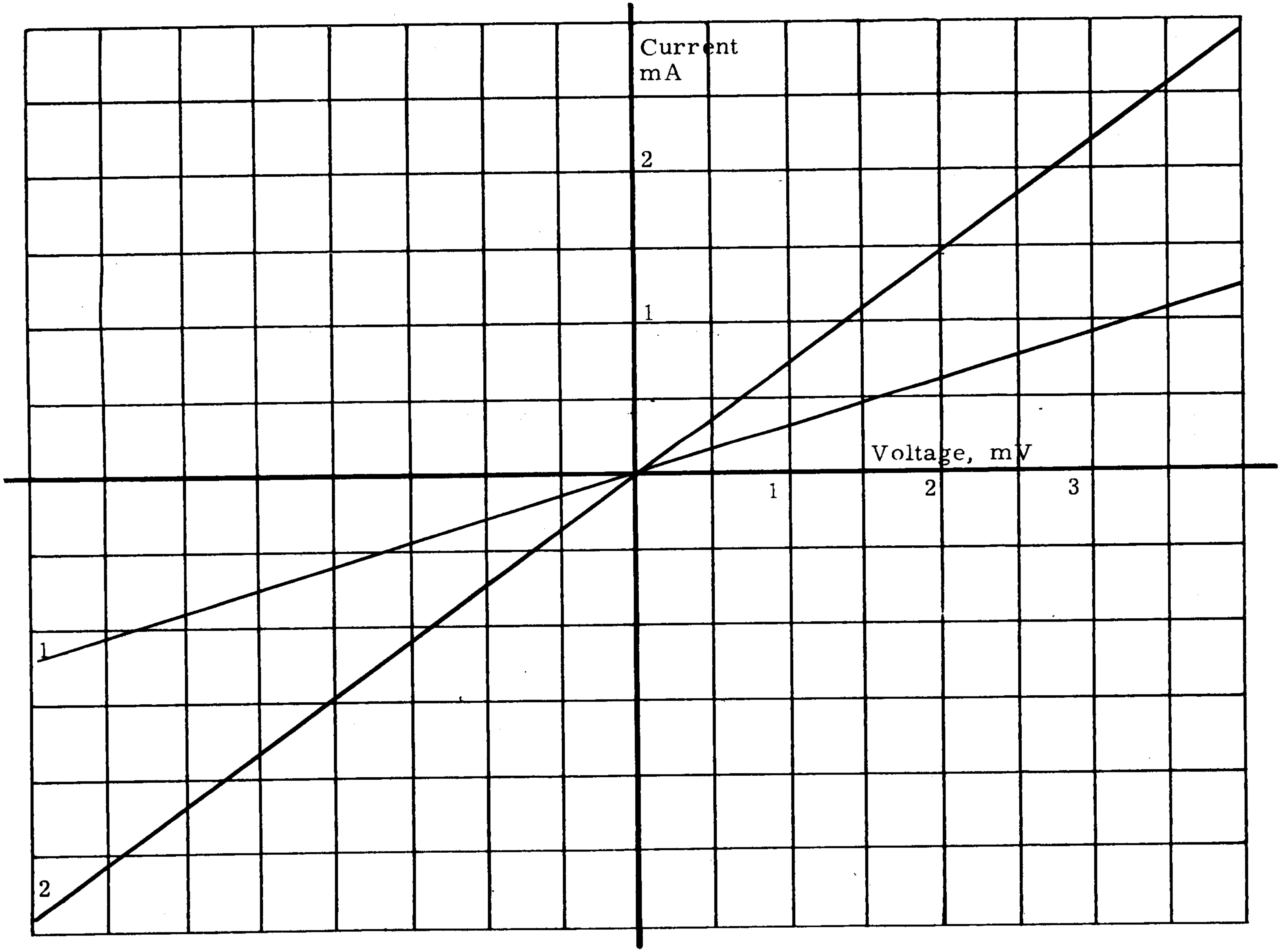


FIG. 6 I-V CURVE OF CdS FILM BETWEEN EVAPORATED GOLD ELECTRODES, AFTER HEATING
(multiply vertical scale by 100 and horizontal scale by 200 for curve 2)

for CdS 147-2 at 1.23 mA and 4 mV, and the slope of curve 2 shows a resistance of 2.76 ohms at 145 mA and 400 mV. The current densities are 1.53 mA-cm^{-2} and 180 mA-cm^{-2}, respectively.

Two indium-mercury amalgam stripes were painted on the films and the measurements repeated for current flowing between the two amalgam stripes, and between one gold and one amalgam stripe. Finally, an overlay of air dried silver paint was placed on each gold stripe and all the measurements repeated. Always, a straight line through the origin was obtained, and invariably, a small change in resistance accompanied a large change in current density. The data are summarized in Table II. It is apparent that the resistance decreases when the current density increases and upon heating the films. The air drying silver paint applied to reduce the resistance of the gold film reduced the measured resistance and resistivity by more than half for CdS 147-2. The two gold stripes were 11/16-inch apart; the amalgam stripes were 5/16-inch apart. The resistivity, determined via the amalgam stripes was 4.1 x 10^{-3} ohm-cm. Therefore, the resistance of an 11/16-inch length of the CdS film should be 0.64 ohm. The resistance of this length of the film, measured via the gold electrodes was 1.27 ohms. Thus one may conclude that evaporated gold electrodes backed with silver paint, have about twice the contact resistance of amalgam electrodes. This does not mean, of course, that gold is the best electrode that one may put on n-type CdS; but merely that it is the most convenient electrode material of those investigated.

Three CdS arrays on H-Film were processed in experiments to evaluate further the n-electrode material and electrode configuration for arrays. Electroplated nickel is used almost exclusively for glass backed cells. It is more convenient to evaporate the n-electrode on H-Film cells. Nickel is difficult to evaporate, while evaporating gold is quite easy. The three arrays on H-Film were to compare evaporated nickel vs evaporated gold as electrode material. From the data of Table III there appears to be no significant advantage of one metal over the other.

TABLE II. Resistance Between Evaporated Gold Electrodes and In-Hg Amalgam Electrodes
(Area of Electrodes was 0.806 cm^2)

	Current Density at Gold Electrode	Resistance Between Gold Electrodes	Current Density At Amalgam Electrode	Resistance Between Amalgam Electrodes	Resistivity of CdS Film Between Gold Electrodes	Resisitivity of CdS Film Between Amalgam Electrodes
CdS 147-2						
Before Heating	1.15 mA-cm^{-2}	4.3 ohm				
	139 mA-cm^{-2}	3.6 ohm				
After Heating	1.53 mA-cm^{-2}	3.3 ohm	2.7 mA-cm^{-2}	0.93 ohm		
	180 mA-cm^{-2}	2.8 ohm	1.1 A-cm^{-2}	0.29 ohm	17.3 x 10^{-3} ohm-cm	4.1 x 10^{-3} ohm-cm
After Applying Silver Paint	0.8 A-cm^{-2}	1.2 ohm	1.1 A-cm^{-2}	0.29 ohm	8 x 10^{-3} ohm-cm	4.1 x 10^{-3} ohm-cm

TABLE III. CdS Cells on H-Film with Evaporated Gold and Nickel Collector Electrodes

Electrode	Cell No.	V_{oc}, volts	i_{sc}, mA	Area, cm^2	Fill Factor	Efficiency %
Evap. Au						
	178Ha	.38	26.2	3.0	.48	1.7
	178Hb	.38	27.2	3.1	.57	1.9
	178Hc	.38	26.4	2.9	.42	1.5
	178Hd	.37	21.5	2.6	.56	1.7
	178He	.37	24.2	2.3	.48	1.9
	178Hf	.37	24.2	2.3	.48	1.9
	178Hg	.37	27.4	2.6	.50	2.0
	178Hh	.36	26.8	2.6	.50	1.9
	178Hi	.35	22.3	2.6	.47	1.4
	Average					1.8 ± 0.2
Evap. Au						
	180Ha	.42	23.7	2.6	.50	1.9
	180Hb	.39	28.6	2.6	.42	1.8
	180Hc	.38	23.0	2.6	.45	1.6
	180Hd	.40	29.6	2.6	.47	2.0
	180He	.40	27.8	2.6	.42	1.8
	180Hf	.38	21.4	2.6	.41	1.4
	180Hg	.37	26.6	2.6	.43	1.6
	180Hh	.34	25.6	2.6	.40	1.3
	180Hi	.37	17.7	2.6	.40	1.0
	Average					1.6 ± 0.2
Evap. Ni						
	183Ha	.43	20.8	2.6	.54	1.9
	183Hb	.43	17.4	2.6	.53	1.6
	183Hc	.44	14.0	2.6	.55	1.3
	183Hd	.42	16.2	2.6	.52	1.4
	183He	.41	21.4	2.6	.48	1.6
	183Hf	.42	17.0	2.6	.54	1.5
	183Hg	.41	18.0	2.6	.61	1.7
	183Hh	.41	16.8	2.6	.42	1.0
	183Hi	.42	16.7	2.6	.54	1.5
	Average					1.5 ± 0.2

In array 178H, the two cells, 178H-c and 178H-i showed very high series resistance in the forward direction. This is not uncommon with evaporated gold electrodes, and is usually denoted by a sharp break in the forward characteristic as the curve crosses the horizontal (voltage) axis. The slope of the curve in the first quadrant may change by an order of magnitude from that in the fourth quadrant. The sharp break in the characteristic usually disappears if the contact is heated, but the overall resistance of the cell remains high.

The sharp break is not as noticeable in array 180H and is not present at all in array 183H, the latter having evaporated nickel electrodes.

Attempts were made to use an evaporated metal grid on the H-Film, beneath the CdS layer, as a current collector from the n-type CdS. Gold had been found to adhere reasonably well to H-Film, so gold grids were vacuum evaporated onto the H-Film and built up in thickness by electroplating nickel onto the gold. The grid consisted of 1/16" wide stripes located on 1/2" centers, stretching across the H-Film from one edge to the opposite edge and interconnected with a single 1/8 " wide central transverse stripe. In the first attempt, the grid was partially removed during cleaning prior to the CdS evaporation. A second attempt was made with extreme care to keep the grid and H-Film clean so that only a distilled water rinse was required prior to evaporation. In this case the evaporated CdS layer pulled the grid free of the H-Film. Similar attempts on glass substrates caused some difficulty with shorts between the barrier layer and grid through pinholes in the CdS layer. However, these difficulties were subsequently overcome and the above described collector grid beneath the CdS layer was successfully used on the large area (4" x 4") cells.

3.2 Barrier Process

3.2.1 Slurry Process

A water suspension of chemically precipitated cuprous oxide is used to form the photovoltaic barriers on the indium doped cadmium sulfide films. The slurry is applied with a soft bristle brush to the CdS film which has been pre-heated to 90-100°C. The slurry is applied liberally to completely cover the exposed area of CdS film, and after drying in place is removed by washing in a stream of distilled water and gently brushing with a soft brush or acetate tissue.

Barrier formation is completed by heating in an oven at 250°C for times of about 2 to 3 minutes. Contact to the barrier is made with a conductive silver paint.

3.2.2 Analysis of Slurry Samples

X-ray identification of copper slurry samples S-9 and S-21 indicates the copper compound to be cuprous oxide, Cu_2O. There was no evidence of any other copper compound. The x-ray patterns were diffused, probably due to lattice disorder and possibly due to particle size.

A qualitative, spectrographic, analysis of slurry samples S-18, S-21 and S-22 showed the following common components: copper, nickel, aluminum, magnesium and silicon. Samples S-21 and S-22 also showed iron. Rough estimates of quantities present indicate copper as the principal component for all samples. S-21 and S-22 contained nickel and silicon in the range 0.01-0.03 weight percent. All other constituents present were less than 0.03 weight percent. All the above elements except aluminum are reported as impurities in the lot analyses of the analytical reagents used in making the copper slurry.

Electron micrographs were taken of the copper slurries. Slurry S-18, used extensively in making cells, had particle sizes in the range of 0.3 to 1.2 micron. The other slurry samples showed approximately the same range in particle size.

3.3 Lamination

A process has been developed for laminating an H Film substrate cell or array of cells to a film of Mylar plastic using a nylon adhesive layer. The lamination is carried out at a temperature of 210-220°C for 4 minutes using a static pressure of approximately 100 psi.

The total package is approximately 0.006" in thickness comprising the following layers, in order:

0.0015"	H-Film (lapped from 0.002")
0.002"	CdS + barrier layer
0.001"	Silver paint (on barrier)
0.0005"	Capran 77c
0.001"	Mylar

This package appears to get around the difficulty which was first experienced with CdS-H-Film composites curling severely. When 0.002" Mylar was used, a reverse curl was experienced.

3.4 Curling Problem

Initially, when CdS was evaporated onto thin H-Film substrates, severe curling of the composite was experienced when the film cooled to room temperature. This appeared to be due to the difference in thermal expansion between the CdS and H-Film plastic. A number of possible methods of counteracting or minimizing the curling were investigated. Several methods such as pre-stressing the H-Film prior to CdS evaporation, and embossing the H-Film to provide greater stiffness to the package were partially successful but were not really satisfactory solutions to the problem.

To eliminate curling it was suggested that the CdS be evaporated on both sides of the H-Film so that the stresses on one side of the H-Film would be counterbalanced by the stresses on the other side. However, this method would be an extremely wasteful process and would add to the weight and thickness of the cell without contributing to cell performance.

A satisfactory solution was developed. This consisted of lapping one surface of the H-Film plastic with 1000 grit abrasive prior to deposition of the CdS onto that surface (which also helped CdS adhesion), and then laminating the finished cell to a single sheet of plastic. Thus, the CdS has an intimately bonded plastic film on both sides so that the stresses from differential expansion are in opposition to each other. By adjustment of the relative thickness and type of plastic used for the two films, the substrate temperature during CdS evaporation, and the temperature of the final lamination, the curling can be varied from concave to flat to convex.

With the present construction and processing conditions as outlined in this report, the curling has been reduced to a negligible level.

4.0 CELL STABILITY

Other workers have studied the degradation of CdS thin film solar cells and have found various degrees of degradation and have ascribed different reasons for it. An attractive hypothesis is that cell deterioration is caused by water vapor attacking the barrier layer, and indeed, in at least one instance,[1] protective, vapor proof encapsulation of CdS thin film solar cells has been effective in eliminating deterioration. On the other hand, Chamberlin[2] reports that no deterioration was observed in six months on unprotected cells. The situation is not so simple in the case of backwall cells fabricated in this laboratory. It has been repeatedly observed that most, but not all, cells left exposed to the laboratory ambient will rapidly decrease in efficiency by as much as 50 percent. To determine whether this was all due to water vapor in the barrier layer, a few cells were placed in a vacuum desiccator immediately after fabrication and obtaining an initial current-voltage characteristic. It was expected that the efficiency of such a cell might at first decrease but that after a few days would recover its initial value. Figure 7 shows that this does not happen. Instead, after an initial rapid decrease lasting 4 or 5 days, the rate of decrease is still significant, albeit a great deal smaller than the initial rate. This is exemplified by the curves for cells 110-8 and 116-2. In order to observe this more carefully, two cells, 111-1 and 111-2, were chosen for the following experiment. The cells were identically and simultaneously

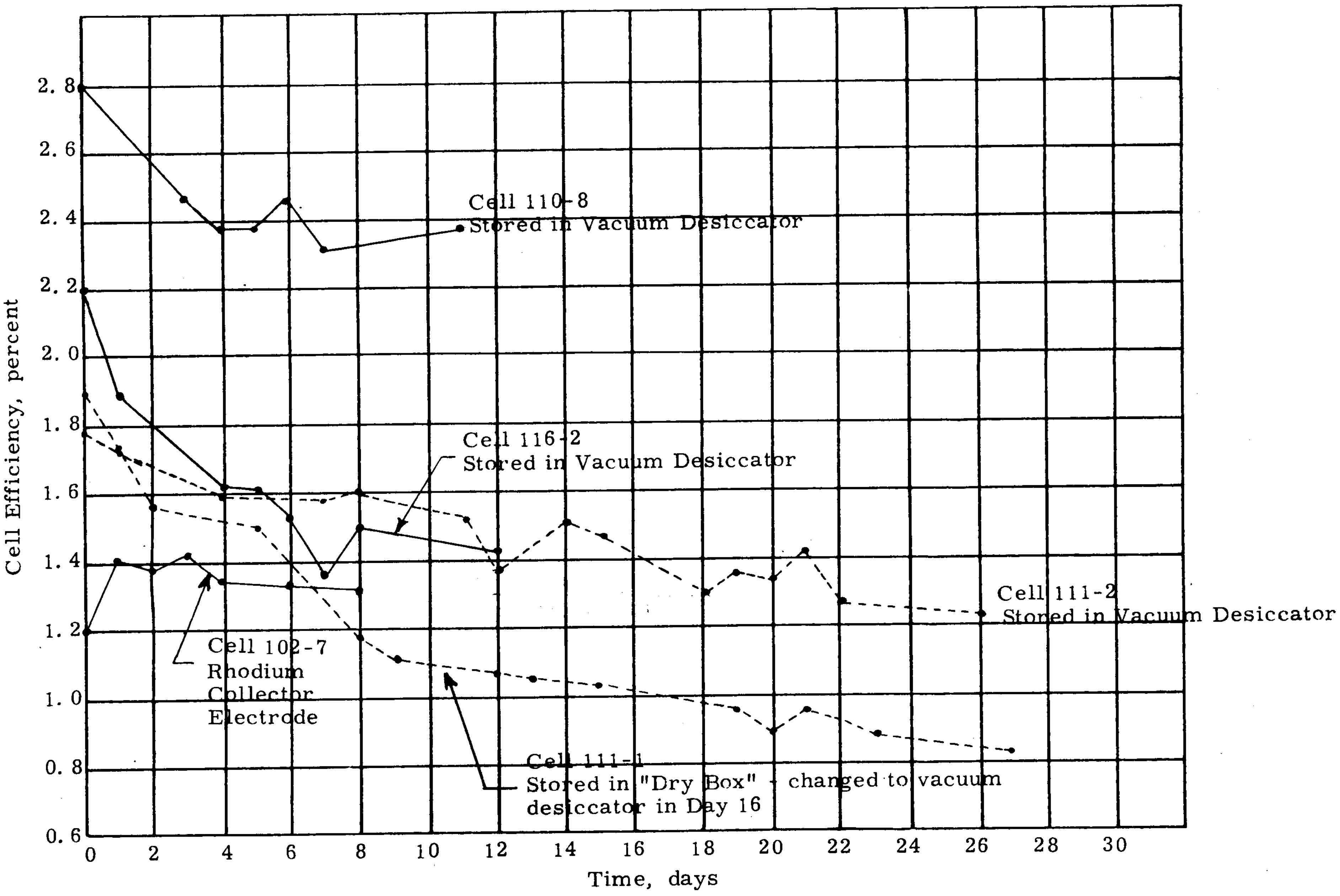


FIG. 7 DETERIORATION OF CdS FILM CELLS

fabricated from films evaporated side by side on a glass substrate. One cell, 111-1, was placed in a "dry" box, the other in a vacuum desiccator. Cell 111-1 deteriorated at more than three times the rate of cell 111-2 for about 10 days (See Fig. 7). Then, cell 111-1 decreased its rate of deterioration while that of 111-2 remained nearly constant. The data are insufficient for accurate comparisons, but it does seem as though the deterioration rate of cell 111-1 between 10 and 16 days is very nearly the same as that for cell 111-2. On the 16th day, cell 111-1 was placed in the vacuum desiccator with cell 111-2. This did not appear to have any effect on the deterioration rate of cell 111-1, for after 27 days, the slope of 111-1 curve does not differ greatly from that of 111-2. It must be emphasized that the data are insufficient for drawing any firm conclusions, but it appears that a dry atmosphere, while retarding the initial rate of deterioration, does not materially affect the long term rate of deterioration.

One might tentatively conclude that water vapor does cause an initial rapid deterioration of a film cell, which is not reversed by putting the cell into a completely dry atmosphere. One may also conclude that one or more other agencies are responsible, at least in part, for the continued deterioration observed in the completely dry atmosphere. Several possibilities come to mind. Among the most likely are donor migration into the barrier layer and impurities introduced with the slurry and not completely removed. To examine the donor migration possibility, a CdS film cell was fabricated without the usual soldered indium peripheral contact to the n-type layer. Instead, a peripheral contact of electroplated rhodium was formed and reinforced with conducting silver paint. Great care was taken while processing this cell to eliminate every possibility of indium contamination other than that deliberately introduced as a dopant during evaporation. The variation in efficiency with time for this cell (cell 102-7) is also shown in Fig. 7. An initial increase in efficiency is observed followed by a much more gradual deterioration of this cell than is observed for the indium electroded cells. This, then, suggests that the "impurities in the barrier layer" agency might also be at work.

It should be mentioned that the first deterioration measurements were made on cell 88-5 and continued for some 70 days. This cell was fabricated November 7, 1963 and had an initial efficiency of 2.2 percent. After 30 days it stabilized at about 1.5 percent. Its curve was not included in Fig. 7 because pressure contacts only could be applied to this cell and contact resistance caused a very wide scatter of experimental points. The cells described above all have terminal leads of silvered copper braid soldered to the peripheral electrode and cemented with conducting silver paint to the silver paint electrode covering the barrier layer. This effectively eliminates contact resistance. It should also be pointed out that the cells described by Fig. 7 (except for cell 111-1) would, most likely, all have deteriorated to less than 1 percent efficiency within a few days had they been left exposed to the ambient atmosphere.

There are other possible causes of deterioration, some of the more likely being: 1) an increase in series resistance, including contact and bulk resistance of the collector electrode; 2) leakage between electrodes due to moisture or similar causes; 3) changes in barrier properties due to temperature extremes or cycling; 4) imperfectly formed barriers containing areas of low resistance, or cracks or crazing leading to low resistance paths; and 5) diffusion of impurities along grain boundaries or precipitation of metallic phases along grain boundaries.

5.0 CELL AND ARRAY CONSTRUCTION AND PERFORMANCE

Seven cadmium sulfide solar cells of the backwall construction were delivered October 1, 1964 to the contracting monitor of the National Aeronautics and Space Administration, Lewis Research Center. Three of the cells were constructed on flexible H-Film substrates and four were constructed on pyrex glass substrates.

5.1 H-Film Cell Arrays

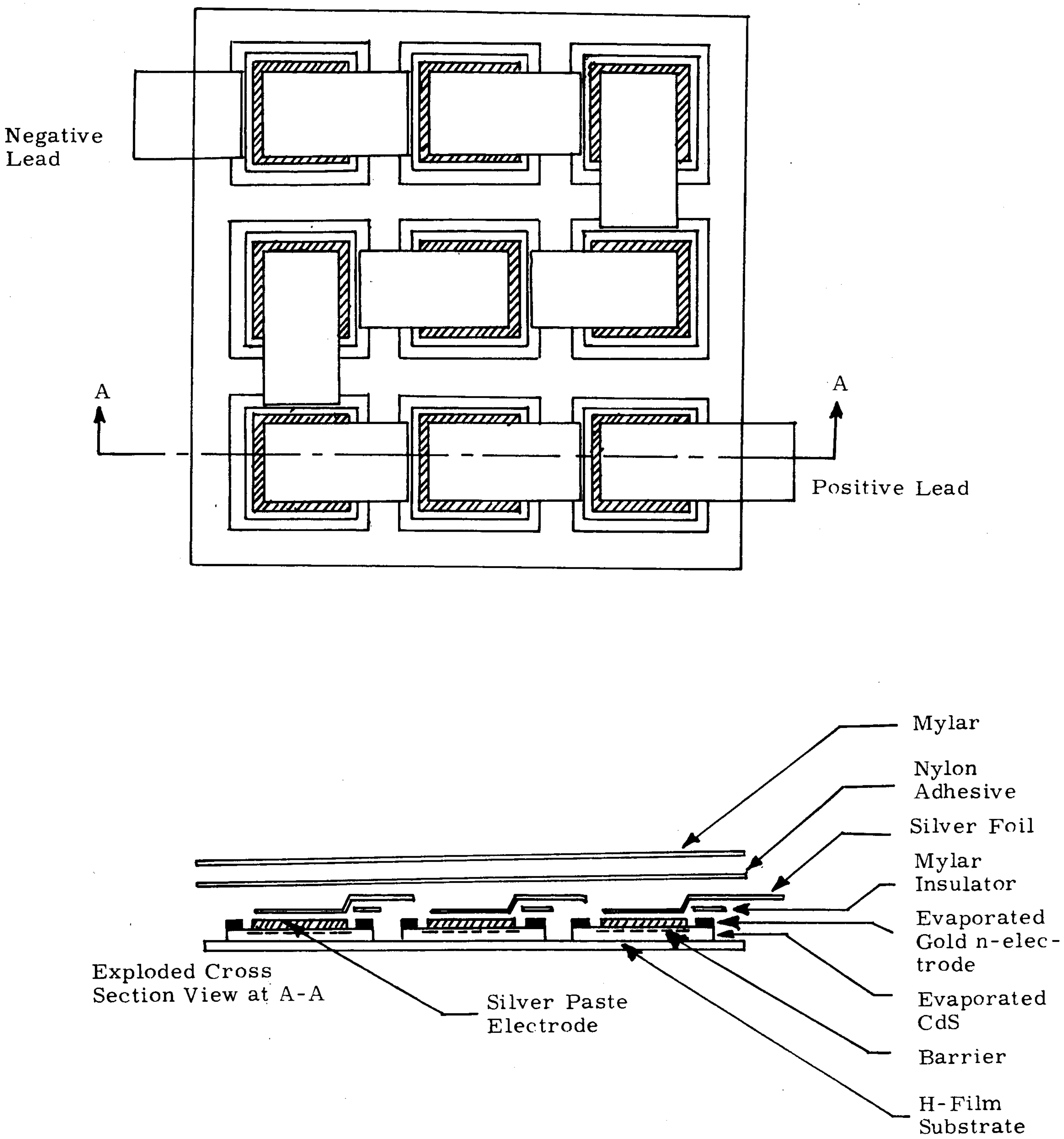
A typical H-Film array consists of nine individual cells in a 3 x 3 array on a 4" x 4" H-Film substrate. These cells are connected in series by a lamination process and constitute a battery. In these prototype batteries no attempt was made to optimize area utilization.

The individual CdS film areas were made by depositing cadmium sulfide through a mask to a thickness of 1. 6-1. 8 mils while the H-Film substrate is held at a temperature of 200°C. A peripheral gold n-electrode is applied to the films by vacuum evaporation. The positive electrode is Waldman's (Joseph Waldman & Sons, 133 Coit Street, Irvington 11, New Jersey) #303 air dry silver paste applied with a brush to the barrier. The barrier is formed by the copper slurry method. The individual cells are connected in series to make a solar battery. Each cell is electrically interconnected with gold plated silver foil. The gold-silver foil connector is insulated with Mylar plastic to bridge over the n-electrode when laminated. The laminated package consists of the following components in order: H-Film substrate, evaporated indium doped cadmium sulfide film, barrier, n- and p-electrodes, a layer of nylon plastic (Capran) and layer of Mylar. The basic construction of the cell array is graphically illustrated in Fig. 8.

The conversion efficiency measurements and other properties of the three solar batteries submitted are given in Table IV.

5. 2 Glass Backed Cells

Glass backed cell components consist of a 1/16th inch pyrex glass plate substrate, evaporated cadmium sulfide film, silver paste electrode on the barrier and an electroplated nickel n-electrode. The nickel n-electrode is electrochemically deposited onto the conductive cadmium sulfide film through a mask of predetermined geometry. The geometry of negative electrodes for a 4" x 4" glass cell is shown in Fig. 9 Two cells of this construction, Number 201 and 202, were submitted. A third cell, Number 176_L, was submitted with a glass covering laminated on the barrier side for the purpose of affording protection against ambients. The fourth cell is similar basically to the first two except smaller in size (1" x 2") and has an electroplated perimeter nickel n-electrode.



(Cells are illuminated from below)

FIG. 8 CONSTRUCTION OF FLEXIBLE H-FILM SUBSTRATE BACKWALL CELL ARRAYS

TABLE IV. Test Data of Backwall Cells Delivered to Contract Monitor

No.	OCV v	SCC ma	V_{mp} v	I_{mp} ma	P_m mw	Area cm^2	Ill. mw/cm^2	Eff. %	Remarks
$234H_L$	3. 2	31. 8	1. 97	20. 1	39. 6	26. 1	100	1. 51	3 x 3 array
$243H_L$	3. 0	31. 6	1. 86	20. 8	38. 7	25. 1	100	1. 54	3 x 3 array
$281H_L$	3. 1	39. 2	1. 87	25. 5	47. 7	24. 4	100	1. 95	3 x 3 array
176_L	. 39	730	. 23	470	109	75. 9	100	1. 43	4 x 4 glass
202	. 39	948	. 25	608	150, 8	75. 2	100	2. 0	4 x 4 glass
201	. 396	1050	. 27	738	200	73. 3	100	2. 73	4 x 4 glass
277-4	. 41	148	. 28	115	32. 2	7. 9	100	4. 1	1 x 2 glass

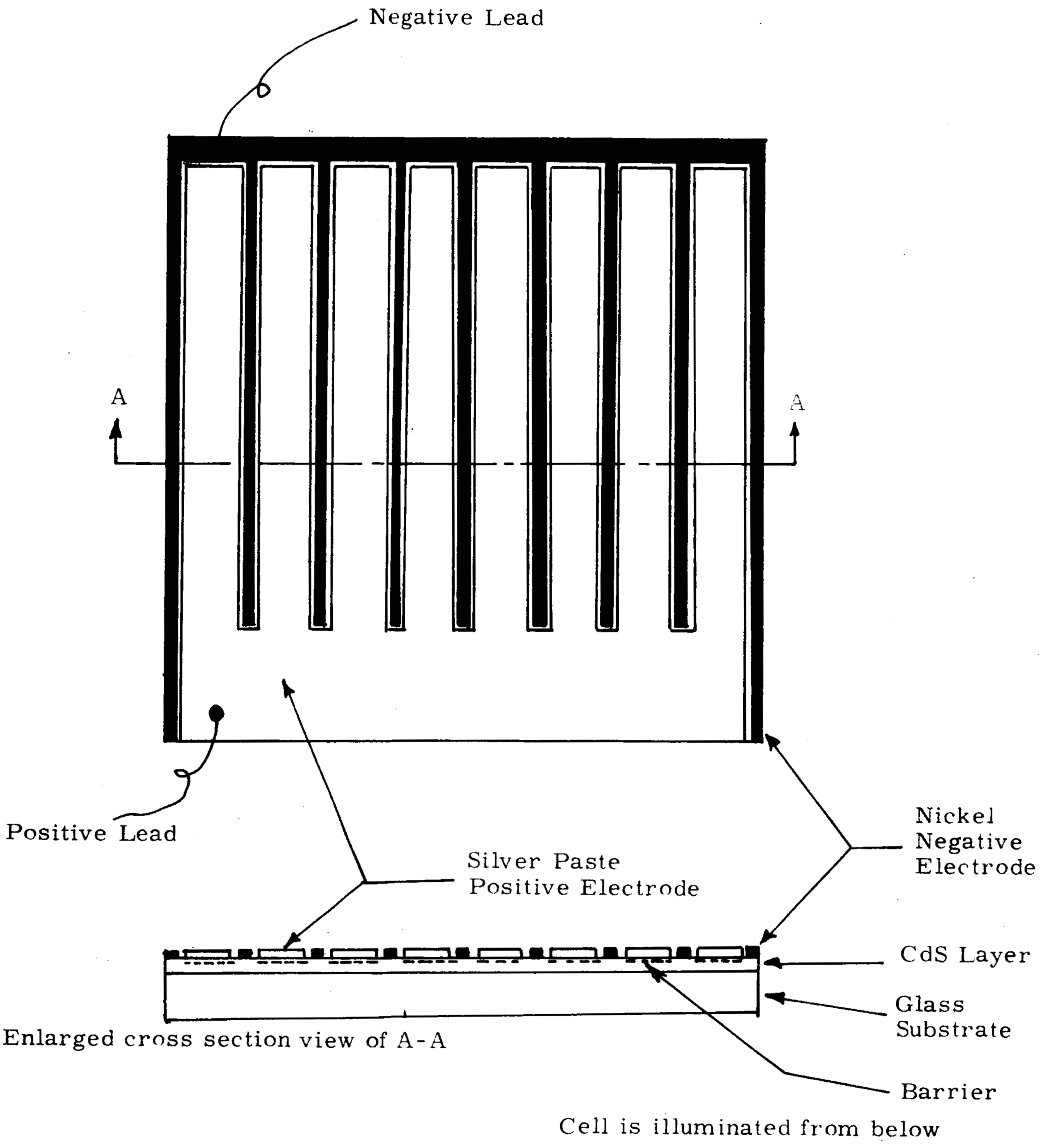


FIG. 9 CONSTRUCTION OF GLASS SUBSTRATE LARGE AREA BACKWALL CELL

5.3 Conversion Efficiency Measurement

The light source for measuring the light conversion efficiency of the cells is four General Electric Photo DXC lamps operated at recommended voltage, having a color temperature at 3400°K. The light from the lamps is filtered through 1 inch of water. The light intensity is set with a silicon solar cell at a value found to be equivalent to 100 milliwatts per square centimeter terrestial sunlight. The light intensity is fixed by adjusting the distance of the lamps from the standard silicon cell.

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NASA CONTRACTOR REPORT

STUDY OF THIN FILM LARGE AREA PHOTOVOLTAIC SOLAR ENERGY CONVERTER

Clevite Corporation

ABSTRACT

Techniques have been developed for vacuum evaporating adherent films of CdS of approximately 0.002" thickness onto specially prepared "H-Film" polyimide plastic foil substrates and for processing these into backwall thin film solar cells. Cell areas have been as large as 4" x 4", but most work has been with arrays of nine 1" x 1" cells connected in series. Highest efficiencies of these plastic foil substrate cells and arrays have been just under 2%. Similar design cells on rigid non-conducting glass substrates have yielded efficiencies greater than 4%. Thus, it is expected that backwall plastic substrate cells can be made at the 4% efficiency level or greater.

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