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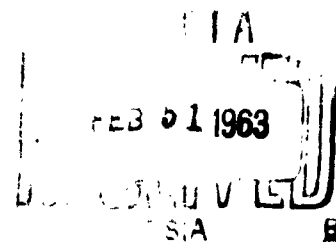
**RESEARCH ON SOLAR-ENERGY CONVERSION
EMPLOYING CADMIUM SULFIDE**

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-69 VOLUME II

December 1962

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

Project No. 8173, Task No. 817301



(Prepared under Contract AF 33(616)-7528 by
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F. A. Shirland, G. A. Wolff, J. C. Schaefer,
G. H. Dierssen, authors)

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FOREWORD

This report was prepared by The Harshaw Chemical Company, Solid State Research Laboratories, as a summary report covering the Research and Development from January through August 1962 on Contract AF33(616)-7528, Project No. 8173. Task No. 817301. The project was funded by the Flight Accessories Laboratory, Aeronautical Systems Division, and initiated and monitored by the Aeronautical Research Laboratory. Mr. Donald C. Reynolds acted as Contract Monitor with Mr. Joseph Wise representing the Aeronautical Systems Division.

The following scientific personnel have contributed to the project during the period of this report: F.A. Shirland, G.A. Wolff, J.C. Schaefer, G.H. Dierssen, R.F. Belt, J.D. Broder, T.A. Griffin Jr., N.E. Heyerdahl, J.R. Hietanen, E.R. Hill, F.N. Lancia, H.E. Nastelin, J.D. Nixon, R.W. Olmsted and D.J. Harvey. Project Direction has been provided by F.A. Shirland. The basic supporting research has been directed by G.A. Wolff. The development work has been directed by F.A. Shirland with J.C. Schaefer supervising the film evaporation, cell fabrication and cell testing phases, and G.H. Dierssen supervising the materials preparation, crystal growth, array fabrication and testing phases. Dr. Richard W. Hoffman of Case Institute of Technology was consulted on problems concerning vacuum evaporation. Radiation damage testing was performed by Mr. Richard Statler of U. S. Naval Research Laboratory.

Volume I of this report was issued January 1962 but was not identified as Volume I. This report is Volume II and is the final report on the contract.

ABSTRACT

Development of a thin film solar cell using vacuum evaporated layers of CdS was continued. Primary emphasis was on the front wall CdS film cell using molybdenum foil substrates. Efficiencies of large area (up to 9 in²) front wall cells have been increased to the range of 2 to 3%. The major factor in this increase was the reduction of sheet resistance by the use of a fine mesh metallic grid laminated to the barrier surface.

Improved vacuum evaporation techniques have made possible a reduction in CdS film thickness and in molybdenum foil substrate thickness - each to about 0.001". With these improvements, power to weight ratios for CdS thin film front wall solar cell arrays, that may be suitable for space applications, of 20 to 30 watts per pound seem assured.

Some tests of CdS front wall film cells and arrays indicate that they should be stable in the high vacuum of space, and that they may be fairly resistant to radiation of the Van Allen types.

Research studies on the structure of CdS single crystals and polycrystalline films were continued with particular reference to grain growth, orientation and polarity effects, and etching and grain boundary studies. There have been indications of a correlation between crystallite orientation and photovoltaic response.

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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INTRODUCTION

The following report summarizes the Air Force sponsored Research and Development at the Solid State Research Laboratory of the Harshaw Chemical Company on the use of CdS for photovoltaic energy conversion for the period from January through August 1962. Previous reports^(1,2,3) have summarized earlier work on the CdS film and single crystal photovoltaic cells.

In this reporting period the efforts were principally directed towards developing the evaporated CdS front wall film cell into a high power to weight ratio solar energy conversion device suitable for space power applications. Appreciable progress along these lines has been made but much work remains to be done before CdS film cells can augment the present dependable high efficiency silicon single crystal solar cell space auxiliary power sources. Plans for continuation of the research and development of the CdS film cell are being made.

MATERIALS PREPARATION

Sinters and Crystal Growth Runs

With the emphasis of this project on the evaporated film cell, the work with single crystal growth of CdS was greatly curtailed during the period of this report. Only a few single crystal growth runs were made and these were run to supply crystals for the basic supporting research program. The method of growth of these single crystals were essentially the same as reported earlier^(1,2,3) with the exception of minor changes in equipment, layout, etc.

For the purpose of supplying starting material for the vacuum evaporation of CdS films, a commercial luminescent grade of CdS⁽⁴⁾ has been used. This material is sintered in vacuum and in inert atmospheres, as outlined earlier⁽²⁾, and then ground to pass a 20 mesh screen prior to charging in the vacuum evaporation boats. The method of preparation has been generally satisfactory and reasonably economic. Attention has therefore been placed on the purity of the CdS material rather than on the method of preparation.

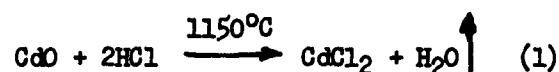
Determination of Oxygen in CdS

It has been found that the CdS powder as received contains about 500 ppm SO_4^{--} , that a standard sinter contained about 50 ppm SO_4^{--} , and that

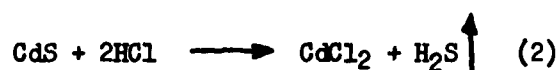
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the SO_4^{--} concentration in grown crystals varies from 0 to 100 ppm. However, sulfur-bound oxygen is only part of the oxygen present. It is to be expected from the physical chemistry of the system that most oxygen at higher temperatures would become bound to Cd as CdO rather than to sulfur as SO_4^{--} , thereby preventing its detection by a SO_4^{--} determination. Therefore a method for the determination of CdO in CdS is also needed. The Harshaw Chemical Company analytical section has developed a method for determining milligram amounts of oxygen as CdO in CdS. While still developmental in character, reproducible results on blanks and actual crystal samples have been obtained. Figure 1 shows the apparatus used for the analysis, and the following is a description of the method.

Anhydrous HCl at a flow rate of 10-15 ml/min. is reacted with the sample after a thorough flushing with dry N_2 . Reaction takes place at 1150°C as per equation(1),



Under these conditions, about 60% to 80% of the sublimed CdS reacts as in equation(2),



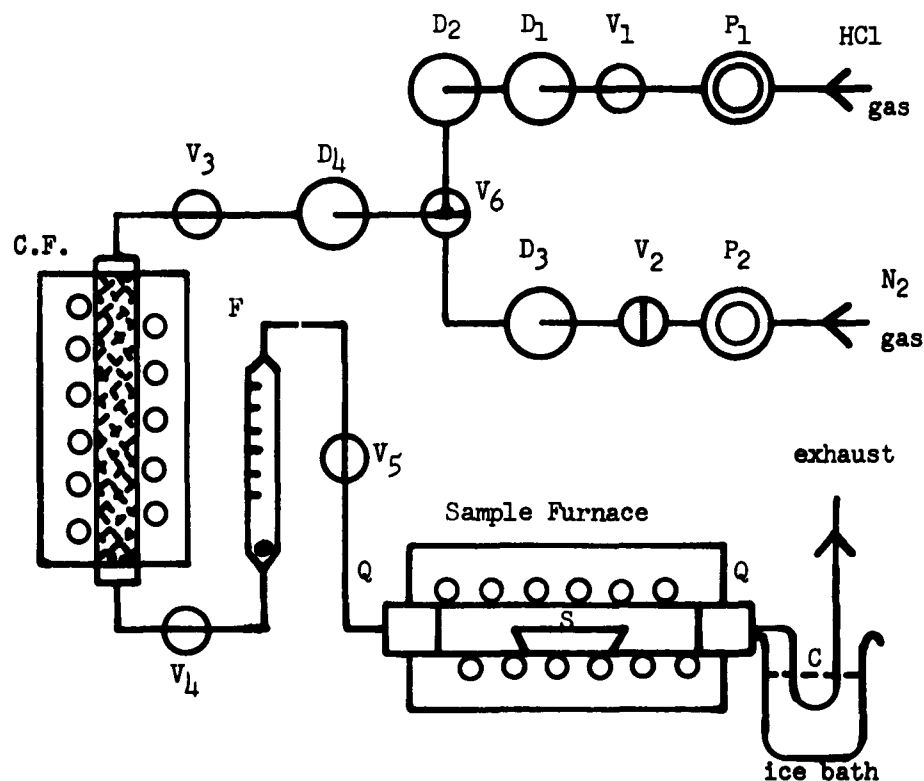
while the remaining CdS condenses in the cooler zones of the furnace along with the CdCl_2 formed.

The water that is formed in equation (1) is condensed in the ice cooled trap and becomes saturated with HCl. After reaction the system is again flushed with nitrogen and the HCl saturated water is washed into a beaker for titration with standard 0.01N NaOH using phenolphthalein as the indicator. One ml. of NaOH is equivalent to 0.9 milligrams of O_2 as CdO.

For the standardization of the NaOH an empirical normality factor is obtained by calibration with known amounts of water. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is a convenient standard. Using such a factor with known amounts of CdO has shown an accuracy of 1%. For a one gram sample of CdS, the lowest concentration of oxygen which can satisfactorily be detected is 0.02% (0.02 milligrams or 200 ppm.) Typical samples gave 0.05 to 0.1% with a deviation of about ± 0.005 .

The equipment consists of two combustion tube furnaces (Hoskins type FH-303A, 230 volt), a Matheson halogen gas regulator, a Rotameter gas flow gauge, and standard bubble columns, valves and connecting glassware. Quartz tubes must be used for the furnaces. All connections must be vacuum tight.

Most of the condensation takes place at the bend in the tubing where it enters the ice bath. Spare collectors and combustion boats are stored in a 100°C oven together with a supply of pyrex glass wool to prevent adsorption of any trace of moisture. The system should be cooled overnight with all of the valves closed and under vacuum, particularly the carbon tube furnace.



Key:

$P_{1,2}$. pressure regulator gauges

V_{1-5} . single bore glass stop-cocks, 1 mm.

V_6 . 3 way glass stop-cock, 1 mm.

D_{1-3} . sulfuric acid bubble columns

D_4 . bubble column with glass wool

F. Flowrator, 3-66 mL/min.

Q. Quartz wool plugs

C. collector tube, 6 mm. Pyrex

S. quartz sample boat

C.F. Carbon furnace - nichrome wire wound furnace,
with activated carbon bed inside quartz tube.

FIGURE 1

APPARATUS FOR DETERMINATION OF CdO IN CdS

Table I lists oxide determinations by the Harshaw method for a number of CdS samples. The amount of oxide detected in the powdered materials as received from General Electric and Sylvania is of the order of 500-700 ppm. It is believed that this is over and above the 500 to 1000 ppm of oxide as SO_4^{--} which has been detected and reported previously.⁽⁵⁾ Preliminary trials have indicated that oxygen bound to sulfur is essentially undetected by this method.

After sintering, the oxide level appears to be reduced slightly to 200-500 ppm. (The sulfur bound oxygen was found to decrease by a factor of 10 during sintering.) During crystal growth, the level of oxide is expected to increase due to such factors as conversion of sulfate to oxide, oxygen impurities added from the growth atmosphere via air leaks, and oxygen being released from growth tubes at the temperature of 1280°C.

This increase is confirmed by data that show the oxide levels present in the crystals vary from 350 to 1900 ppm (as compared with 200 to 500 ppm in the starting materials). The variance appears to be due to differences in seal perfection during crystal growth. In every case analyzed, the secondary seed plate crystal contained more oxide than the primary seed plate crystal confirming the belief that oxygen is introduced from the open end of the system during growth.

Although the method has not yet been developed to a point where a complete distinction between oxide and sulfate content of crystals can be established, the correlation of the effect of oxide contamination to electrical and optical characteristics of CdS is now possible, and steps can be taken to improve the growth conditions by eliminating the oxygen contamination.

Preparation of High Purity CdS

It has been recognized⁽¹⁾ that the CdS materials available up to this time have contained appreciable quantities, in the range of ppm to tens of ppm, of electrically active impurities, plus larger quantities of impurities such as zinc, oxygen, carbon, silicon and other elements whose electrical effects are not known. In addition, non-stoichiometry, is a source of further impurity that has been difficult to measure, quantitatively, but which is known to have major effects on the electrical properties of CdS crystals.

Following the experience with semiconducting silicon, it is believed by many that a real breakthrough in CdS for semiconducting purposes will be made only after ultra purification makes possible the determination of its fundamental properties and its accurately controlled doping. Previous experience at Harshaw⁽⁶⁾ has indicated that wide variations in spectral response of CdS photovoltaic cells has been attributable to variation in trace impurity content, giving rise to differences in the density and distribution of trapping centers.

Preliminary attempts have been made to obtain a higher purity CdS material by the direct combination of highly purified forms of the constituent elements. Work at the Eagle-Picher Research Laboratories and

TABLE I

OXIDE DETECTED IN VARIOUS POWDERS, SINTERS AND SINGLE CRYSTALS OF CdS

Lot No.	Raw Material Source	Dopant	Growth Atm.	Detected ppm O
<u>POWDERS</u>				
104 S20	G.E. Lum. Grade Sylvania CA-754A	-	-	700 580
<u>SINTERS</u>				
10-27-60 S-49 O-71	Eagle-Picher Ultra Pure G.E. Lum. Grade G.E. Lum. Grade	- None None	- H ₂ S Argon	210 530 260
<u>CRYSTALS</u>				
H-7 Primary H-7 Secondary O-19 Primary O-31 Primary O-45 Primary 1S-64 Primary 1S-64 Secondary OS-83 Primary OS-83 Secondary	G.E. Lum. Grade G.E. Lum. Grade E.P. Ultra Pure Sylvania C-676 CUV G.E. Lum. Grade L69 G.E. Lum. Grade L104 G.E. Lum. Grade L104 G.E. Lum. Grade L104 G.E. Lum. Grade L104	None None None None None O.03% In O.03% In None None	Argon Argon Argon Argon Argon H ₂ S H ₂ S H ₂ S H ₂ S	380 1900 460 350 900 980 1040 890 1030

at Harshaw has resulted in higher purity material than is obtainable commercially, but, such material appears to be still appreciably short of the goal of a really ultrapure CdS, and the problem of non-stoichiometry remains.

EVAPORATED CdS FILMS

Light Weight Construction

One figure of merit for space power conversion systems is the power to weight ratio. While there will always be applications where the high efficiency solar cell (e.g.-silicon and gallium arsenide) will be required, it is expected that lower efficiency solar cells will be preferred in many instances if they can produce more power for less system weight.

The vacuum evaporated CdS film cell shows promise of being capable of high power to weight ratios compared with single crystal solar cell systems. While there are a number of design possibilities utilizing vacuum evaporated films of CdS for solar cells, the front wall film cell using a metallic foil substrate has seemed to offer the best prospects for the immediate future and has therefore received the major portion of the developmental effort at Harshaw.

Initial work⁽¹⁾ employed .003 to .005" thick CdS layers vacuum evaporated onto .002 to .005" thick molybdenum foil substrates. Power to weight ratios of such cells (complete with leads and plastic encapsulation) up to 10 watts per pound were obtained. Subsequent efforts have therefore been directed at reducing the thickness of the CdS film required to secure good conversion efficiency cells and the thickness of the metal foil substrate - since these comprise most of the weight of such arrays. Concurrent efforts were continued to increase the conversion efficiency of the cells.

It was found that the thickness of the molybdenum substrate could be easily reduced, but that unless the thickness of the CdS film was also reduced, the slight difference in the thermal expansion coefficient between CdS and molybdenum caused curling of the combination. This curling became too severe for a practical film solar cell device if the molybdenum substrate thickness was reduced to .001" while the CdS layer remained at .002".

During this period attempts were made to improve the properties of the evaporated CdS polycrystalline films so that thinner films would yield cells of good photovoltaic conversion properties. By increasing the temperature of the substrate during evaporation (at the expense of an increase in the time required to complete the evaporation) it was found that the minimum practical CdS film thickness could be reduced from .002" to .001". This made possible a reduction in the minimum molybdenum metal foil substrate thickness from .002" to .001", and thus approximately doubled the attainable power to weight ratio.

Substrate Materials

Molybdenum metal foil was tried initially as a substrate for the CdS front wall cell because its coefficient of thermal expansion matched that of CdS fairly closely. However, at a specific gravity of 10.2 molybdenum is fairly heavy. Titanium and zirconium also have thermal expansion coefficients nearly the same as CdS, and they are much lighter, with specific gravities of 4.5 and 6.4 respectively. However, when these metals were tried as substrates for CdS film cells, the cells had appreciably lower conversion efficiencies and a higher incidence of shorted cells. The problem appeared to be associated with difficulties in cleaning these metals prior to vacuum evaporation of the CdS. Titanium and zirconium were both embrittled by acid etching or sandblast cleaning methods. Any less vigorous cleaning procedure resulted in poor adherence of the CdS film.

When aluminum metal foil was tried as substrate material for CdS it was found that the CdS films would flake off from the aluminum while they were cooling to room temperature after completion of the vacuum evaporation step. This is undoubtedly due to the very great differences in thermal expansion coefficients.

Film Evaporation Conditions

Attempts to reduce the thickness of the molybdenum metal foil substrate without simultaneously reducing the thickness of the CdS film caused trouble with excessive curling of the combination, as discussed earlier. Therefore, attempts have been made to reduce the thickness of the CdS film needed for good cell performance. At first CdS film thicknesses less than about 0.002" gave rise to loss of rectangularity of the I-V characteristic curve traceable to a lowering of the equivalent shunt resistance. This was believed due to imperfections in the CdS film permitting local shorting of the barrier region through to the substrate.

Therefore attempts were made to improve the structure of the CdS films by increasing the substrate temperature during the period of vacuum evaporation. An experiment was run in which the substrate temperature was increased from 220°C, which had been adopted as standard, to 300°C. Secondary problems were encountered due to a greatly reduced rate of CdS deposition which required more CdS to be evaporated, and for longer periods of time. However, film thicknesses up to .001" were obtained, and it did appear that these thinner films deposited at higher substrate temperatures were better structured. There were a number of cells made from such films of CdS in the range of .001" thickness that yielded cells as good as had previously been obtained from thicknesses of .002". Films as thin as .0005" yielded cells with I-V characteristic curves about the same as had been obtained previously with CdS films .0015" thick formed at the lower substrate temperature.

There have been other improvements in processing that may have contributed to the above experience, including improved methods of substrate cleaning and of barrier electrode formation. However, there are strong indications that higher substrate temperatures are beneficial and more work is needed in this area in an attempt to correlate the structure of the CdS film with conditions of evaporation, and to optimize the evaporation conditions.

There are a number of practical problems to the use of higher substrate temperatures, including substrate temperature measurement and control, deposition rates, and low yield of CdS condensed on the substrate.

The attaining of thinner CdS films, however, is well worthwhile since it makes possible the use of thinner substrates and gives increased flexibility of the finished arrays, as well as higher power to weight ratios.

CdS FILM CELLS

Barrier Formation Studies

Conditioning of Barrier Plating Solution

During the operation of the pilot line it was noticed that there was a variation in cell quality that corresponded to the number of cells that had been processed in a given barrier plating bath. Closer examination revealed that the first few films plated in a given bath always resulted in poor cells.

Obviously some type of bath conditioning was taking place. Since conditioning has been found necessary in many other plating baths, it seemed reasonable to expect the same problem to be present in the production of solar cells. The conditioning could consist of gradual bath purification by the removal of a contaminant such as cadmium or sulfide ions, or it could consist of the oxidation or reduction of the organic addition agent (polyethylene glycol) during electrolysis. The latter appears to be the mechanism, since an analysis of a fresh, unused plating bath and that of a well-used bath revealed only one difference; the appearance of a carbonyl group showing a partial conversion of the glycol. The presence of this group appears to be a desirable agent for the formation of a good barrier layer by our present methods. Present procedure is to condition the bath with a pre-electrolysis for one hour at the normal current density. The first few films are no longer detectably different.

Chemical Deposition Utilizing CuCl

A comparison has been made of barriers produced on CdS films by the regular electrodeposition method, and a purely chemical method. For this study barriers produced on films by the conventional electrodeposition method were removed in a KCN solution and a new barrier was deposited by dipping the crystal into a hot CuCl solution (95°C) for a few seconds. In a number of initial trials, the magnitude of open circuit voltage and short circuit current of the resultant small area cells were the same. Cells of poor efficiency remained poor and those of higher efficiency remained high. Because this method would obviously be advantageous in production further trials were conducted on larger area films. However, while good dark rectification curves were obtained from these larger area (1 x 3" size) cells, little or no power was obtained. The reasons for

this experience are not at all clear.

Electrophoretic Deposition of Cu_2O

A technique that could place Cu_2O directly onto a CdS film, (in place of depositing elemental copper and then oxidizing to Cu_2O), is the electrophoretic deposition of particulate Cu_2O from a non-aqueous medium. The general method involves the deposition of charged particles, which can be either metals or compounds, from a solution containing the material in the form of a suspended sol or colloidal powder, by means of an applied DC voltage. The charged particles will usually deposit very rapidly on the electrode of opposite charge when a sufficient electric field is applied. The particles must, of course, be insoluble in the solvent and must remain in suspension for a reasonable length of time.

Solvents chosen for this effort were: tap water, distilled water, alcohol, CCl_4 , and acetone. CCl_4 seemed to be the only suitable solvent of those tested. Various electrode materials were used initially to determine whether deposition of the Cu_2O could be accomplished and what effect, if any, the electrode may have on the system. Cu_2O was deposited on molybdenum producing a thin, very uniform continuous coating. About 500 volts DC was required for a period of 6 minutes. The current, of course, was negligible. Several CdS films were plated on molybdenum under these conditions. When contacted with silver print stripes and tested, they showed rectification but no appreciable power output.

Electrolytic Formation of Cu_2O

Another method of interest is a procedure for the formation of Cu_2O films on a metallic cathode by electrolysis, at very low current densities, from solutions containing copper and certain organics. The original method was developed as a means of forming colored coatings of Cu_2O on various metallic objects, and the author⁽⁷⁾ noted that the coatings exhibited unilateral conductivity and photoelectric properties. It was felt that the process could be modified to form Cu_2O layers on CdS films.

The method followed was the immersion of a suitably masked 1" x 3" CdS film into a solution of CuSO_4 and NaOH, and plating for various periods of time up to 64 minutes.

The current and voltage had to be kept low, less than one milliamper, with an applied voltage of about 0.25 volts. If the voltage exceeded about 0.35 volts, the electrode potential for the formation and deposition of Cu_2O was exceeded and copper metal plated out. The results obtained varied quite widely. High current densities produced metallic copper deposits, while low current densities made it possible to produce large area cells ranging from 0.1% efficient to 0.7%. Under similar experimental conditions, a CdS single crystal yielded a cell of 1.2% efficiency.

The barriers produced were always transparent and generally exhibited a blue color due to light interference. The Cu_2O coatings were essentially

uniform in thickness over the entire CdS film. Other colors are obtained occasionally in certain small areas but never over an entire film. Attempts were made to obtain these other colors, such as gold, orange, and green, since they are related directly to the thickness of the deposit and would permit a comparison of Cu₂O layer thickness with cell characteristics, and might possibly provide a better insight into the barrier's nature. Colors other than various shades of blue were not obtained.

Other baths of this nature have been tried, but there were no indications of better results than what was experienced above.

Hull Cell Study

Difficulties experienced with the tests of the Starek type bath and the difficulty of producing various thicknesses of Cu₂O, led to the use of a Hull Cell to facilitate the study of this bath, and also the determination of the optimum current density for the present barrier plating bath. The Hull Cell⁽⁶⁾ is a very useful tool for the analysis of plating baths of all descriptions for control, research and development.

The Hull Cell consists of a container that holds an anode, a cathode inclined toward the anode, and a plating solution. When a potential is applied, plating occurs and a gradation of current densities laterally across the entire face of the cathode results according to the equation.

$$A = C (27.7 - 48.7 \log L)$$

where:

A = current density
C = total current
L = distance along the cathode

An examination of the deposit permits the determination of the optimum current density needed for a given effect. (Such effects might be brightness, color formations, powders, matte finishes, or the lack of these.) The results of various concentrations, temperatures, degrees of agitation, addition agents, or impurities can also be readily determined.

The Hull Cell was used to check the performance of the regular barrier plating bath. During one of these tests, it was found by sectioning the plated CdS film and testing each section separately that the high current density area (~ 200 ma per cm²), measuring about 1" x 3/8", was a cell of 1.5% efficiency while the entire film cell was only 1.1% efficient. This indicated that better barriers might be formed at higher current densities than those presently employed. Subsequent experiments have given similar indications, but conclusive data have not been obtained. An optical examination of the cells after barrier plating, (before the removal of the excess material) showed dense dendritic growth over the high current density surface of films. These areas later proved to yield the better cells. The areas that gave only moderate efficiency cells showed fewer dendrites and

had very small areas of smooth copper and areas of exposed CdS. The areas that gave very poor results were those where the smooth copper and exposed CdS comprised the major portion of the surface.

Barrier plating experiments run at the same conditions but using metal cathodes in place of CdS films have not given the same dark mossy deposit. This indicates wide local variations in current density over the surface of the evaporated CdS films. This seems to be related to the work done on the CdS surface. This is borne out by the observation that certain grains appear at times to form a barrier more readily than others. More effort is needed in this area.

Pilot Operations

As part of the effort to achieve reproducibility a small scale laboratory pilot line was started about a year ago to fabricate front wall CdS film cells on molybdenum substrates. This line has operated continuously since then and has provided a base line against which presumed improvements in design and processing could be compared. More than 300 1 x 3" cells have been made on this pilot line, and there has been a gratifying improvement in average cell efficiency as a direct result of this effort.

A degree of reproducibility was gradually achieved as a result of the pilot line operation, and a set of standard operating procedures for the various processes evolved.

One result of the pilot operation was the observation that there might be a correlation between average cell efficiency and room humidity. A number of cells of appreciably higher conversion efficiency were obtained during one week when the humidity was at a minimum (20 to 30). Records of humidity were therefore kept and carefully compared with average pilot line cell efficiencies. There did indeed appear to be a correlation but there were other factors that complicated the interpretation of these data, and prevented a definite conclusion.

It is planned to run a carefully controlled experiment in an effort to arrive at a definite conclusion regarding the influence of humidity during processing on cell efficiency. The pilot line operation will be moved for selected periods to a humidity controlled room (20 to 30%) and the results compared with periods when normal room humidities prevail. If indicated, dry box operations of the critical processing steps can then be evaluated.

Another test that is planned is the use of dry heated air to accomplish the heat treatment of cell barriers. It has been found that heat treating the film cells after barrier electroding by using a low temperature oven gives more reproducible results than the faster higher temperature "heat shot" on an electric hot plate. (Oven treatment for 30 minutes at 150°C has been found to give more uniform cells with higher efficiencies on the average.) The use of really dry air fed to a mechanical convection oven for heat treating barriers on large area film cells may lead to higher efficiencies and greater uniformity.

A second, but smaller scale, pilot line was started for the fabrication of rear wall CdS film cells on 1/16" thick conducting pyrex glass substrates. This was done to facilitate studies of the differences between front wall and rear wall CdS film cells - and to provide higher efficiency cells than were achievable with the thin light weight construction. A standard procedure for the fabrication of these rear wall CdS film cells was developed and a degree of reproducibility was achieved. Average conversion efficiencies of 3.0% in equivalent terrestrial sunlight are obtained. The process is essentially the same as outlined earlier.⁽¹⁾

Higher Efficiency Cells

At times it has been observed that portions of a larger area CdS film cell will produce appreciably higher power output per unit of area than the cell as a whole. The evaporated thin film CdS cell lends itself readily to the isolation of smaller areas, or to sectioning into a number of smaller area operating cells. In an effort to determine just what levels of conversion efficiency might be physically attainable from the CdS front wall photovoltaic cells, a number of standard 1 x 3" sized front wall cells on molybdenum substrates were cut into smaller areas and tested. At a time when a maximum conversion efficiency of only 1.1% had been obtained from a larger area front wall cell, a number of smaller area cells were found that had appreciably higher conversion efficiencies. A maximum of 2.5% was observed. Table II shows the results of 5 smaller area cells that were cut from larger area cells. The efficiencies ranged between 1.5 and 2.2%.

TABLE II

SMALL AREA FRONT WALL CdS FILM CELLS

Film No.	Voc (Volts)	Isc (ma)	Area (cm ²)	Eff. (%)
1	0.49	1.16	0.17	1.5
2	0.49	1.40	0.16	1.7
3	0.50	.82	0.10	2.1
4	0.49	.72	0.12	1.6
5	0.50	1.30	0.12	2.20

While these small area cells are of little practical value they do prove that higher efficiencies are feasible. Also, they emphasize the lack of uniformity existing under certain conditions across the surface of individual large area cells. Sectioning of more recent front wall cells has shown a much better degree of uniformity across the surface of the cell, but the small areas of relatively high conversion efficiency seem to have been sacrificed in obtaining the uniformity. It is noteworthy that all of the higher efficiency smaller area cells had an open circuit voltage of 0.49 to 0.50 volts. This is about 5% higher than normally attained on the larger area cells. This may be an indication of better current collection and less sheet resistance.

Spectral Response

In the operation of front wall CdS film cell pilot line a number of cells were produced, all at about the same time over a period of a week, with appreciably higher conversion efficiencies. It was noted that these cells, that ranged from about 1.4 to 1.8% efficient, were also characterized by an improved spectral response. Figure 2 shows the spectral response, both in monochromatic light and with white light bias, for what was at this time a typical 1% front wall film cell (No. 265). Figure 3 shows corresponding spectral response curves for one of these higher efficiency cells (No. 263). There is greater response at all wave lengths, but particularly at those wavelengths longer than the absorption cut-off on CdS. In addition, there is greater "enhancement" from white light bias.

At present the reasons for this improved spectral response of a few cells remain a matter of conjecture. There have been some improvements in processing introduced at about this time including a refined method of heat treating the barriers. However, these improvements do not correlate closely enough with the presumed processing improvements and the higher efficiencies have not remained, though the process refinements have. It seems likely that the phenomenon may be connected either with the location and distribution of trapping centers giving rise to the two stage transition from valence to conduction band, or to some rate determining factor such as recombination centers at the front surface or quenching mechanism in the crystal. From the curves of Figures 2 and 3, the latter possibility seems more likely and further studies of these factors are strongly indicated.

A few experiments were conducted involving the evaporation of a 0.05% Ag+0.01% In-doped CdS (Lot 1-72) in an attempt to enhance the spectral response of the CdS film cells to correspond to what was obtained in the high efficiency cells. Film thicknesses of about 2 mils were evaporated onto 0.002" molybdenum and produced darker but well adhering films. However, subsequent cell fabrication invariably resulted in shorted cells. Dilution of lot 1-72 to 0.005% Ag+0.001% In concentration permitted cells of 0.5 and 0.6% efficiency to be produced. The I-V curves still revealed low shunt resistance, however, Lot No. 1-63E (0.003% In) also produced 0.5 and 0.6% cells of low voltage, and no increase in spectral response was noted.

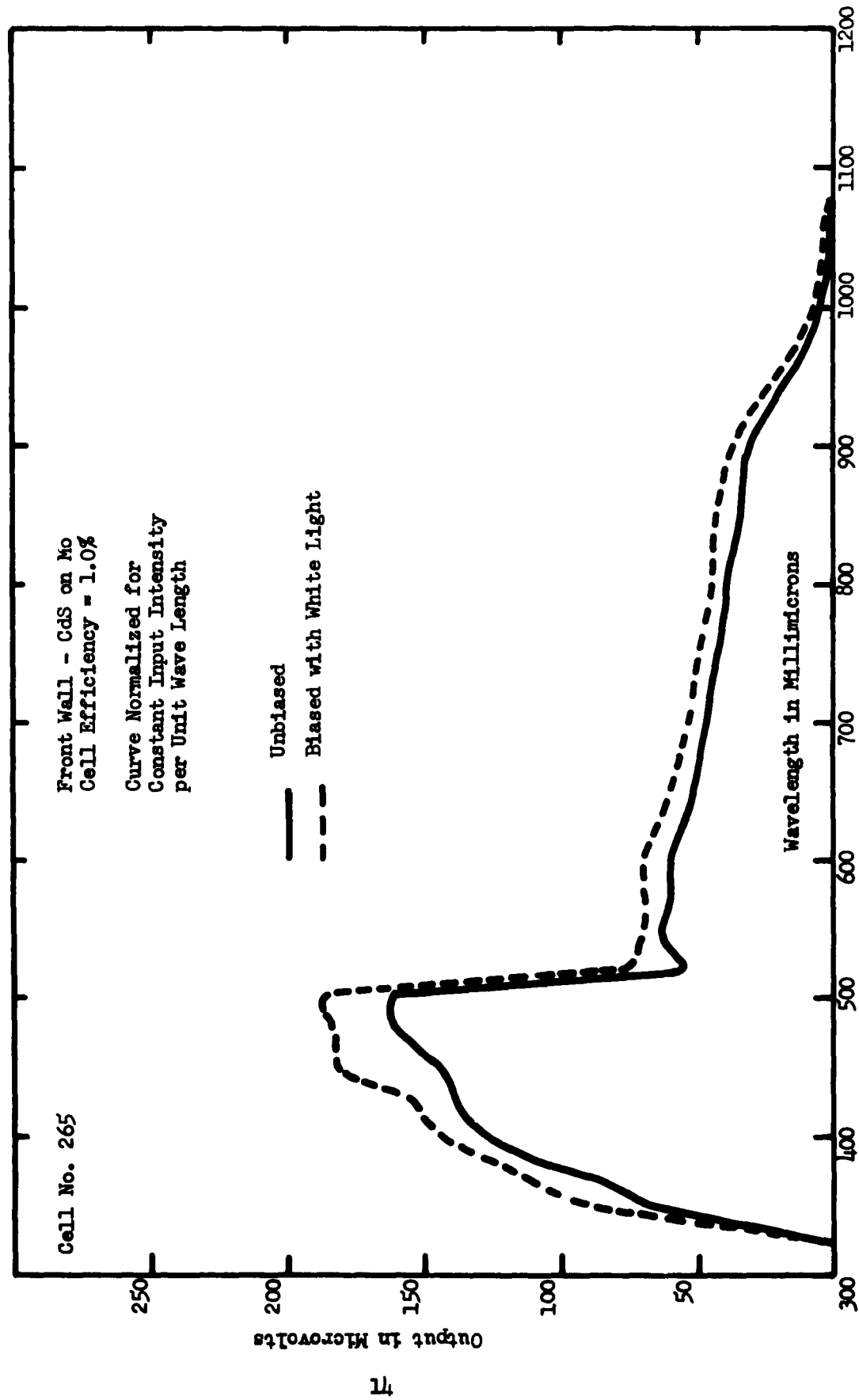


FIGURE 2
SPECTRAL RESPONSE OF TYPICAL LOW EFFICIENCY FRONT WALL FILM CELL

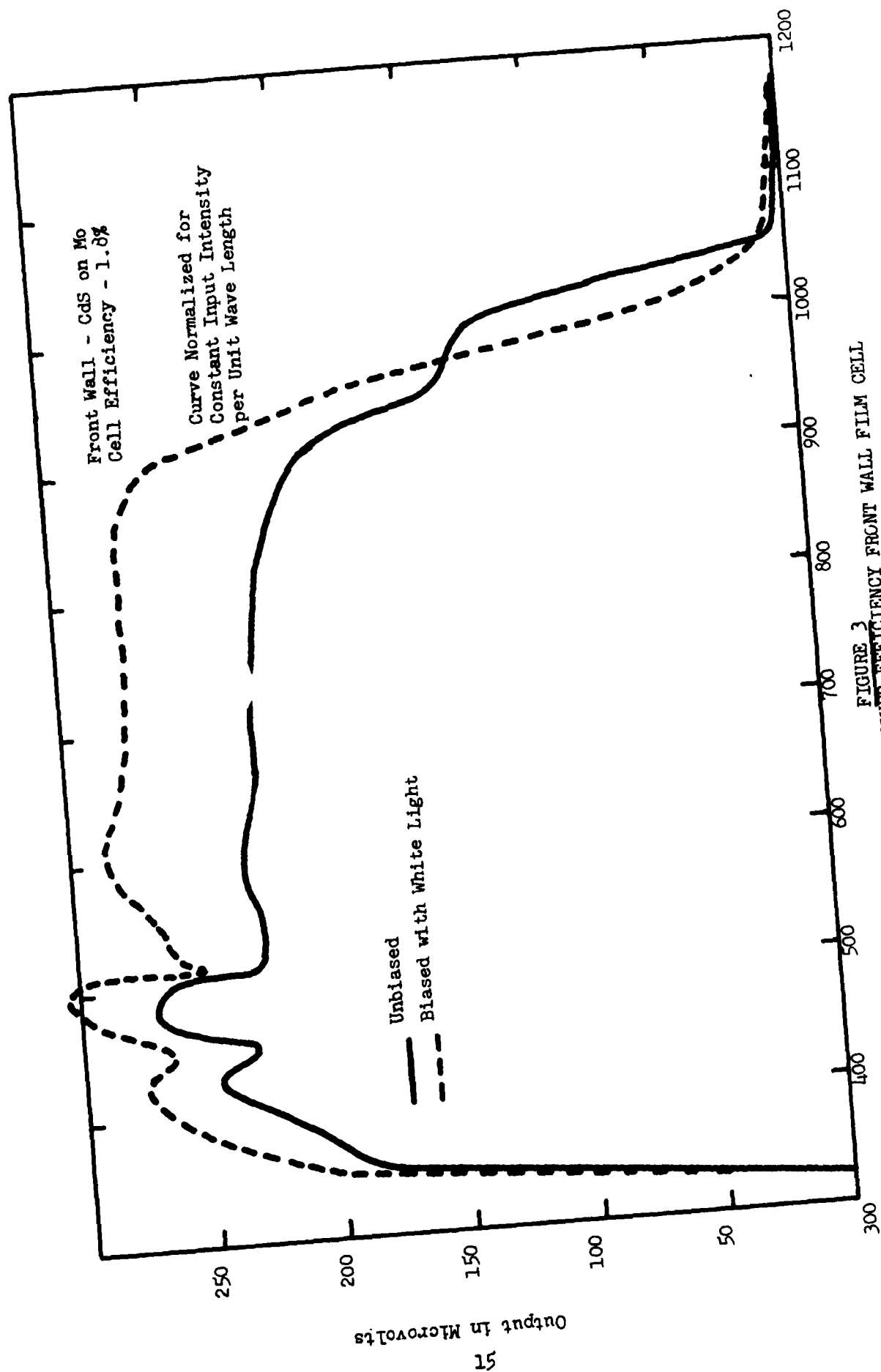


FIGURE 3
SPECTRAL RESPONSE OF HIGHER EFFICIENCY FRONT WALL FILM CELL

Sheet Resistance and I-V Curve Analysis

The front wall CdS cell requires a partially transparent electrode for contact to the positive barrier surface. No highly conductive transparent film compatible with the barrier layer has been found as yet. Therefore, grids of conductive silver paint have been used. The barrier surface exhibits a sheet resistance, so that current generated some distance from the electrode will produce a voltage drop due to the surface resistance in passing to the electrode. Assuming uniform current generation over the surface, the voltage drop produced will be a function of the distance from the point of generation to the electrode, and will influence the shape of the I-V curve of the cell. To determine the expected magnitude of the effect, an analysis has been made.

Consider an elementary cell, as shown in Figure 4.

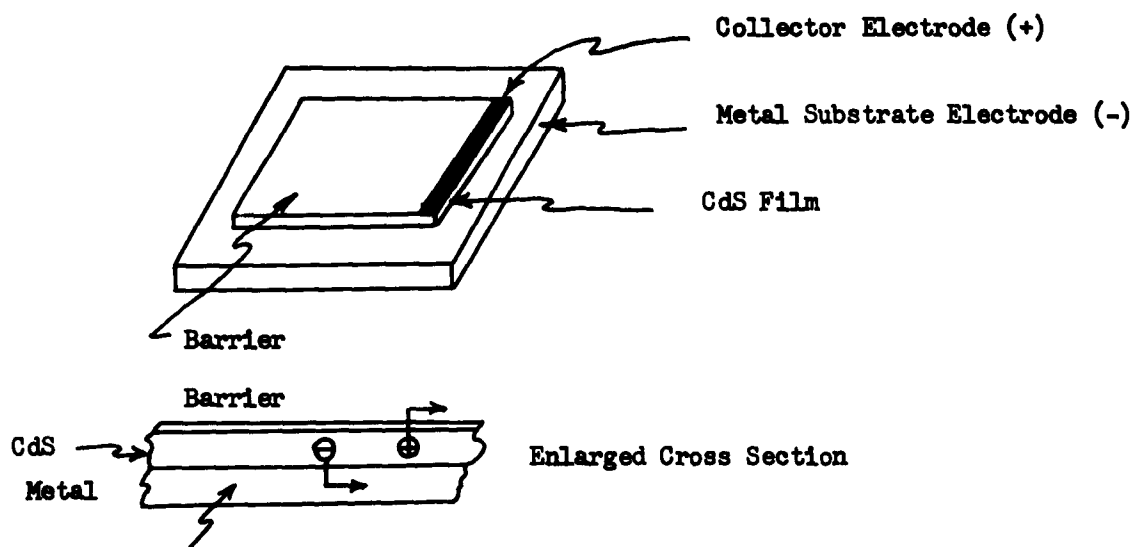


FIGURE 4

Elementary CdS Front Wall Film Cell

Charge is generated in the cell. Negative charge passes through part of the CdS film into the metal substrate and out to the external circuit. It re-enters through the positive collector electrode, passes through the sheet resistance of the barrier and back into the film. (Positive charge can be traced in the opposite direction). The resistive components of this circuit are the CdS film, the metal substrate, the barrier layer sheet, and the external resistance.

The ideal cell has an I-V characteristic described by

$$I = I_s \left[e^{\frac{qV}{nkt}} - 1 \right] - I_{sc}$$

I_s = saturation current

n = constant, usually $1 \leq n \leq 2$

I_{sc} = light generated current

The equivalent circuit for this is shown in Figure 5.

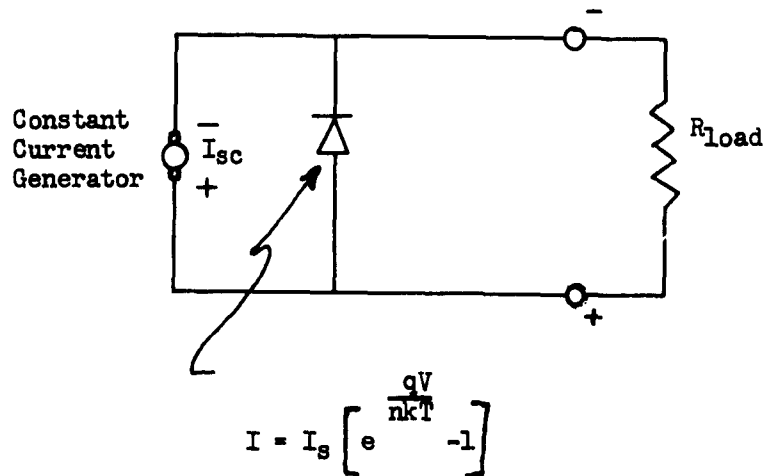


FIGURE 5

Equivalent Circuit for Ideal Cell

The addition of the resistances in the film, substrate and barrier alters the equivalent circuit as shown in Figure 6

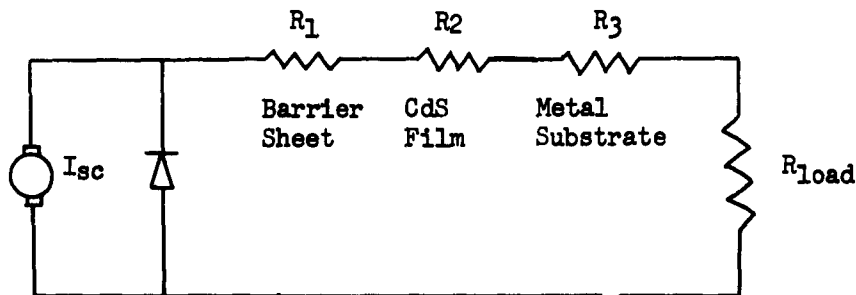


FIGURE 6
Equivalent Circuit for Cell After Addition of Resistances

In a practical cell, R_1 and R_3 are not linear impedances when seen from the output terminals, since they are distributed along the physical length of the cell. The physical effect of these resistances is to produce a voltage drop which is added to that across the load.

To proceed with the analysis, two assumptions are made.

- 1) The barrier layer impedance is a resistance and can be characterized by a sheet resistivity ρ_s .
- 2) The resistances due to the metal substrate and CdS film are neglected. The metal substrate sheet resistivity will be about 10^3 ohms per square for 2 mil molybdenum whereas the barrier layer has a sheet resistivity of the order of 10^3 ohms per square. The resistance due to the CdS film will have the effect of a constant resistance in series with the load.

The equivalent circuit of the practical cell is now formed from distributed parameters, as shown in Figure 7.

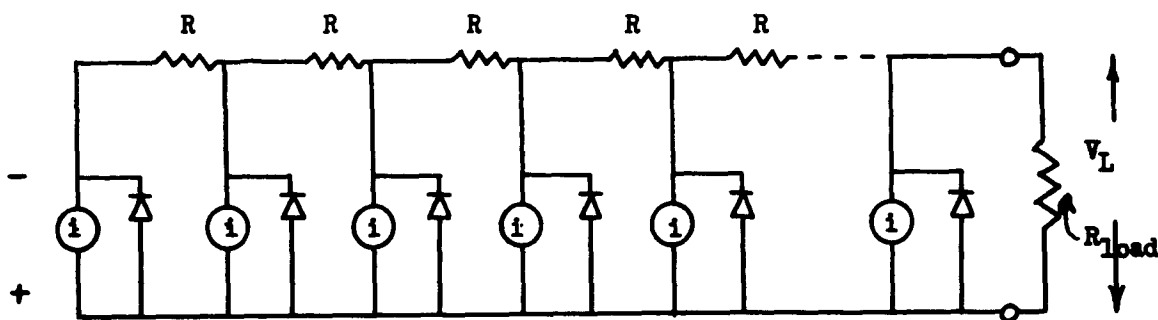


FIGURE 7
Equivalent Circuit of Practical Cell

$$\sum i = I_{sc}$$

$$\sum R = \rho_s \left[\frac{\text{length}}{\text{width}} \right] = \rho_s \left[\frac{L}{W} \right]$$

Because of the exponential relation for the I-V equation of the diode, the analytical solution of the circuit in Figure 7 leads to a non-linear differential equation which can be solved only by numerical methods. However a useful approximation can be made if it is assumed that the I-V curve for the diode is as shown in Figure 8.

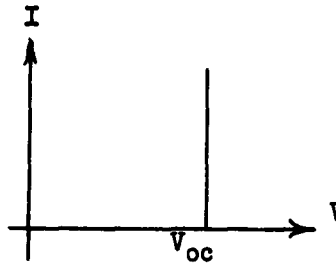


FIGURE 8
Assumed Diode I-V Characteristic

Under this assumption, each current generator will supply all its current to the external load if it sees a voltage less than V_{oc} . If it sees more than V_{oc} , all its current passes thru the diode.

An equation relating the current and voltage can now be set up. Referring to Figure 4, the assumption of a uniform sheet resistance means that for a current generation which is uniform over the entire cell area the equipotential lines are parallel to the collector electrode. The only dimension of interest is the distance along the length of the cell, so the elementary cell is redrawn as in Figure 9.

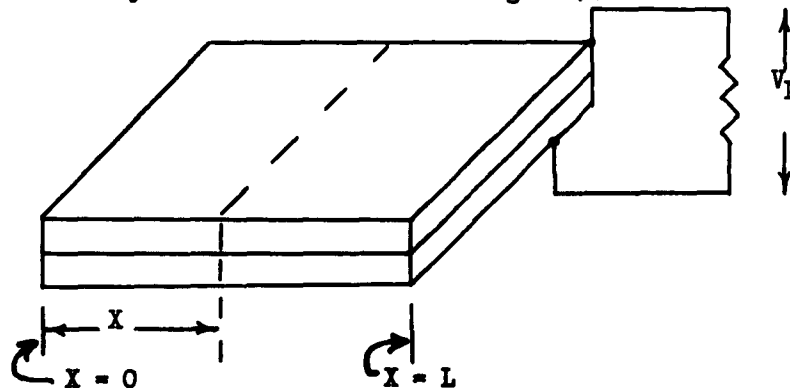


FIGURE 9
Revised Elementary CdS Front Wall Film Cell

At point x, the current generated by the area to the right is I (x)

$$I(x) = I_{sc} \left(1 - \frac{x}{L}\right)$$

The current generated by a stripe of width Δx is :

$$I = I_{sc} \left(\frac{\Delta x}{L}\right)$$

This is independent of x.

The resistance seen by this element of the cell is

$$R(x) = \rho_s \left[\frac{L - x}{W} \right]$$

The voltage this produces across the sheet resistance is

$$\Delta V = R(x) I = \frac{\rho_s I_{sc}}{LW} (L-x) \Delta x$$

The voltage developed across the sheet between the electrode at $X = L$ and any point X is

$$V(x) = \int_x^L \frac{\rho_s I_{sc}}{LW} (L-X) dX = \frac{\rho_s I_{sc}}{2LW} (L-x)^2; I(x) = I_{sc} (X-L)$$

Eliminating X

$$V_s = \frac{\rho_s L}{2WI_{sc}} I^2 \quad I^2 = \text{voltage developed across the sheet resistance}$$

Now

$$V_{oc} = V_s + V_{load}$$

and

$$V_{load} = V_{oc} - V_s = V_{oc} - \frac{\rho_s L}{2WI_{sc}} I^2$$

A similar analysis can be made for a different collector electrode geometry, namely an elementary square cell with a peripheral electrode as in Figure 10. This would be representative of a collector electrode in the form of a screen grid.

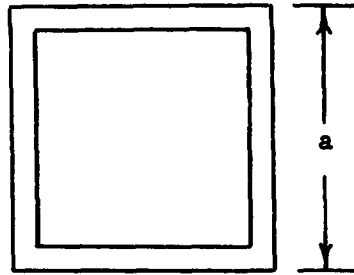


FIGURE 10

Elementary CdS Front Wall Film Cell With Peripheral Electrode

In this case, the area is divided into four triangular quadrants by the diagonals of the square. The current from each triangle is assumed to go to the electrode along its hypotenuse. This is equivalent to assuming that the equipotential curves are also squares. The elemental generator is then as shown in Figure 11.



FIGURE 11

Elementary Generator of Cell With Peripheral Electrode

By mathematics and reasoning similar to the previous case, the resulting equation is:

$$V_{\text{load}} = V_{\text{oc}} - \frac{Ja^2 \rho_s}{16} \left[(1 - \frac{I}{Ja^2}) \ln (1 - \frac{I}{Ja^2}) + \frac{I}{Ja^2} \right]$$

where J = generated current per unit area

It is now possible to compare two grid structures illustrated in Figure 12.

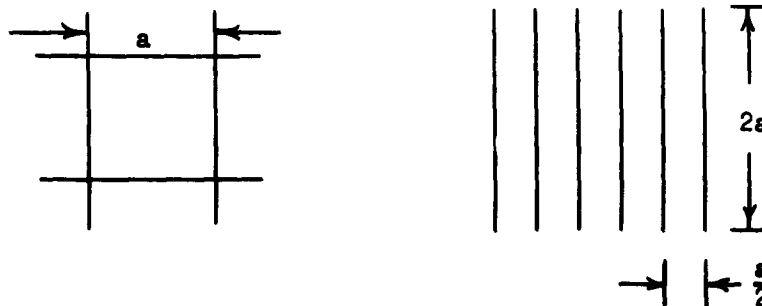


FIGURE 12
Two Collector Electrode Grid Patterns for CdS Front Wall Film Cells

The two cells are equal in active cell area and in surface area of the conductors, since the horizontal conductors of the square grid pattern are taken out and placed midway between the vertical conductors of the parallel pattern.

Assume the following values

$$V_{oc} = 0.5 \text{ volts}$$

$$P_s = 10^5 \text{ ohms per square}$$

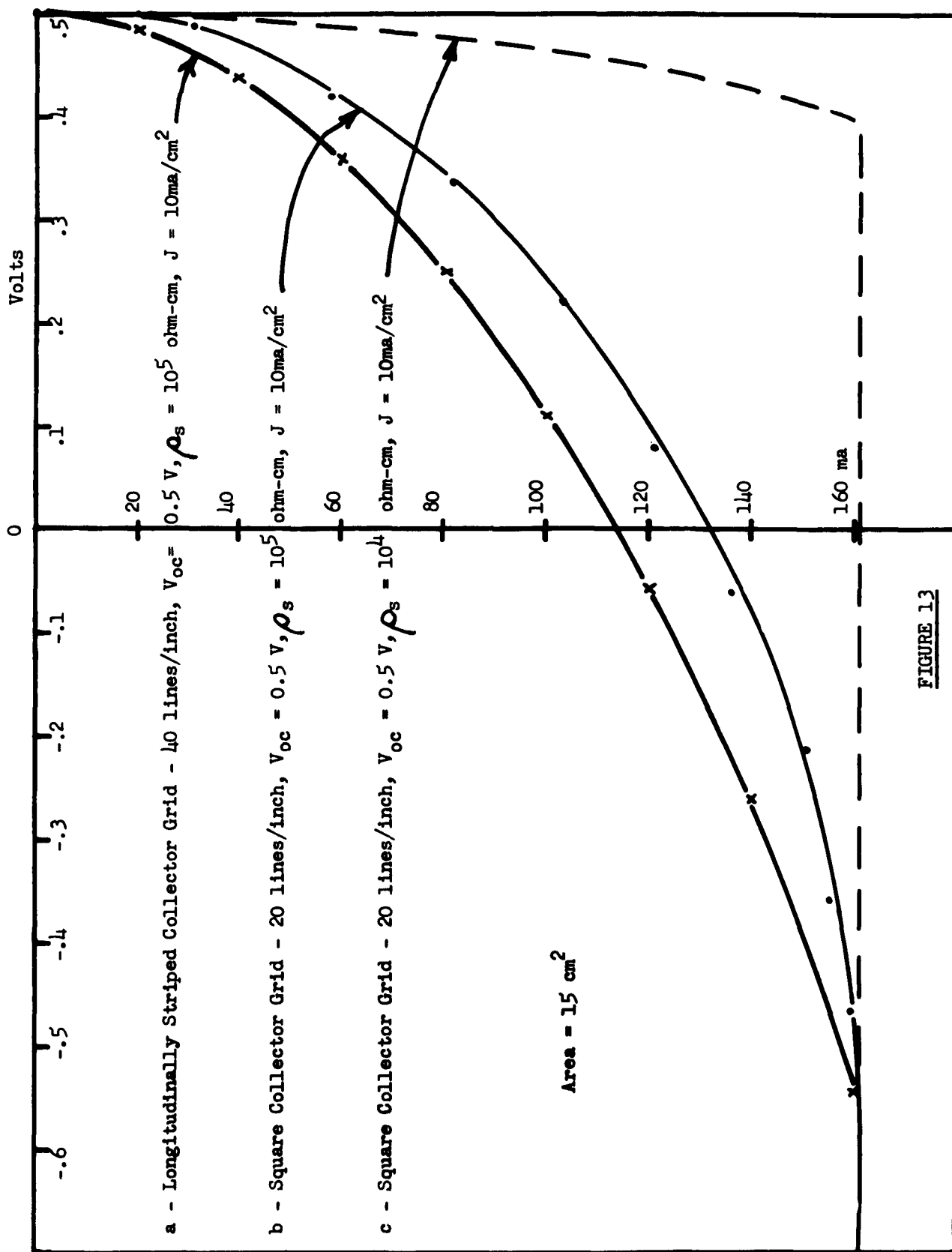
$$J = 10 \text{ ma/cm}^2$$

$$a = 1/20 \text{ inch}$$

Figure 13 shows the calculated I-V curves for the cells of Figure 12 with areas equal to a^2 and the above assumed parameters. Clearly, the square grid is superior. In the same figure, the dashed curve shows the calculated I-V curve for the square grid pattern with an assumed sheet resistivity of 10^4 ohms per square, the rest of the parameters remaining the same.

If the dimension a is decreased by using a grid with 100 lines per inch, the value of Ja^2 decreases by a factor of 25. For $P_s = 10^4$ ohms/square, and a grid of 100 lines/inch, the voltage drop due to the sheet resistance at maximum current is 0.4 millivolts. In this case, the effect of sheet resistance should be negligible.

Measurements of the sheet resistance of typical CdS film cells have ranged from 100 to 10,000 ohms/square with the majority less than 1000 ohms/square.



CALCULATED I-V CHARACTERISTIC CURVES FOR CELLS OF FIGURE 12 WITH ASSUMED VALUES OF PARAMETERS

Collector Electrode

In the above analysis it was shown that the effect of sheet resistance should be greatly lessened by increasing the number of grid lines and going to a square grid pattern. For purposes of comparison it was assumed that as more grid lines were used, the width of each decreased in proportion so that the current carrying capacity of the collector electrode remained the same as well as the total active area of cell barrier surface. In practice this is not so easy to accomplish with the conductive silver paint used up to this time for a collector grid for the front wall CdS film cell. With the techniques in use it would be very difficult to go to mesh grids with more than about 10 lines per inch.

However, another technique was developed at this time which got around the difficulties inherent in the use of conducting silver print. This technique used a screen of silver metal laminated against the barrier surface and held in intimate pressure contact to the barrier by a transparent plastic layer heat sealed in place. The lamination process was the same as described earlier⁽¹⁾ for encapsulating CdS front wall film cells in plastic envelopes.

At first silver grids were laboriously fashioned from fine silver wires, flattened and formed into desired geometries. Then it was found that screen grids could be obtained commercially that were formed from metal foils by etching away the metal between the desired grid lines. Grids of silver, gold, copper and other metals with lines as thin and narrow as .001", and with line spacings as much as 280 to the inch could be obtained from the Buckbee Mears Company of St. Paul, Minnesota. These are expensive, but the results obtained when they were applied as collector grids to CdS front wall film cells were spectacular. Cell efficiencies of $1\frac{1}{2}$ to $2\frac{1}{2}$ times what had been attainable with silver paint grids were secured with this technique.

With the silver paint collector electrodes, cell efficiencies of 0.6 to 1.4% were obtainable reproducibly on 1 x 3" and 3 x 3" front wall film cells using molybdenum foil substrates. Using the metal foil collector grids laminated in place, cell efficiencies of the same size cells increased to between about 1.5 and 2.9%. There have not as yet been sufficient cells fabricated by this technique to determine the average reproducible cell efficiency obtainable by the method.

One series of experiments were run, utilizing this technique of laminating the collector grid in place, in order to check the series resistance - I-V characteristic analysis of the previous section of this report. Nine front wall film cells were contacted by laminating various square grids. Four were contacted with 90 line per inch grids of silver, three with 20 line per inch grids of silver, and two with 70 line per inch grids of gold. I-V curves under simulated sunlight illumination were taken with an oscilloscope and camera. Using the measured values of open circuit voltage and short circuit current, the curves were fitted to the following equation.

$$I = I_0 \left[e^{\frac{qV}{nkT}} - 1 \right] - I_{sc}$$

The values of n & I_0 were chosen to give the best fits to the various curves. Figures 14, 15, 16, and 17 show the curves for cells with the 90 line per inch silver grid. These are all fitted well with a value of n between 3 and 4. Figures 18, 19 and 20 show the I-V curves for cells with the 20 line per inch silver grids. These are also fitted well with a value of n between 3 and 4. Figures 21 and 22 show the I-V curves for cells with 70 line per inch gold grid. These also fitted very well with a value of n between 3 and 4.

Some conclusions can be drawn from the above as follows:

- 1) Fixed series and shunt resistance elements are not present in these cells since their presence in an appreciable degree would cause large deviations from any exponential curve at the short circuit current and open circuit voltage points.
- 2) Sheet resistance in cells with these collector grid contacts is negligible since there is no noticeable change in the fits of the curves from 20 to 90 lines per inch grids.
- 3) Since the I-V curves are all of the same general shape, the major variation between cells is the generated short circuit current. It is possible that the mesh electrode does have an effect on the barrier geometry in the manner of a point contact diode. That is, the metal electrode may change the character of the barrier region, making a deeper junction than exists with no electrode. This may account for the two cells with gold electrodes having such high short circuit current. The other possibility is that the gold electrodes were placed on superior cells.
- 4) Whichever of the foregoing possibilities is true, the key to still higher power output now lies in the inner workings of the device. The external collector grid geometry now appears to be adequate.

Cell Testing

One disadvantage of the new method of contacting the cells is that a cell must be laminated before its electrical characteristics are known. This makes it inconvenient to match cells in a larger array or to eliminate occasional shorted cells.

Therefore work has been started to develop a method of testing such cells by pressing a collector grid against the barrier surface without actually laminating it in place. Placing a grid between a glass plate and a cell and backing the cell up with a rigid steel plate was not successful in reproducing the conditions existing when the grid was actually laminated in place. The indicated efficiencies obtained by shining the light through the glass plate in this manner were much less than when the same cells were actually laminated.

The next step was to design a unit that would press the cell by means

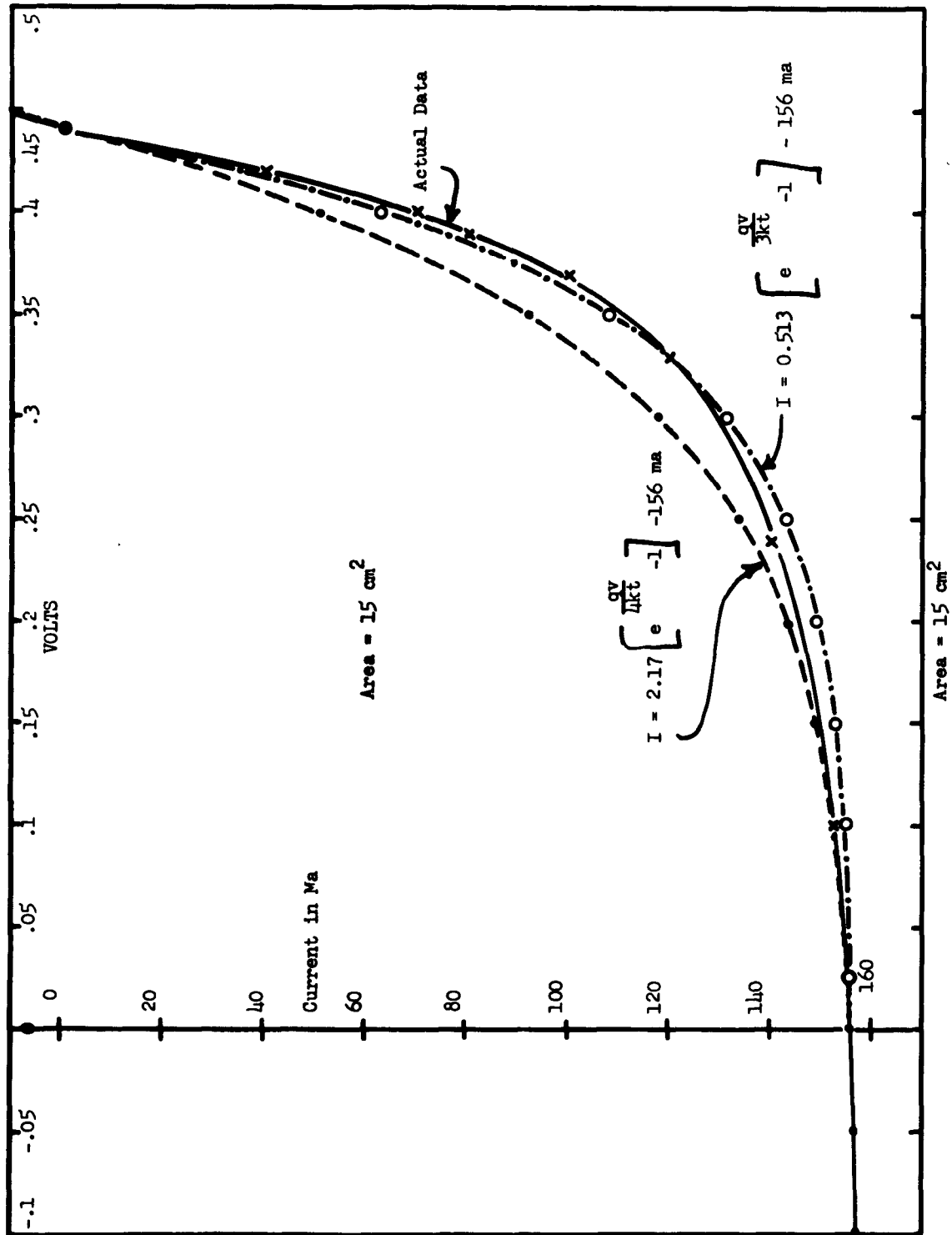


FIGURE 14. ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 50 WITH 90 LINES PER INCH SILVER SQUARE GRID CONTACT

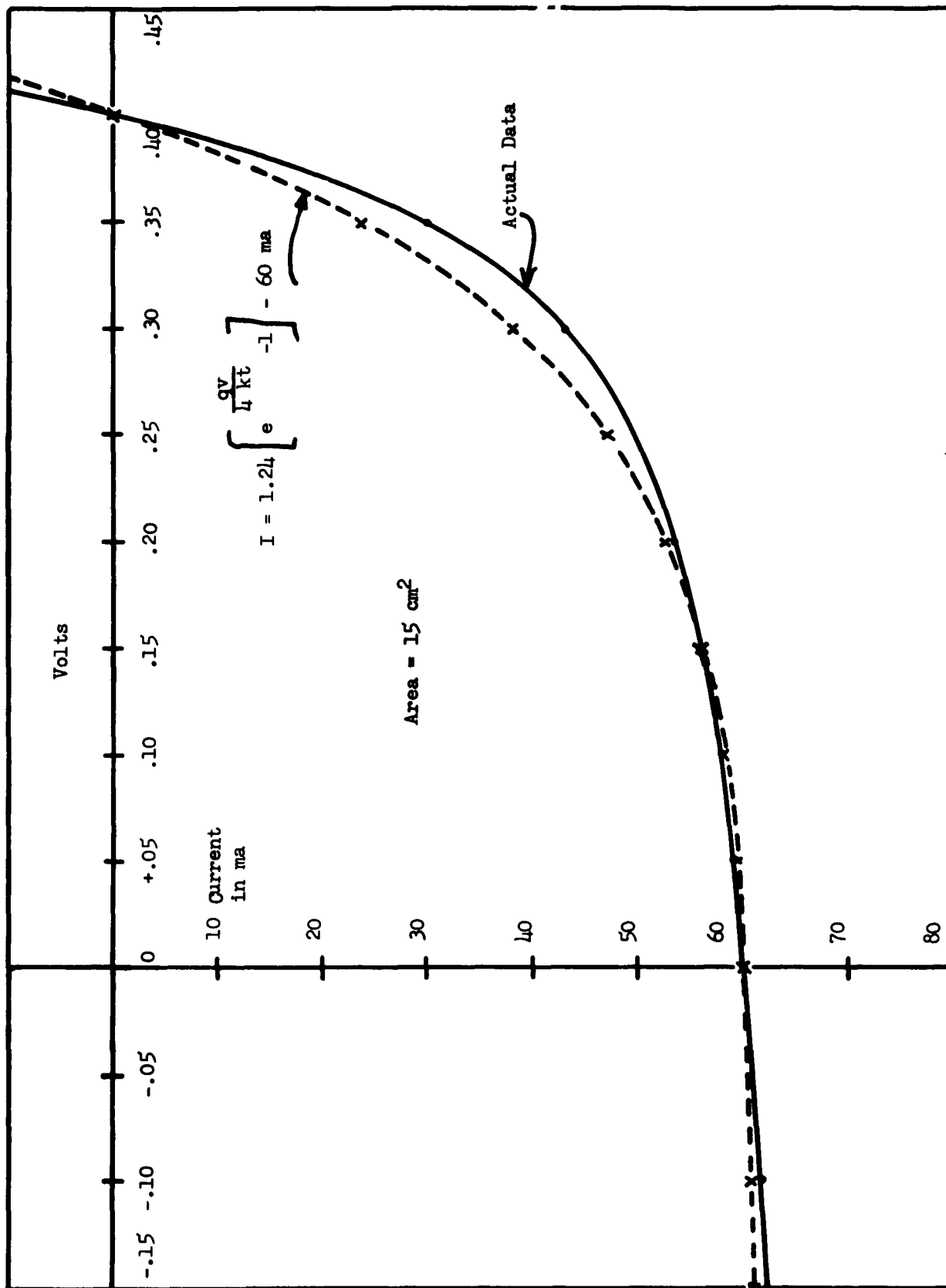


FIGURE 15
ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 51 WITH 90 LINES PER INCH SILVER SQUARE GRID CONTACT

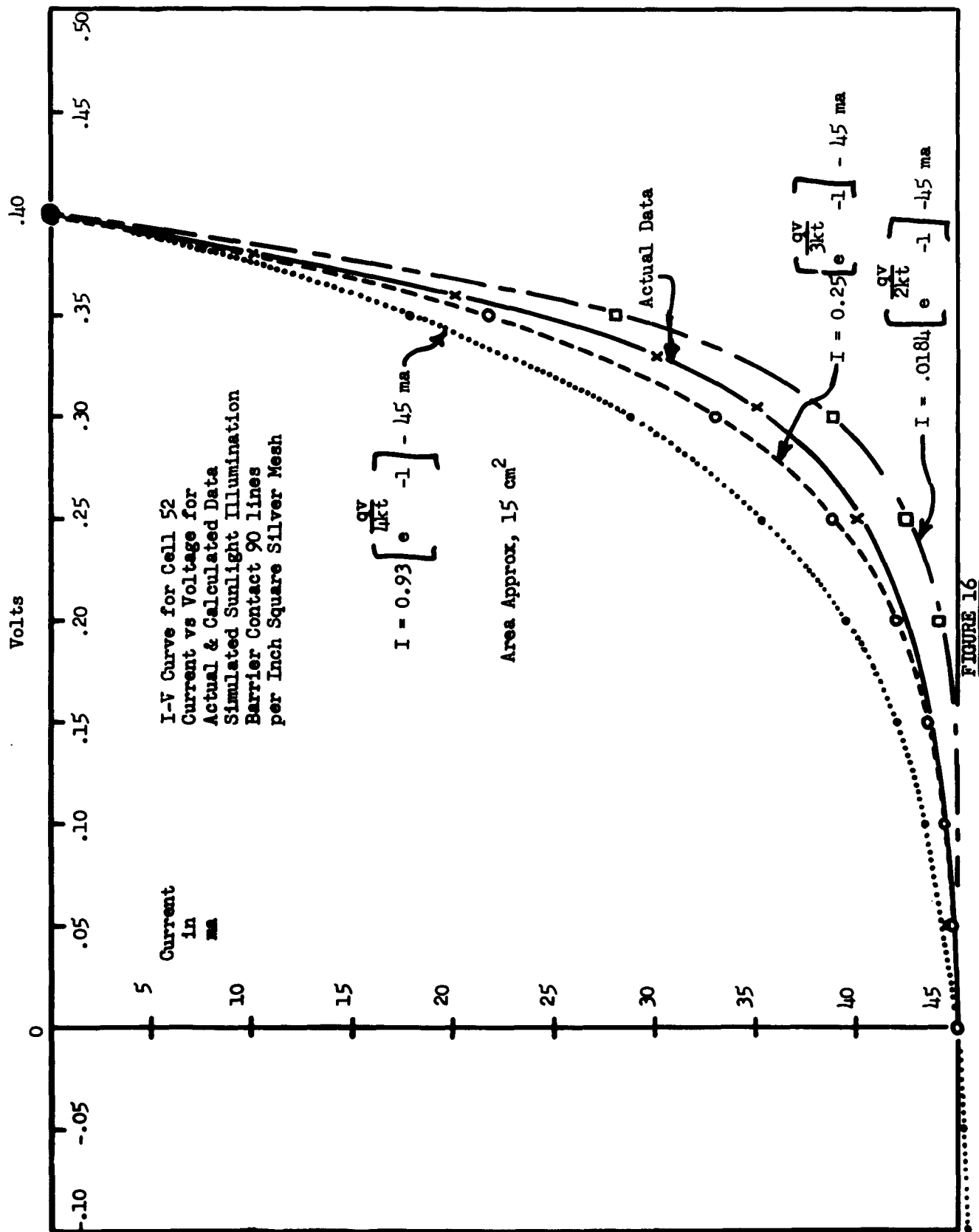


FIGURE 16
ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 52 WITH 90 LINES PER INCH SILVER SQUARE GRID CONTACT

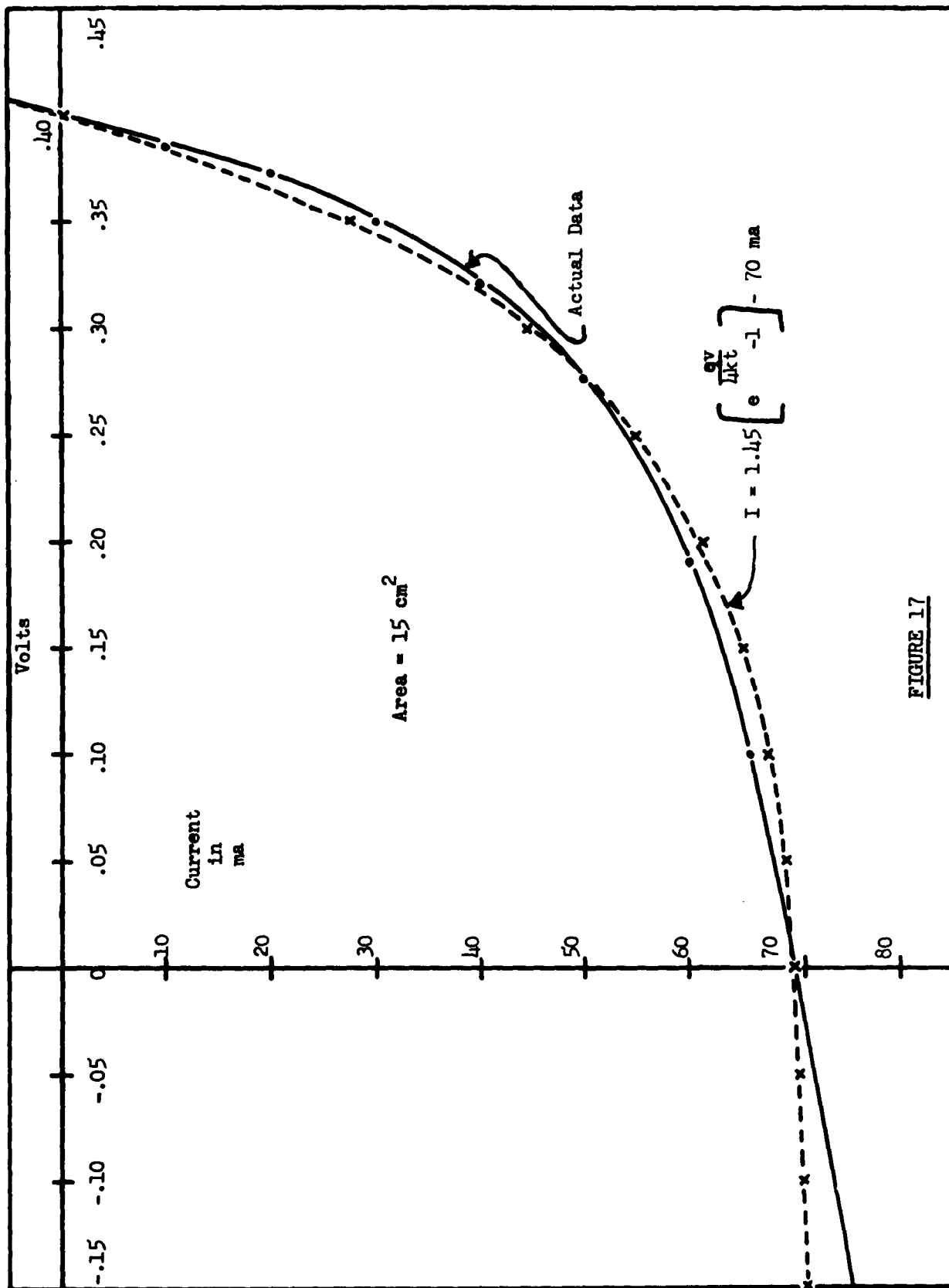


FIGURE 17

ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 53 WITH 90 LINES PER INCH SILVER SQUARE GRID CONTACT

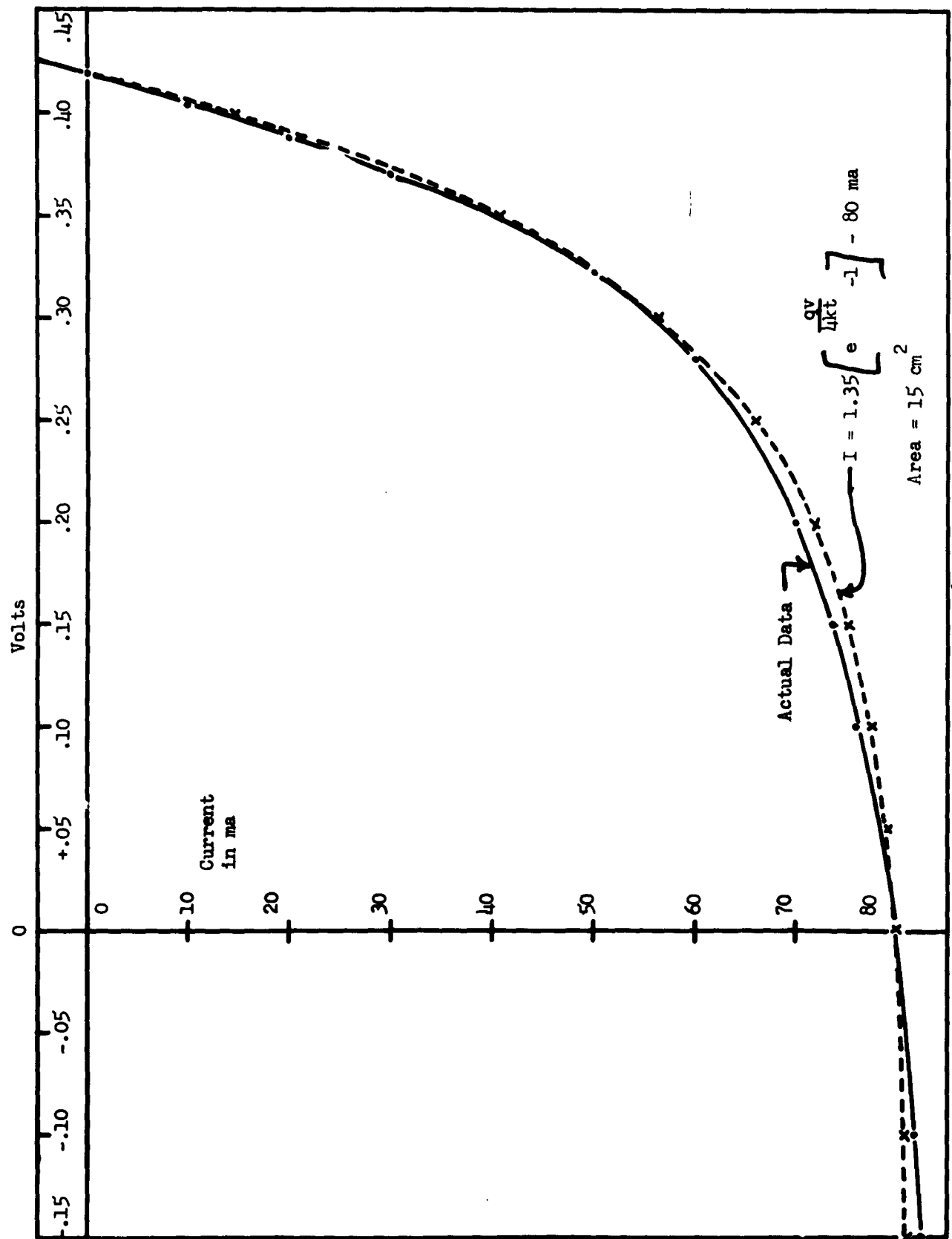
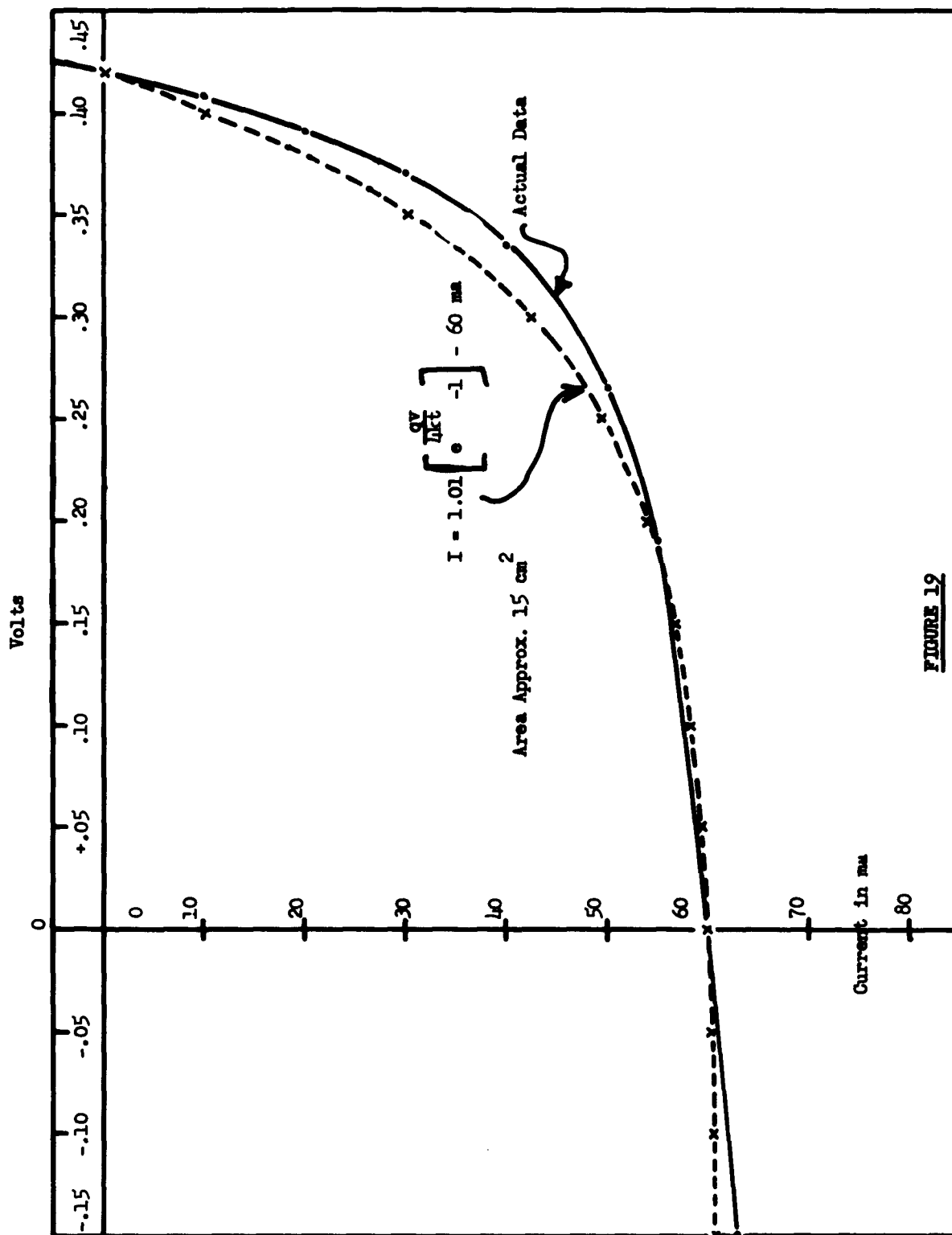


FIGURE 18
ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 54 WITH 20 LINES PER INCH SILVER SQUARE GRID CONTACT



ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 55FN WITH 20 LINES PER INCH SILVER SQUARE GRID CONTACT

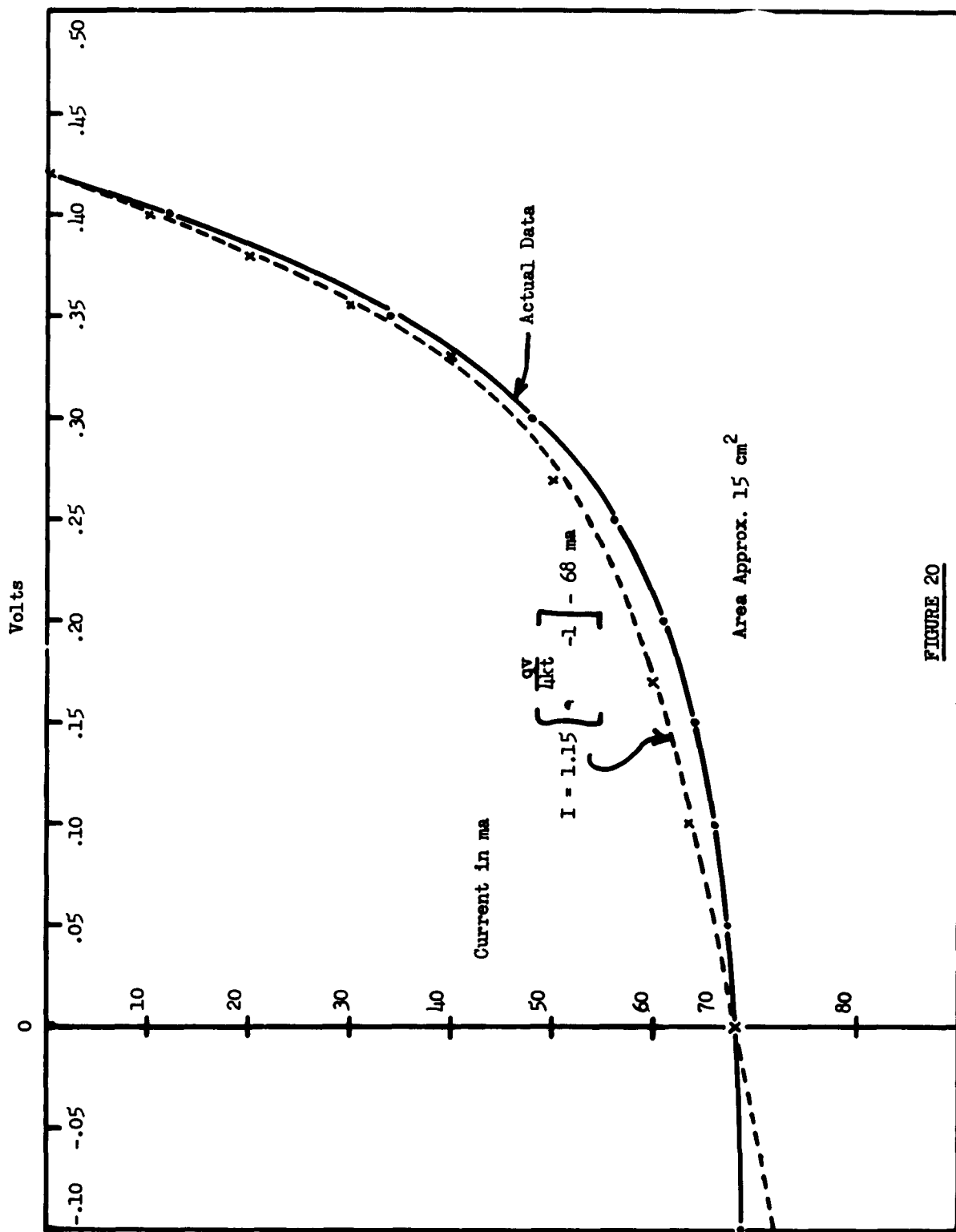


FIGURE 20

ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. 59 WITH 20 LINES PER INCH SILVER SQUARE GRID CONTACT

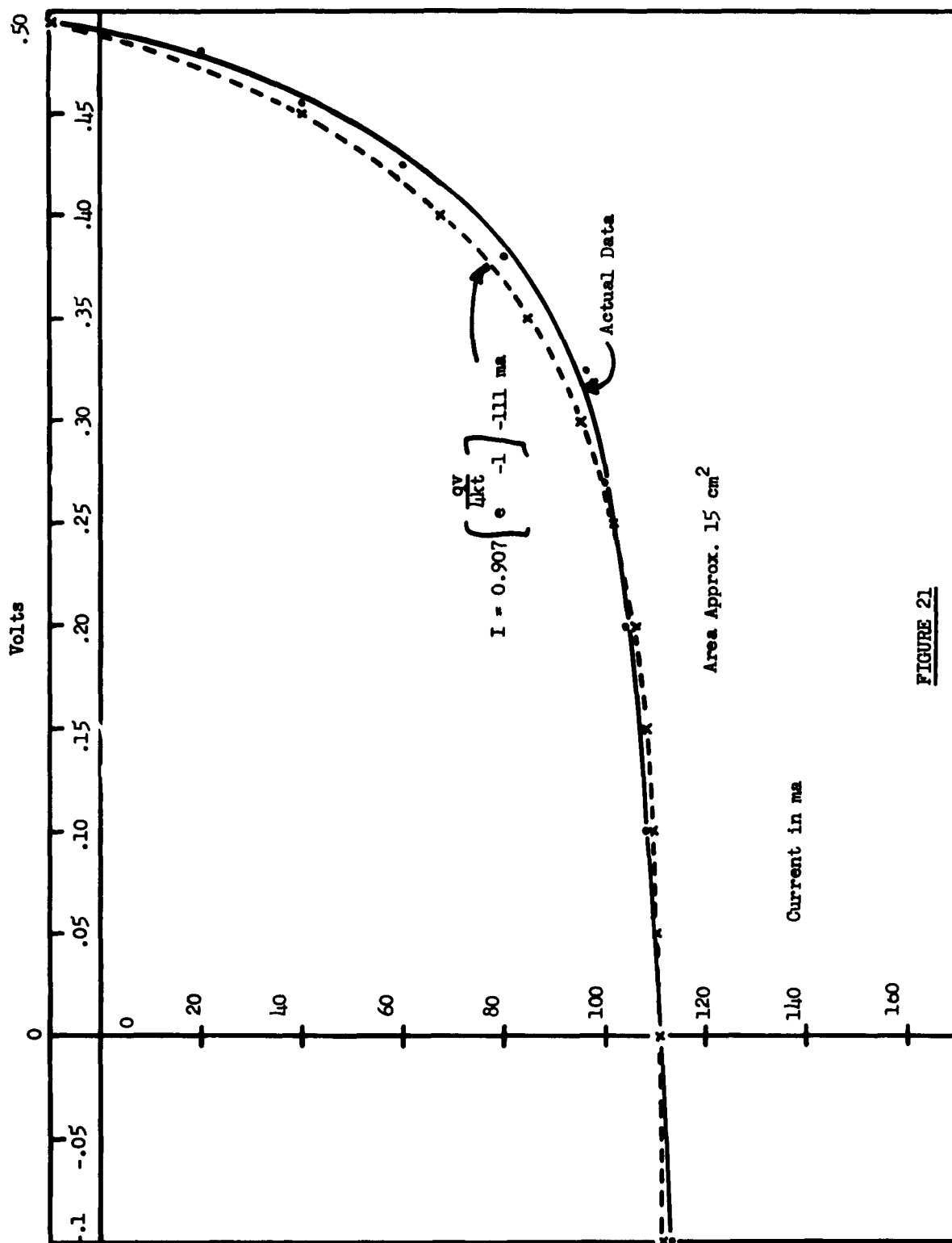


FIGURE 21

ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. X108 WITH 70 LINES PER INCH GOLD SQUARE GRID CONTACT

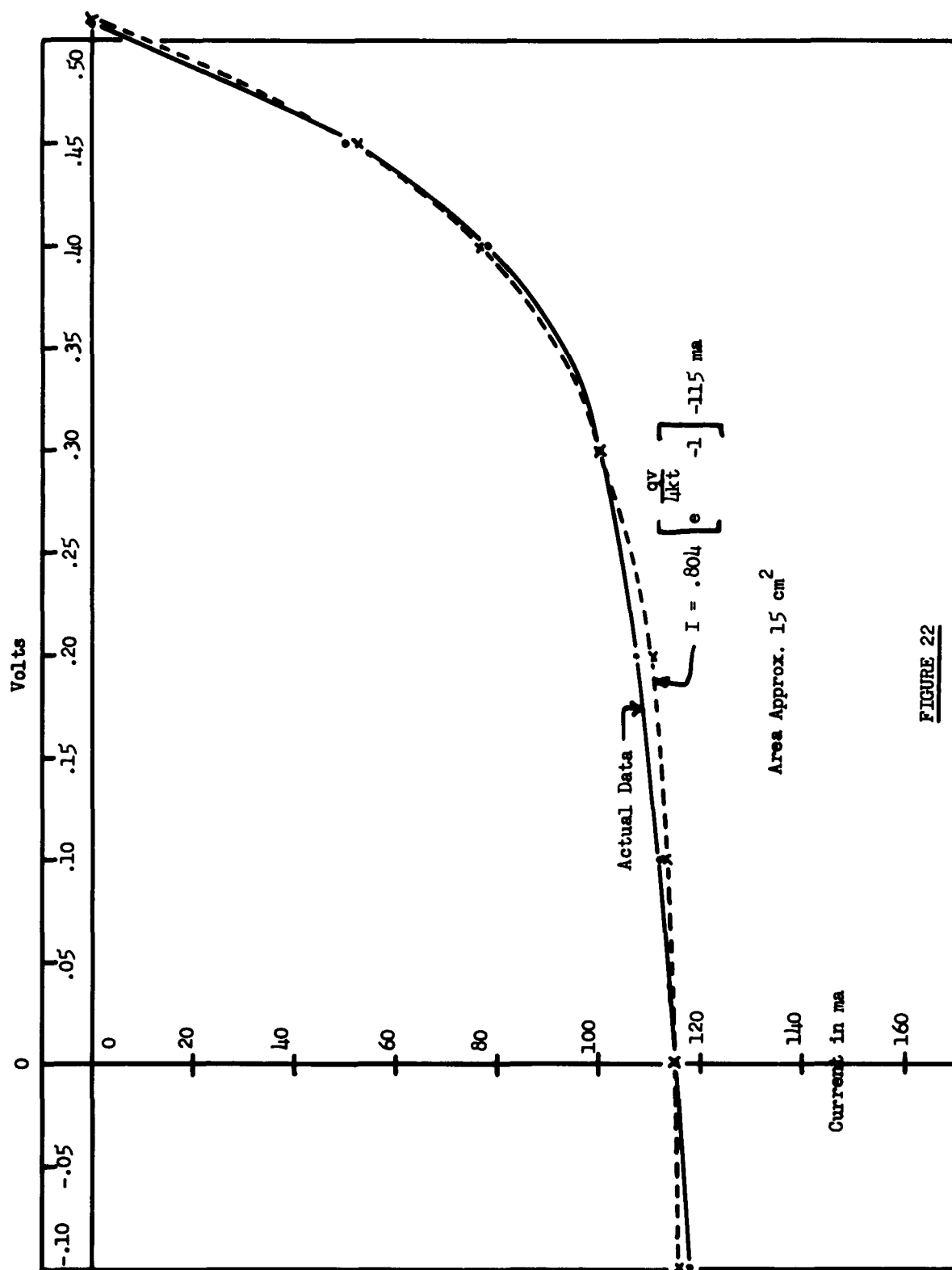


FIGURE 22

ACTUAL AND CALCULATED I-V CURVES FOR CELL NO. X107 WITH 70 LINES PER INCH GOLD SQUARE GRID CONTACT

of a back up rubber diaphragm and gas pressure against the grid and thick glass plate. The unit was designed to operate with pressures of up to 50 psi; and is illustrated in Figure 23. Tank nitrogen controlled by a pressure regulator was applied behind the rubber diaphragm to press the cell against the collector grid and glass plate. A steel frame retained the glass plate. Leads were brought out from the silver collector grid and from the back of the molybdenum substrate. Table III shows the results of testing one cell on this apparatus.

TABLE III
EFFECT OF DIAPHRAGM PRESSURE ON INDICATED CELL OUTPUT USING
EXPERIMENTAL TEST APPARATUS

<u>Pressure</u>	<u>Voc</u>	<u>Isc</u>	<u>Efficiency</u>
0	0.43 V	80 ma	1.0% (hand striped)
0	0	0	0
20	.47	80	1.1
30	.48	84	1.2
40	.48	86	1.3
50	.48	88	1.4

It appears that more pressure is needed in order to adequately duplicate the effect of laminating a collector grid in place. A new apparatus of improved design is being made because the temporary unit was found to be rather cumbersome and inconvenient to use. It does appear that this method of initial cell evaluation can probably be made to work satisfactorily.

ARRAYS OF CELLS

Design of CdS Front Wall Thin Film Cell Arrays

The method of encapsulating thin large area CdS cells by laminating them complete with their interconnections and output leads between two sheets of transparent plastic was described earlier⁽¹⁾. While minor improvements in technique have been made since then, the method remains essentially the same.

Because of the lack of stability of the CdS film cell in the presence of water or water vapor, arrays designed for use where water vapor is present

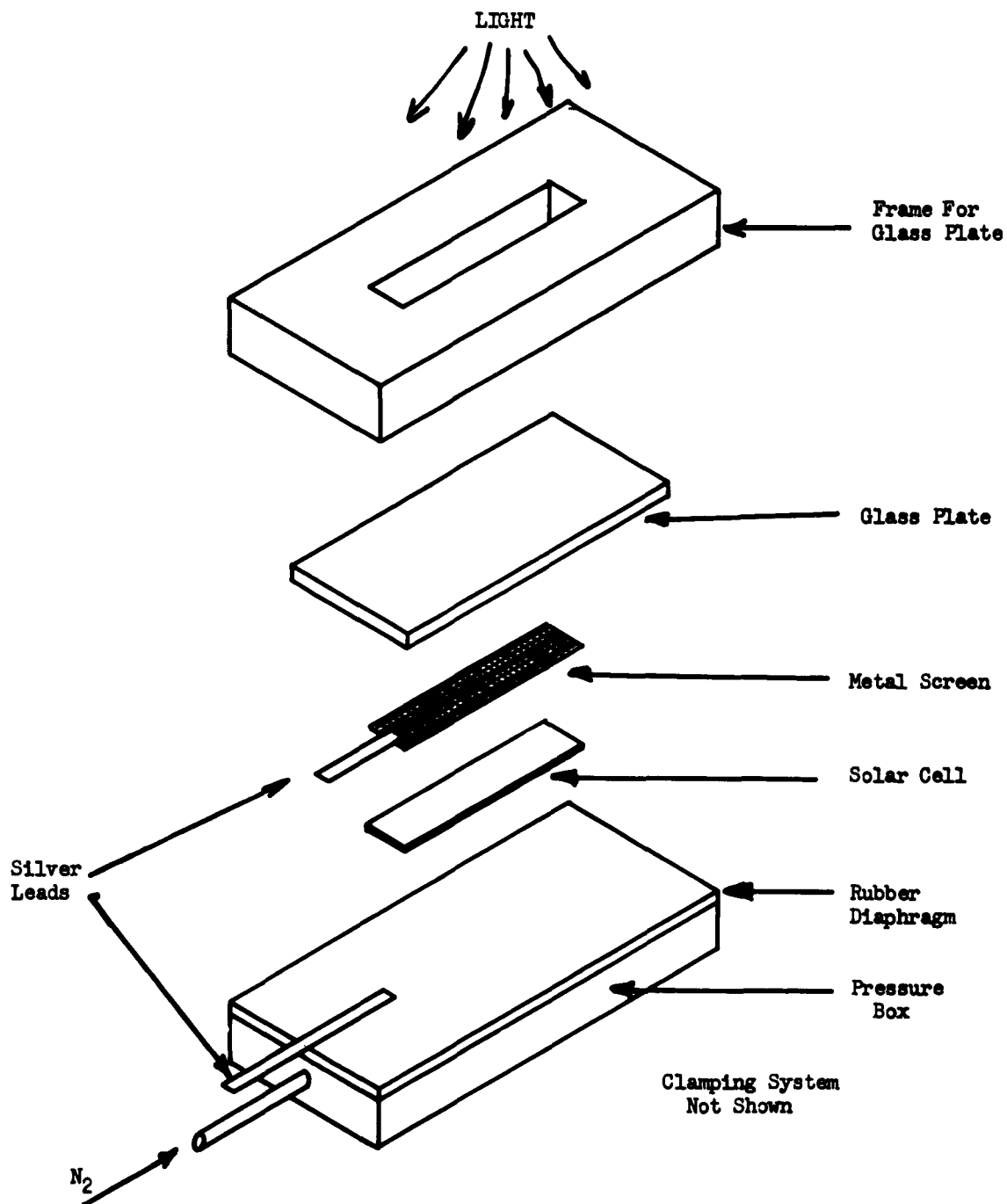


FIGURE 23
 DESIGN OF APPARATUS TO TEST FRONT WALL FILM CELLS
 WITHOUT PERMANENTLY LAMINATING COLLECTOR GRID

(Exploded View)

must be protected from the water vapor. For terrestrial use CdS front wall film cell arrays must be protected by a transparent humidity proof package. Glass or thick plastic layers are possible materials for such a package.

For photovoltaic arrays used in outer space applications the requirements are different. Since there is no water vapor in outer space, the photovoltaic arrays could be stored in a passive state while on earth. They could, for instance, be folded into a small sealed capsule of aluminum foil until they were transported to outer space, and then the capsule could be broken and the array unfolded. The main consideration for a solar cell array in space applications is a high power to weight ratio, and a small volume in its passive state, together with a long life and dimensional stability in its active unfolded state in outer space. There are many design possibilities which would satisfy these requirements. One can visualize a space structure as an array of cells held together by a light plastic film-wire lead structure folded into a capsule and unfolded in space like an umbrella or a sail. Many plastics lend themselves as structural elements for a light weight film type structure; thin films of Mylar, Kel-F, Nylon, Polyethylene, Cellulose Acetate and rubber could all be considered. Although atmosphere is not a factor in outer space, several other factors could have detrimental effects upon a photovoltaic array and must be considered in evaluating a space structure. Cosmic radiation, impact from micrometeorites, temperature cycling between earth shade and sun exposure are some of the more obvious.

Performance of Arrays

There have been a number of 1 x 3" and 3 x 3" area front wall thin film cells laminated into arrays during the period of this report. These were done for a number of different reasons including evaluation of the lamination process, evaluation of various laminating materials, production of arrays for life and environmental storage tests, for demonstration units, etc. Smaller cells were laminated for radiation damage testing studies. During the last few months of the period, the revised collector grid design was evaluated and was made standard as soon as larger supplies of the grids could be obtained.

Because of the wide variety of sizes, designs and purposes involved, the arrays constructed over the 8 month period are definitely not comparable. Table IV lists some of the better arrays constructed towards the end of the period using improved designs and procedures. Included is a 1 square foot array that was delivered to the Contract Monitor. This array is shown in the photograph of Figure 24. The array consisted of 4 smaller arrays of 4 - 3 x 3" cells connected in series. These 4 arrays were connected in parallel to form the square foot array. Under equivalent terrestrial sunlight this 1 square foot array yielded 0.75 watts at 1.3 volts and 0.75 amperes. Its open circuit voltage was 1.75 volts and its short circuit current was 0.80 amperes. At a total weight of 136 grams the array should deliver 3.5 watts per pound in extraterrestrial sunlight.

The maximum power to weight ratio obtained during the period of this contract was measured on a single 3" x 3" cell that was formed on an 0.001" molybdenum metal foil substrate and encapsulated between two 0.00075" thick "Capran" (nylon) plastic sheets. This "array" gave an

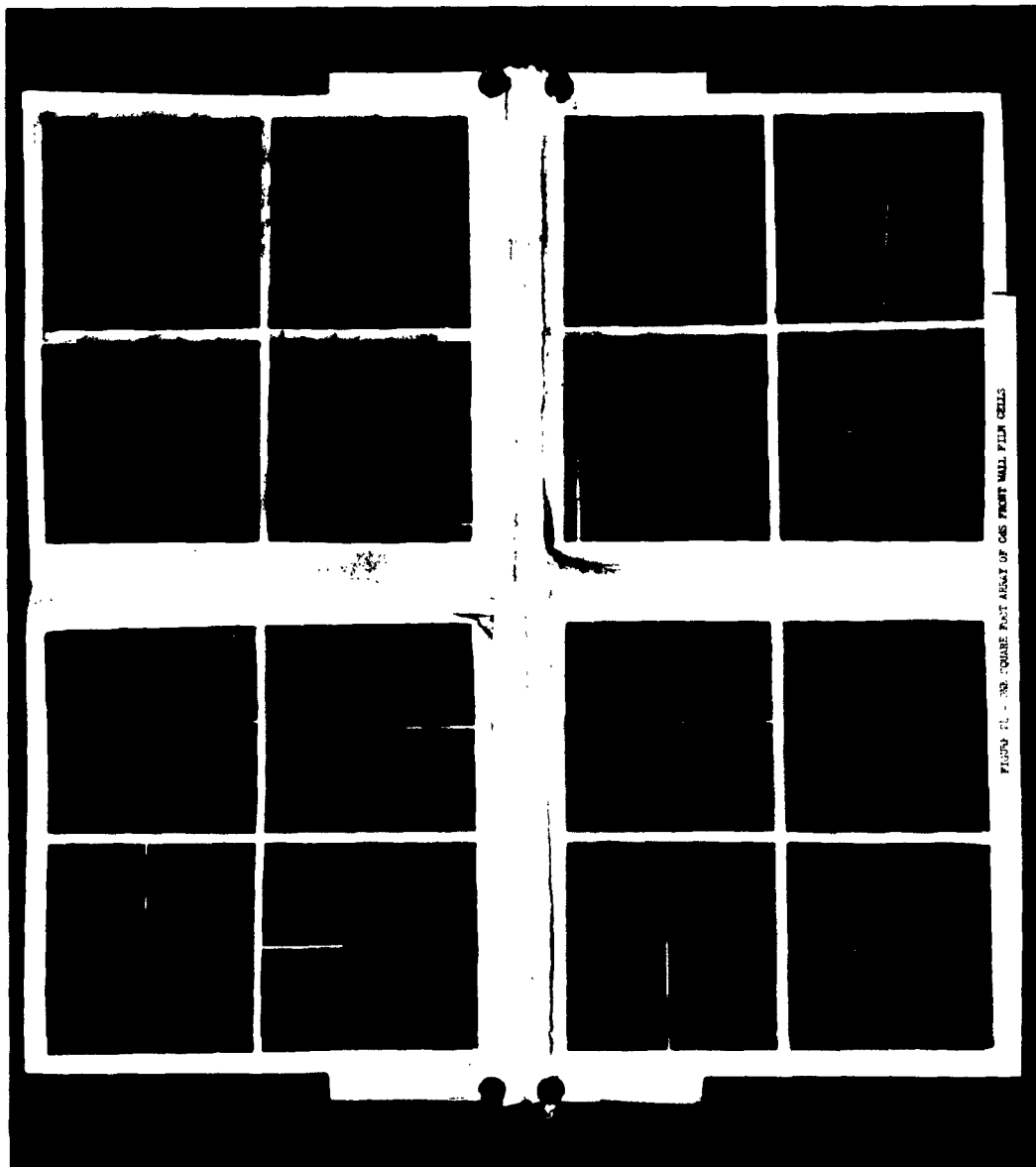


Figure 24. ONE SQUARE FOOT ARRAY OF GAS FRONT WALL FILM CELLS

TABLE IV
PERFORMANCE OF VARIOUS CJS FRONT WALL FILM CELL ARRAYS

<u>Cell No.</u>	<u>Collector Grid</u>	<u>Voc (Volts)</u>	<u>Isc (ma)</u>	<u>Efficiency (%)</u>	<u>Area (cm²)</u>	<u>Wt. (gms.)</u>	<u>Power/weight₂ (at 140 mw/cm²) (watts/lb.)</u>
187 N	Ag	.45	260	<u>3" x 3" Arrays</u> 1.7	39.8	2.5	17.1
138 FN	Au	.49	355	2.6	42	3.1	22.6
139 N	Au	.48	405	2.6	46.8	2.37	33
<u>6" x 6" Arrays</u>							
130 FN	Ag	1.85	300	1.85	184.5	28.3	7.64
135 FN	Ag	1.9	290	1.7	201.6	30.19	5.04
136 FN	Ag	.45	1000	.5	180	31.9	1.76
140 FN	Ag	1.7	260	1.3	194.6	30.69	5.07
141 FN	Ag	.42	840	1.1	168	30.5	3.9
143 FN	Ag	1.7	300	1.5	200.8	30.5	6.45
<u>12" x 12" Array</u>							
197 AN	Ag	1.75	800	1.0	753	136.	3.5

indicated maximum specific power to weight ratio of 33 watts per pound. It is of course to be emphasized that these are merely individual small area components and not large area complete systems. Also, it is not known as yet whether the components as designed will be suitable for the environment of outer space. The data are indicative of progress being made towards the goal of large area high watts per pound devices for space solar energy converters.

Considerations for Unfurling Arrays in Space

Many unfurling film structures are designed for use in daily life applications. Examples are: a roll, a sail, an umbrella, a fan, a window shade, a parachute and a balloon. In space, a mechanical unfurling would probably have to be based on a mechanical means such as spring action or a rotational force such as centrifugal force since gravity forces or air pressure would not normally be available.

The general design of an unfurling device will depend on the design of the space system for which it is intended. The characteristics of the thin film CdS cell including light weight, large area, thinness, flexibility and possible resistance to radiation damage may well give additional degrees of freedom to the design of unfurlable solar cell arrays for space systems. In addition to such readily suggested designs as a rolled film, telescoped fan, inflated balloon, umbrella and an articulated accordion, more sophisticated designs will probably occur to designers in this field.

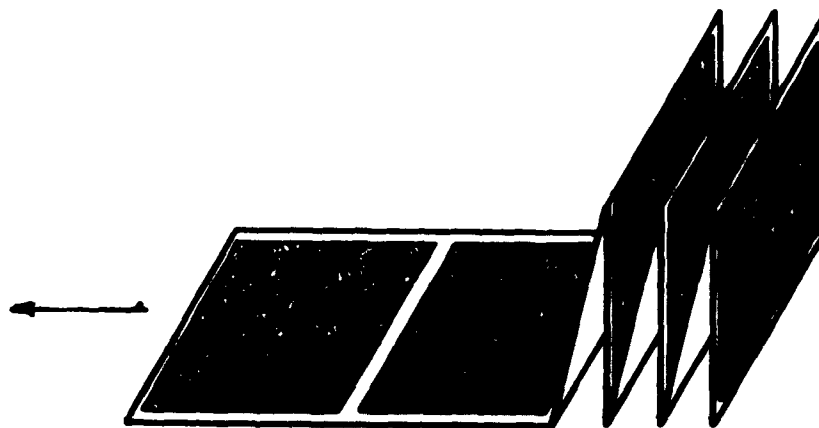
Figure 25 shows two simple methods of furling and unfurling that might be applied to arrays of CdS film cells. Figure 25A shows an articulated design folded like a map and unfurled by applying a force in the direction of the arrow. Figure 25 B shows a rolled rug design with metal springs laminated into the edges of the array. These springs would unroll the array and hold it flat and rigid as soon as the restricting capsule is broken. In this design the metal springs could also be used as conducting leads to carry the electrical current from the array.

Stability Studies

It has been past experience that exposure to humidity reduces the output from CdS single crystal photovoltaic cells. This effect has been remedied by a bake-out, or it has been prevented by protecting the barrier of the cells from moisture. Similar degradation effects from water vapor have been experienced with the CdS thin film cells. Hence, it has been necessary to protect the film cells by storing them in desiccators and/or by encapsulating them in plastic of low water vapor permeability.

At an early stage of this program cells were encapsulated and stored in various atmospheres to determine the long term effects on efficiency. Figures 26, 27, and 28 are plots of the data of cells kept in normal room atmosphere, in a desiccated atmosphere, and in a partial vacuum for approximately 200 days. Table V lists the various encapsulating materials used.

Figure 26 shows typical depreciation curves for CdS film cell arrays



A



B

FIGURE 25
TWO POSSIBLE DESIGNS FOR UNFURLING THIN FILM SOLAR CELL ARRAYS IN SPACE

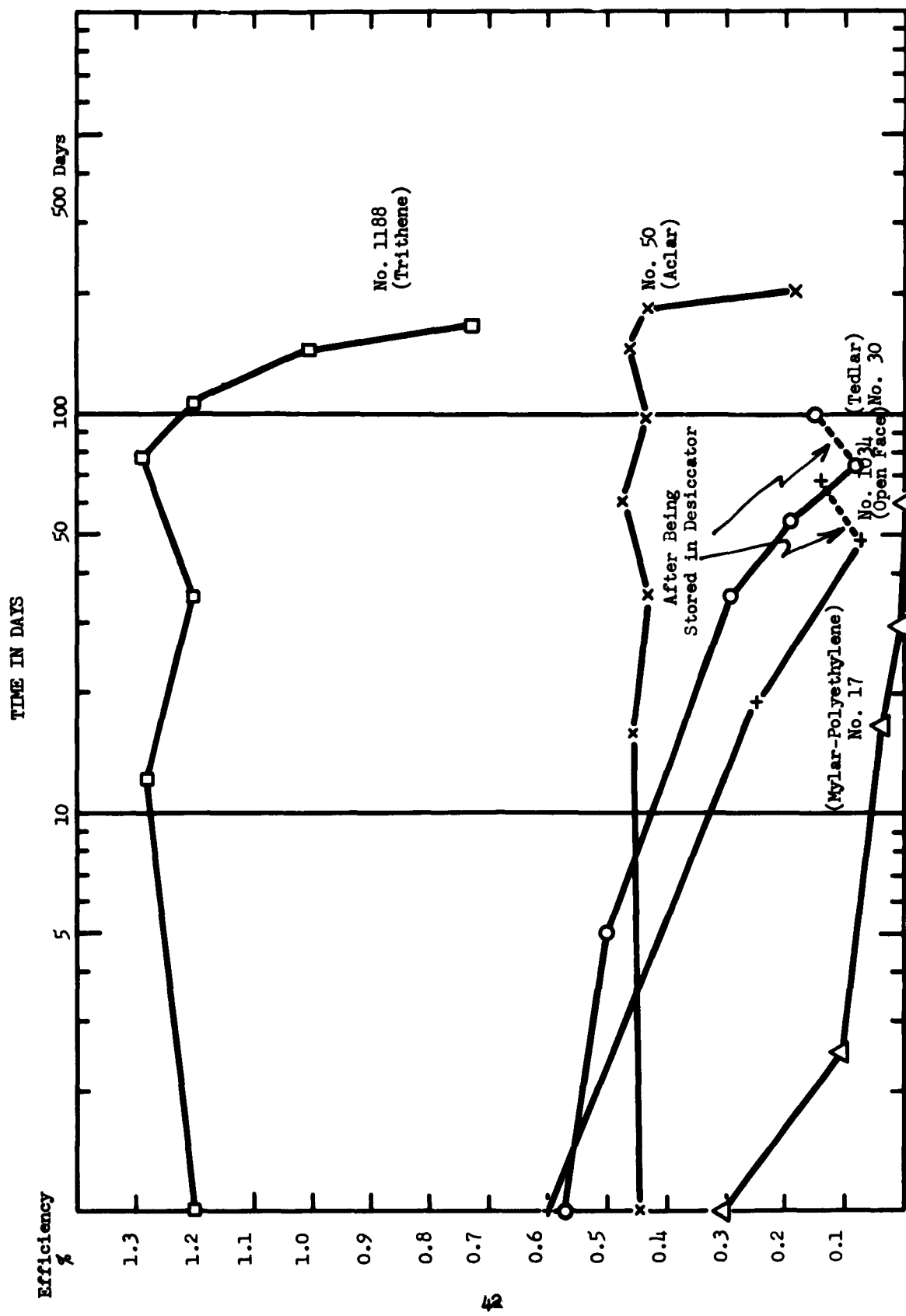


FIGURE 26
ARRAY EFFICIENCY AS A FUNCTION OF TIME FOR CELLS STORED IN NORMAL ROOM ATMOSPHERE

TABLE V
ENVIRONMENTAL LIFE TEST UNIT SPECIFICATIONS

Unit No.	Active Area cm ²	<u>Lamination Plastic</u>		<u>Encapsulation</u>	
		Type	Thick-ness mil	Type	Thick-ness mils
17	14.7	Polyethylene	2	Mylar	1
30	14.0	None	-	Tedlar	2
50	14.0	None	-	Aclar	5
60	15.0	Capran	3/4	Trithene B	4
61	15.0	Capran	3/4	Trithene B	4
62	15.0	None	-	Visotherm	5
1034	15.9	None	-	None	-
1040	15.0	None	-	None	-
1188	7.5	Capran	3/4	Trithene A	1-1/2

exposed to the normal room atmosphere for about 200 days. It is very apparent that the efficiency will decrease in proportion to the amount of moisture that can come in contact with the CdS material. The unprotected cell (No. 1034) and those laminated in plastics that are relatively permeable to water vapor such as Mylar-Polyethylene (No. 17), and Polyvinyl Fluoride (No. 30), depreciated to 10 percent of their initial efficiency within 1 to 2 months. Contrast this with the curves obtained for cells encapsulated in plastics of low moisture and water vapor permeability such as the Polychlorofluoro-ethylenes, Trithene and Aclar, where little or no depreciation has taken place over the test period.

Figure 27 illustrates the improvement that is obtained by storage of thin film large area CdS cells in a desiccated atmosphere. Cell number 62 encapsulated in 5 mil Polyethylene, and cell No. 60 encapsulated in Trithene B, exhibited significant efficiency increases with time indicating a removal of detrimental moisture from the cells. Cell No. 62 increased in efficiency more rapidly probably due to the higher water vapor permeability of the Polyethylene. Cell number 17, 30, and 1034 were taken from the room atmosphere test after about 2 months and were placed in a desiccator. As can be seen in Figure 27 numbers 30, and 1034 immediately began to recover. Cell No. 17 has not responded, and is not plotted. This correlates well with the laboratory atmosphere tests with respect to the plastics and water vapor permeability when it is remembered that in the first instance the

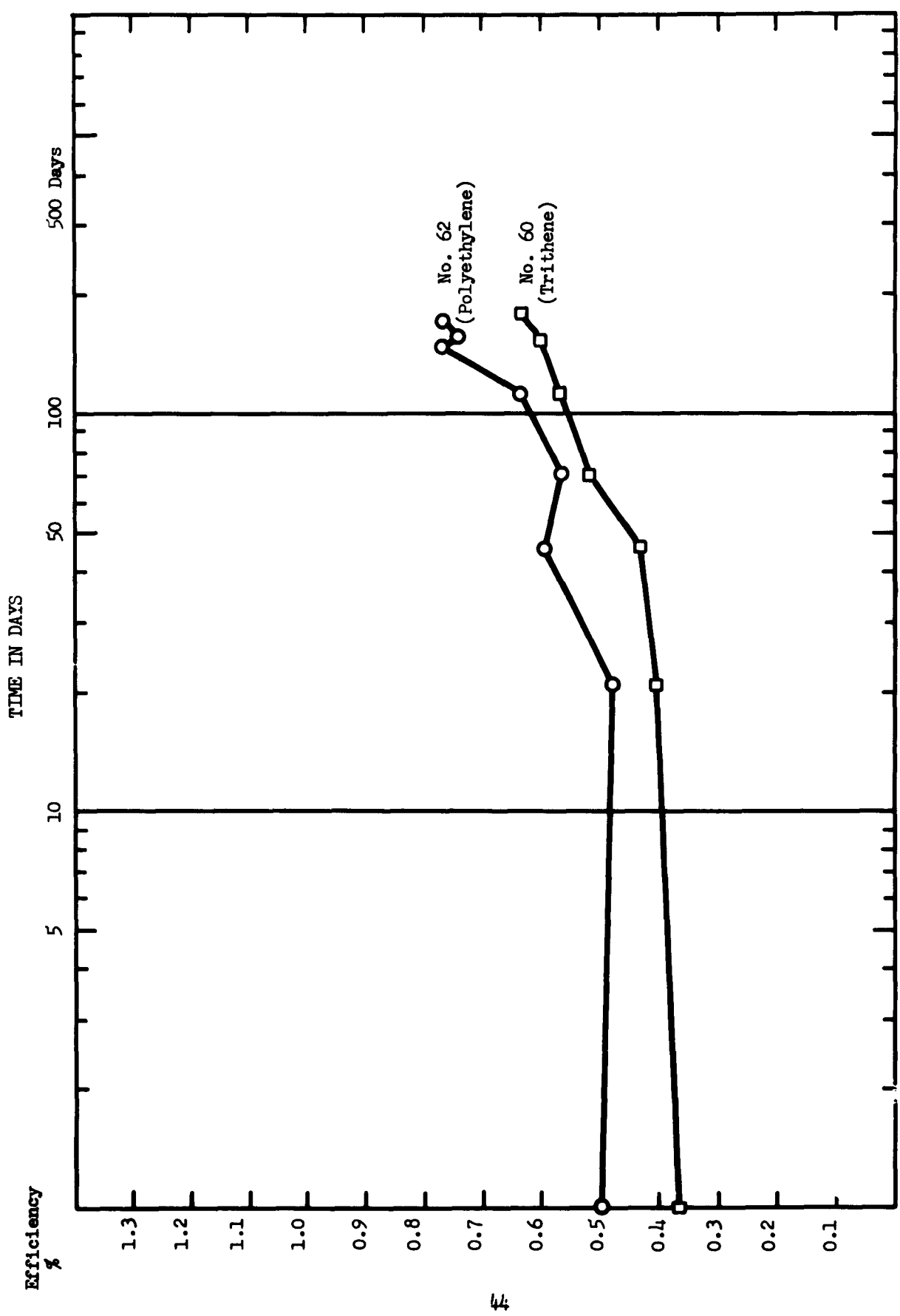


FIGURE 27
ARRAY EFFICIENCY AS A FUNCTION OF TIME FOR CELLS STORED IN A DESICCATOR

water vapor is entering and in the second case the water vapor is leaving the cell.

Figure 28 illustrates a preliminary vacuum storage test to determine the stability of CdS cells in such an environment. Unfortunately, the seal of the system was not completely tight, and as a result air leaked into the system slowly. The vacuum was maintained intermittently only, since a pump was not permanently attached to the system. Thus the test was not completely satisfactory.

Cell No. 1140, Figure 28, was unprotected, while No. 61 was encapsulated in Trithene. Both cells held up well. During the test period, Cell No. 1140 behaved somewhat erratically. This might be expected with an unprotected barrier where water vapor could be adsorbed or released freely depending on the state of the vacuum. In general, the three tests confirm previous experience that moisture has an adverse effect on the CdS photovoltaic barriers.

Radiation Damage Tests

Initial radiation damage tests on CdS film cells were run at the RCA Laboratories and reported at the IAPG sponsored conference on Radiation Damage Testing of Solar Cells held at NASA Hq. February 28, 1962.⁽⁹⁾ The indications from these very preliminary tests were that CdS film cells might possess appreciably greater resistance to radiation damage than higher efficiency silicon cells - even of the n-on-p type.

Since CdS photovoltaic cells have an extremely thin barrier region - on the order of 0.1 microns, it is conceivable that damage effects would not be localized in this very thin region as readily as they would be for cells with appreciably thicker barrier regions. Also, it is entirely possible that different degrees of radiation resistance might be exhibited by the three types of cells, i.e. front wall film, rear wall film, and by the single crystal CdS cells. The RCA tests were apparently run on the back wall film cells on conducting glass substrates. It is not known whether the radiation was incident directly on the cell barriers or through the glass substrate and CdS film.

During this period, accelerated radiation damage tests were kindly conducted on Harshaw fabricated CdS evaporated film cells by the U. S. Naval Research Laboratory. These tests were run by Mr. Richard L. Statler of the Insulation Section, Electromagnetic Materials Branch, Solid State Division through the cooperation of Mr. E. L. Brancato, Head of the Insulation Section.

Two series of tests were run. In the first series, CdS front wall film cells on molybdenum substrates were laminated in different plastic film encapsulating materials and exposed to 1.5 Mev electrons while other samples were exposed to 1.1 to 1.2 Mev radiation from a Co⁶⁰ source. The results are summarized in Table VI. While the results are somewhat scattered, it can be seen that the initial indications for possible radiation resistance with the CdS film cells are favorable. This is the case in spite of a complicating feature of these tests - i.e. that the cells were not cooled

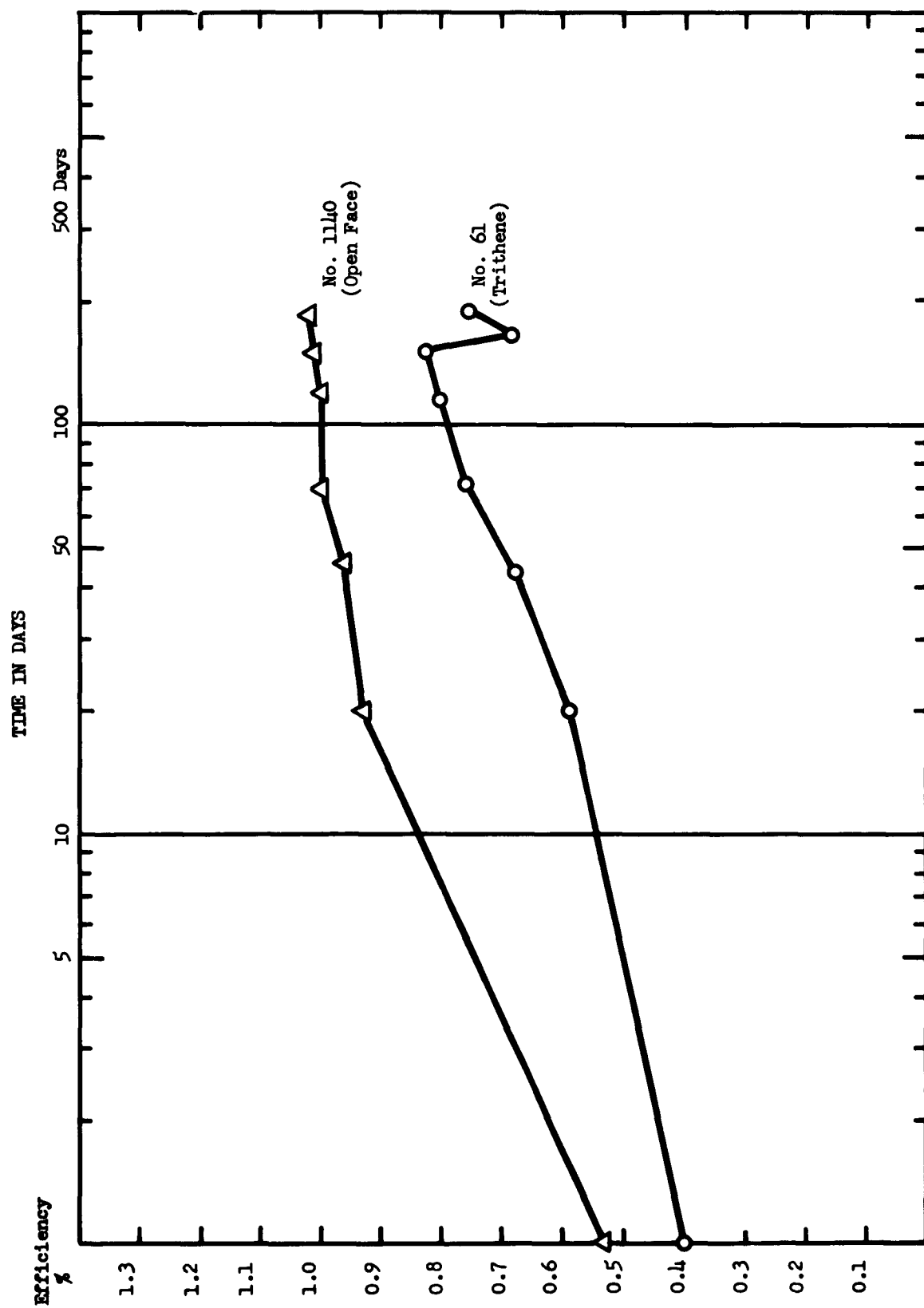


FIGURE 28
ARRAY EFFICIENCY AS A FUNCTION OF TIME FOR CELLS STORED IN PARTIAL VACUUM

TABLE VI
FIRST RADIATION DAMAGE TEST
(CdS Front Wall Cells On Molybdenum Substrates)

<u>Cell No.</u>	<u>Material Between Barrier and Radiation</u>	<u>Damage as Percent Decrease in I_{sc}</u>	<u>Radiation</u>	<u>Total Flux</u>
N-94	0.00075" Capran	20	1.5 Mev electrons	1.5×10^{17} electrons/cm ²
MP-97	0.001" Mylar + 0.002" Polyethylene	20	1.5 Mev electrons	1.5×10^{17} electrons/cm ²
F-87	0.004" Trithene	20	1.5 Mev electrons	1.5×10^{17} electrons/cm ²
FN-91	0.004" Trithene + 0.00075" Capran	15	1.5 Mev electrons	1.5×10^{17} electrons/cm ²
FN-89	0.004" Trithene + 0.00075" Capran	20	1.1 to 1.2 Mev gammas	Co ⁶⁰ 1.3×10^8 Roentgens
MP-96	0.001" Mylar + 0.002" Polyethylene	3	1.1 to 1.2 Mev gammas	Co ⁶⁰ 1.3×10^8 Roentgens
N-95	0.00075" Capran	25	1.1 to 1.2 Mev gammas	Co ⁶⁰ 1.3×10^8 Roentgens
F-83	0.004" Trithene	25	1.1 to 1.2 Mev gammas	Co ⁶⁰ 1.3×10^8 Roentgens

NOTE: Temperature of samples was not regulated.

during the tests and consequently there was considerable charring of the plastic encapsulating layer due to overheating of the plastic at the high radiation intensities employed. This charring and delamination of the plastic must have made it much more difficult to get the light to the cell for the final cell efficiency tests and hence have probably indicated a greater drop in output of the cells than actually occurred due to radiation damage of the barriers.

Therefore, a second series of tests were run and during this test the cells were cooled so that in no case did the temperature of the cells exceed 30°C. These data are given in Table VII. Here the results are scattered even more widely than in the first series of tests. It does appear that the type of plastic encapsulant may have a considerable influence on the degree of radiation resistance imparted to the arrays. The Kel-F Nylon combination seems to have performed best in this respect.

One back wall single crystal cell was included in this test series, and in effect this cell was protected by 2 mm of CdS. As expected, it stood up to the radiation fairly well. Some of the completely unprotected cells showed the greatest deterioration from the bombardment.

While these tests are highly preliminary, it does appear that at least in a few instances, and in a few configurations, the CdS evaporated thin film photovoltaic cell could possess appreciable resistance to radiation damage of the types normally associated with the Van Allen belts. Certainly many more tests of radiation resistance are needed before this factor can be defined with any reasonable degree of accuracy.

CRYSTAL STRUCTURE STUDIES

The overall aim of the structural studies program has been to determine the influence of crystal structure on the thin film CdS solar cell now being developed in this laboratory. The influence of such structure parameters as orientation, grain boundaries, and dislocations have been and are now being studied. Enough data has been accumulated so that some tentative conclusions can be made as to the influence of crystal orientation and a program has been devised to examine this influence further. Experimental techniques necessary for the investigation of the influence of grain boundaries and dislocations are nearing a stage where they may be directly applicable to the examination of these influences on thin films.

Grain Growth

Grains up to 100 microns in diameter have been observed to grow on films of CdS deposited on both glass and molybdenum substrates when these films are heated to 800°-900°C for 3 to 5 minutes in open atmospheres. To date, the easiest method of accomplishing this growth has been to heat the films with a Bunsen burner, letting the flame of the burner pass over the surface of the film. This technique appears to have the effect of

TABLE VII
SECOND RADIATION DAMAGE TEST
(CdS Front Wall Cells On Molybdenum Substrates)

<u>Cell No.</u>	<u>Material Between Barrier and Radiation</u>	<u>Damage as Percent Decrease in Isc</u>	<u>Total Flux</u>
M-6	0.001" Mylar + 0.002" Polyethylene	10	1.4×10^{16} electrons/cm ² (1 Mev)
M-4	0.001" Mylar + 0.002" Polyethylene	79	1.4×10^{16} electrons/cm ² (1 Mev)
FN-2	0.005" Trithene + 0.00075" Capran	0	1.4×10^{16} electrons/cm ² (1 Mev)
FN-5	0.005" Trithene + 0.00075" Capran	5	1.4×10^{16} electrons/cm ² (1 Mev)
O-6	None	41	1.4×10^{16} electrons/cm ² (1 Mev)
O-2	None	14	1.4×10^{16} electrons/cm ² (1 Mev)
37	2 mm CdS (Potted Single Crystal)	9	1.4×10^{16} electrons/cm ² (1 Mev)
FN-3	0.005" Trithene + 0.00075" Capran	13	6×10^{15} electrons/cm ² (1 Mev)
FN-6	0.005" Trithene + 0.00075" Capran	59	6×10^{15} electrons/cm ² (1 Mev)
M-2	0.001" Mylar + 0.002" Polyethylene	13	6×10^{15} electrons/cm ² (1 Mev)
O-5	None	48	6×10^{15} electrons/cm ² (1 Mev)
FN-7	0.005" Trithene + 0.00075" Capran	15	1.3×10^{12} protons/cm ² (5 Mev)
O-4	None	88	1.3×10^{12} protons/cm ² (5 Mev)

NOTE: Temperature of all samples kept below 30°C.

a-As Received From Evaporator

(500 X)

b-After Heating

(500 X)

FIGURE 29
CdS FILM ON MOLYBDENUM SUBSTRATE - BEFORE AND AFTER HEAT
TREATMENT TO CAUSE GRAIN GROWTH

minimizing the formation of CdO which forms quite rapidly when films are heated in a furnace. Figure 29 a and b shows a CdS film on a molybdenum substrate before and after a heat treatment, respectively.

This method of grain growth has an apparent advantage over that used by van Cakenberghe⁽⁶⁾ in that no predeposition of metal atoms has been used to initiate the grain growth. Thus during the heat treatment, none of the metal atoms which are detrimental to the production of a photovoltaic cell are present. The use of this grain growth method has in fact produced a workable photovoltaic cell (Figure 30,) while all attempts in this laboratory to fabricate a workable cell from CdS films treated by the van Cakenberghe method have not succeeded.

Observations of films on which grains have been grown by the above method and on which a barrier has been fabricated by a chemical means, i.e. by dipping the film into a hot aqueous solution of CuCl, show a very obvious difference between the darkening of various grains of the film. This variation in darkening, which in the past has shown a correlation with photovoltaic efficiency on both single crystals and on polycrystalline films, suggests an orientation dependence of cell photovoltaic output. A program has therefore been started to investigate whether this dependence exists and if it does how it can be best used.

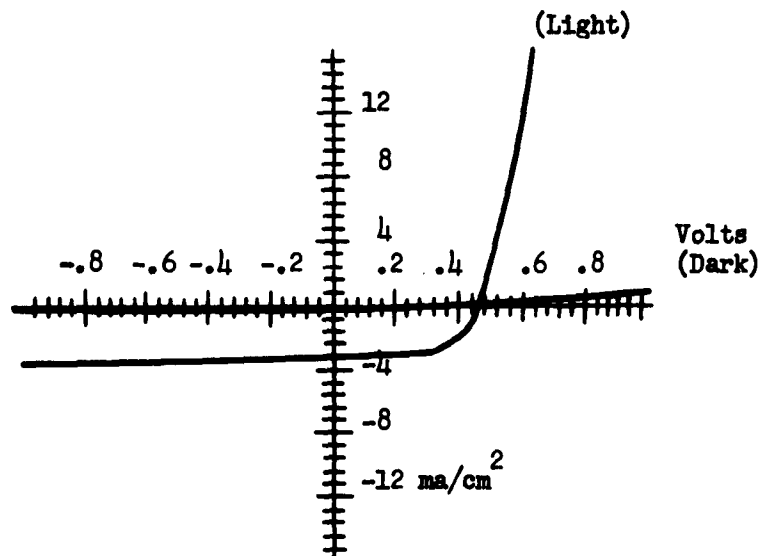


FIGURE 30
I-V CURVE OF CELL PRODUCED FROM HEAT TREATED EVAPORATED
CdS FILM ON MOLYBDENUM SUBSTRATE

Orientation Studies

Orientation investigations have been made on CdS single crystals from two different growth runs. Both runs were indium doped. The samples used were cut into 2 mm x 5 mm x 10 mm parallelepipeds with their large face containing the (0001), (10 $\bar{1}$ 0), and (10 $\bar{1}$ 1) planes respectively. Because the crystals are noncentrosymmetric along the c-axis, both positive and negative planes of (0001) and (10 $\bar{1}$ 1) planes were used, i.e. (0001) (000 $\bar{1}$), (10 $\bar{1}$ 1) and (10 $\bar{1}$ $\bar{1}$). The barrier was applied to these crystals by a chemical deposition process whereby the crystals are dipped into a saturated boiling solution of CuCl. After measurements were completed, the barriers were removed by lapping and the crystals reused.

Figure 31 shows the graphs of photovoltaic efficiency for varying times of dipping in the barrier producing solution for crystals of the different orientations for both growth runs. It can be seen that higher efficiencies were obtained on the (10 $\bar{1}$ 0), (10 $\bar{1}$ $\bar{1}$), and (10 $\bar{1}$ 1) planes of both crystals for short dip times. Longer dip times produced different results; in one group of crystals a marked decrease in efficiency on these same planes was noted while in the other case no decrease was noted. No appreciable decrease was noted in either group of crystals for barriers made on the basal planes.

The efficiency differences noted need further investigation. The contribution of surface pre-treatment should be examined to determine what effect various pre-barrier treatments have on cell efficiencies and to see if the apparent efficiency differences are associated with any specific pre-barrier treatment.

Etching Studies

The etching studies have been directed toward the determination of the orientation of grains in CdS films and toward an understanding of the influence of dislocations on the electrical properties of the cells. To date single crystal slices have been employed whenever possible since it is easier to use single crystals of the desired orientation to determine and study pit shape development. A great deal of information has been gathered on the etching behavior of CdS and as a result, work is now being directed toward finding an etchant and a technique of etching that will be suitable for orientation and dislocation studies on thin films.

Both crystal grain orientation and dislocation content in various grains are being investigated. The grain orientation studies are necessary in light of the difference in cell efficiencies noted on single crystals of different orientations and the observed differences in darkening of different grains on films on which grain growth has occurred. Dislocation studies are necessary because of the known influence dislocations have on many single crystal devices. Particular attention will be placed on the determination of the effect electrically active α and β dislocations have on the cell performance.

Various etchants have been used to reveal etch pits and light figure patterns on different crystallographic planes of CdS crystals. HCl and

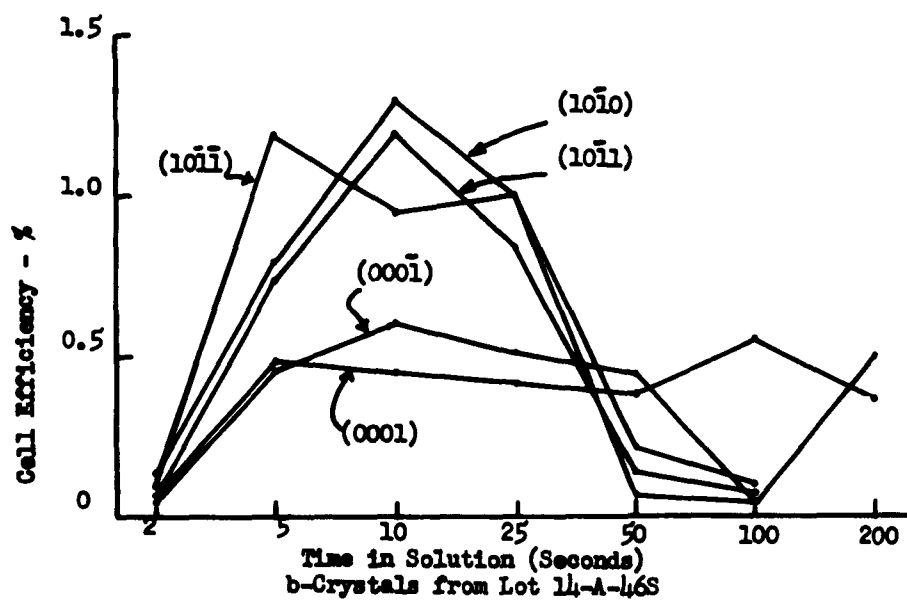
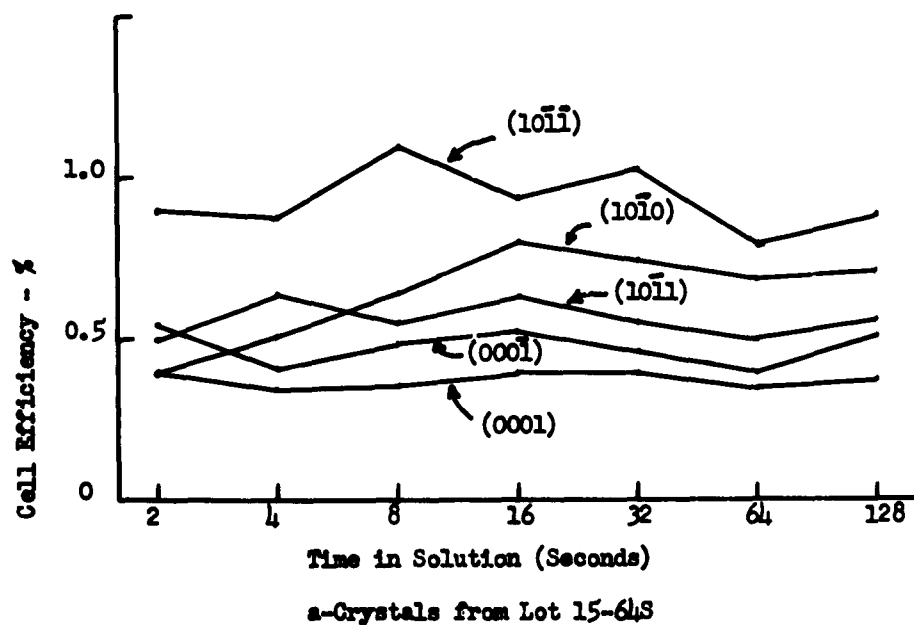


FIGURE 31
 OUTPUTS FROM CHEMICALLY DEPOSITED BARRIERS ON VARIOUS Cds SINGLE
 CRYSTAL PLANES FOR DIFFERENT IMMERSION TIMES

HNO_3 in their concentrated form have been used to expose etch pits on the (0001) and (1011) planes. The etch pit shape and their light figure patterns are shown in Figure 32. These pit shapes are characteristic of the surfaces in question and can be used quite effectively to determine orientation. Etch pits have also been revealed on the (0001) and (1010) planes by the use of an AgNO_3 -fuming HNO_3 etchant. These pit shapes and their corresponding light figure patterns are shown in Figure 33. It is to be noted that dislocations are revealed on both the (0001) and (0001) planes by the etchant in question.

The latter etchant (AgNO_3 -fuming HNO_3) is slow acting. This makes it applicable to the etching of polycrystalline films. Work is now being undertaken to determine the proper concentrations of AgNO_3 needed in the fuming HNO_3 to produce recognizable etch pit forms on polycrystalline films.

Other etchants such as H_2SO_4 are being studied for possible use on CdS thin films. This etchant has been used successfully as a polishing etch, a preferential etch, and a dislocation revealing etch. CdS etched in boiling H_2SO_4 - H_2O (3:1) solutions resulted in polished surfaces. Preferential etch forms (solution forms) result when CdS is etched in boiling dilute H_2SO_4 - H_2O (1:6) solutions. Dislocations have been revealed when CdS is etched in concentrated H_2SO_4 at room temperature. It too is a slow acting etchant and will be used to etch polycrystalline films.

Grain Boundary Studies

When CdS is grown by vapor deposition onto seed plates, grains of various orientations nucleate and grow. Some grains expand and grow at the expense of others. It would be interesting and perhaps useful to know what influence neighboring grains have on each other. A program has, therefore, been initiated to investigate the growth of seed plate crystals.

One seed plate crystal containing five grains has been investigated. The orientation of the various grains was determined by etching the crystals with concentrated HCl and determining their orientation with respect to the substrate by use of the light figure technique. Figure 34 shows a picture of the crystal ingot. The size of the crystals at the substrate and after growth was completed have been compared and the effective orientation of their interfaces determined. From these results a tentative correlation has been made between the grain orientation of neighboring grains and spreading or receding of each grain as the growth front of the ingot moves away from the substrate. First indications are that: (1) when two neighboring grains have their c-axes parallel to the axis of the seed plate, the interface is also parallel to that axis; (2) when the c-axes of two neighboring grains are perpendicular to the axis of the substrate (parallel to the plane of the substrate), their interface will also be parallel to the substrate axis; and (3) when the c-axes of two grains are perpendicular to one another, the grain with its c-axis perpendicular to the axis of the substrate will expand and spread at the expense of the other grain.



(500 X)

a - Etch pits formed on the (0001) plane from a 1 minute etch in Conc. HNO_3

INSERT - Light figure pattern which results when parallel light beam is reflected onto a screen parallel to the (0001) plane. Note that the "spokes" of the light figure represent light reflected from the side walls of the etch pits.

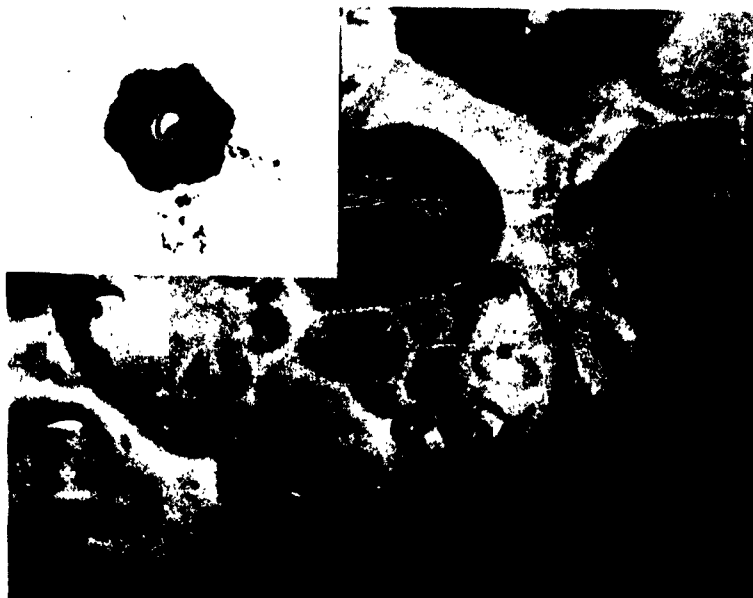


(500 X)

b - Etch pits formed on the (1011) plane from a 1 minute etch in Conc. HNO_3

INSERT - Light figure pattern characteristic of reflections from the (1011) plane of CdS crystals.

FIGURE 32
ETCH PITS AND LIGHT FIGURE PATTERNS FROM (0001) and (1011) PLANES OF CdS SINGLE CRYSTALS



(500 X)

a - Etch Pits formed on the $(000\bar{1})$ plane after a 5 minute etch in a fuming HNO_3 - AgNO_3 Solution

INSERT - Light figure pattern characteristic of reflections from the $(000\bar{1})$ plane of CdS crystals



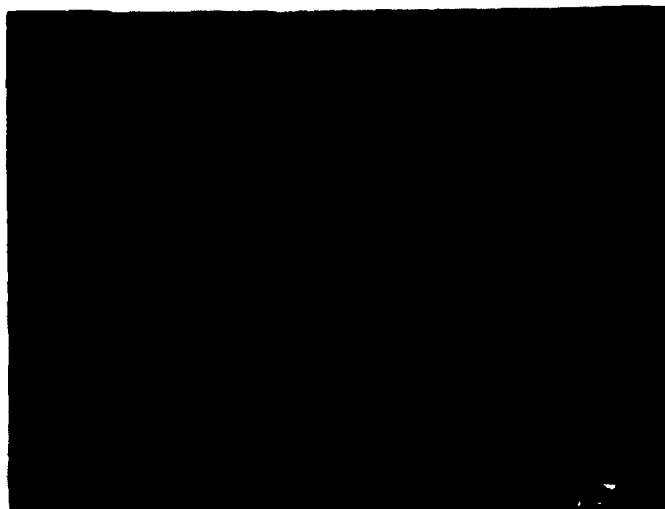
(500 X)

b - Etch Pits formed on the $(10\bar{1}0)$ plane after a 5 minute etch in a fuming HNO_3 - AgNO_3 solution.

INSERT - Light figure pattern characteristic of reflections from the $(10\bar{1}0)$ plane of CdS Crystals.

FIGURE 33

ETCH PITS AND LIGHT FIGURE PATTERNS FROM $(000\bar{1})$ AND $(10\bar{1}0)$ PLANES OF CdS SINGLE CRYSTALS



(Actual Size)

FIGURE 3:

CdS POLYCRYSTALLINE INDOT CONTAINING 5 CRYSTALLITES

Further analysis of this ingot is under way to determine the influence of the substrate on the orientation of the various grains and to better understand the influence of the slight tilts of the grain axes with the substrate axis on the orientation of the interface. Another ingot containing many more grains is also being prepared for investigation.

It is hoped that the results obtained from these ingot studies can be applied in a similar way to CdS films. It seems entirely likely that this will be possible if the conclusions regarding the influence of grain orientation on grain boundary interfaces are shown to hold.

Polarity Studies

In the CdS crystals under study the structure is of the wurtzite type and is noncentrosymmetric. The diatomic layer structure along the $[0001]$ direction can be unambiguously determined only by x-rays. If the crystallographic parameters are defined so the Cd atoms are located at the origin, the (000ℓ) planes will then consist of Cd atoms. The x-ray (000ℓ) reflections will be indicative of the scattering of the Cd layers along this particular direction. In a similar manner the $(000\bar{\ell})$ reflections will represent the S atom layers. The intensity difference of the (000ℓ) and $(000\bar{\ell})$ reflections arises from the dispersion corrections when the x-rays have a wavelength in the vicinity of an absorption edge.

Polarity can also be determined by etching studies, piezoelectric, and pyroelectric measurements. In these cases reference must always be made to the x-ray techniques because they alone are absolute. However the others are of value because of time saving, availability of apparatus, and simplicity. This is particularly true of etchants because of their wide use in dislocation studies, crystal growth and orientation, and identification of selected planes. In the Harshaw Laboratories these are constantly being applied to both single crystals and polycrystalline films in connection with photovoltaic effects. It therefore became imperative to run determinations of polarity to provide a consistent and independent correlation with etching behavior.

The general method chosen was patterned after that of E.P. Warekois et al.⁽¹⁰⁾ Single crystals were cut into plates of about 1 cm x 2 cm by 2 mm thick. The cuts were performed as nearly as possible parallel to the (000ℓ) planes with the large faces in the plane. The crystals were carefully mounted in the holder of a fluorescent x-ray spectrometer. Chromium radiation was utilized for all measurements and was obtained from a suitable salt. A Geiger counter was the detector and the counting rate was adjusted to fall in the linear range. Integrated intensities were obtained by the moving crystal-moving counter technique. In the wurtzite structure the (000ℓ) reflections for $\ell = 4n$ should be equivalent in intensity while for $\ell = 2n$ the measurements should be different for opposite faces. The data were taken to be significant only if the (0004) and $(000\bar{4})$ reflections actually proved to be equal within a few percent. Under these conditions the intensity ratio $I(000\ell)/I(000\bar{\ell})$ proved to be very close to the computed values. Two determinations were made on each of two crystals of a different origin. The results are actually given in Table VIII. The calculated ratios were obtained from extrapolations of published dispersion corrections for Cr $K\alpha$. In most crystals examined the data were significant to positively identify the polarity. However some crystals gave poor results which could only be attributed to misorientation, perfection, or other unknown difficulties.

TABLE VIII
INTEGRATED X-RAY INTENSITIES FROM (000 ℓ) PLANES OF CdS

<u>Crystal</u>	<u>Reflection</u>	<u>Integrated Intensity</u>	<u>Experimental Ratio (000 ℓ)/(000 $\bar{\ell}$)</u>	<u>Calculated Ratio (000 ℓ)/(000 $\bar{\ell}$)</u>
1	(0002)	41300	0.80	0.82
	(000 $\bar{2}$)	51400		
	(000 $\frac{1}{4}$)	21300	1.06	1.00
	(000 $\frac{1}{4}$)	20000		
2	(000 $\frac{1}{2}$)	36850	0.89	0.82
	(000 $\frac{1}{2}$)	411400		
	(000 $\frac{1}{4}$)	9520	1.03	1.00
	(000 $\frac{1}{4}$)	9250		

Pole Figure Studies on Polycrystalline Films

Similar to many other vacuum deposited films, the structure of CdS may be greatly influenced by the nature of the substrate, the vacuum preparation conditions, and the type of post treatment. It has been found in these laboratories, and in reports of other workers, that most CdS films deposit with the c-axes of the grains perpendicular to the substrate. An X-ray photograph with the beam perpendicular to the plane of the deposit shows a random orientation of all crystallographic planes (Figure 35). X-ray photographs with the beam parallel to the plane of the film give a single crystal type pattern which could only arise from a nearly perfect preferred orientation (Figure 36). The nature of this preferred orientation is quite analogous to that in large crystalline ingots grown from the vapor phase. In order to investigate the orientation in a more quantitative manner, a pole figure of the (0002) planes was constructed. This is eventually to be performed for CdS films deposited on amorphous and crystalline substrates. Figure 37 shows the (0002) pole figure for a film deposited on a molybdenum substrate. The pole figure indicates that only a small fraction of crystallites have their C-axes not perpendicular to the substrate. The exact cause of this is not readily determined but must come from the mode of nucleation and growth. It may be pointed out here that the choice of substrate may not be influenced by the "critical misfit condition" namely that the deposited layer should have the same type structure and lattice parameter as the substrate. However the main purpose of the work is for an accurate description of orientation in relation to the origin, type, and study of dislocation phenomena.

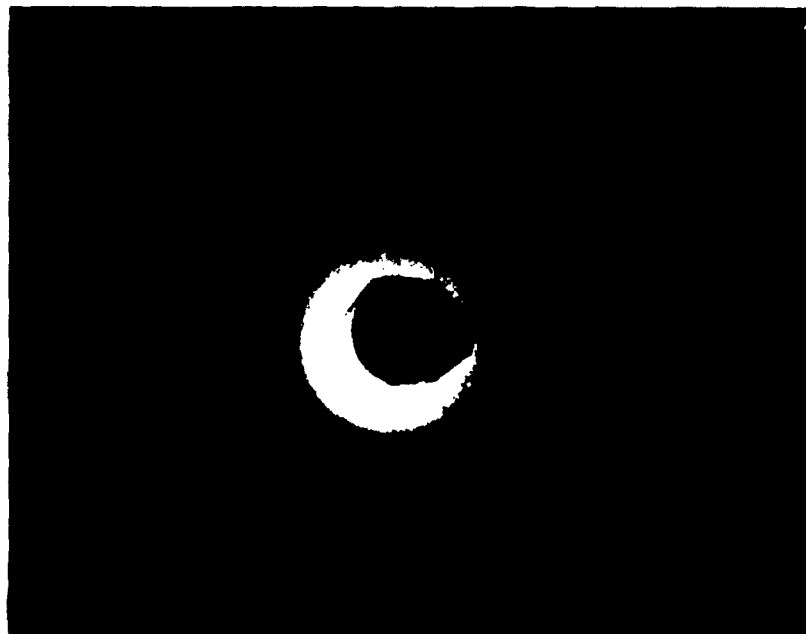


FIGURE 35
X-RAY DIFFRACTION PATTERN OF VACUUM DEPOSITED FILM SHOWING RANDOM
ORIENTATION OF GRAINS - BEAM PERPENDICULAR TO PLANE OF FILM

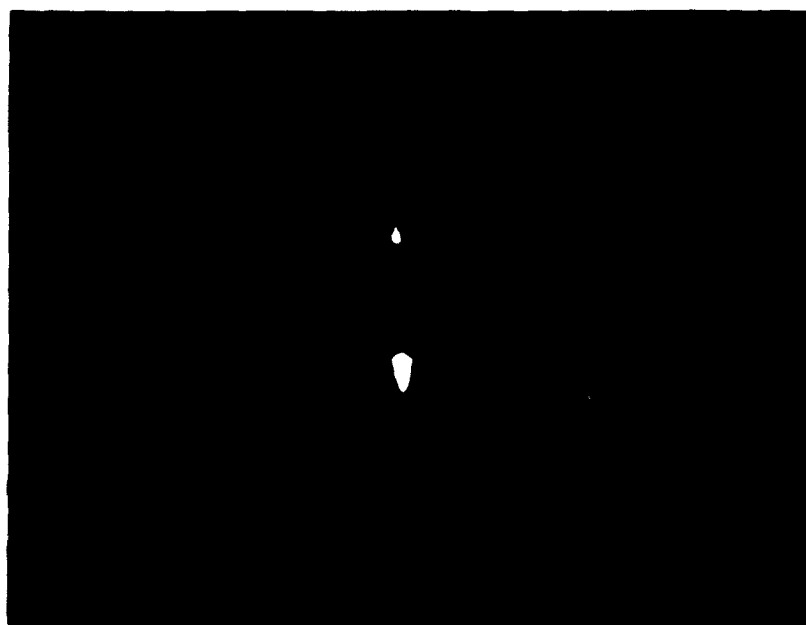
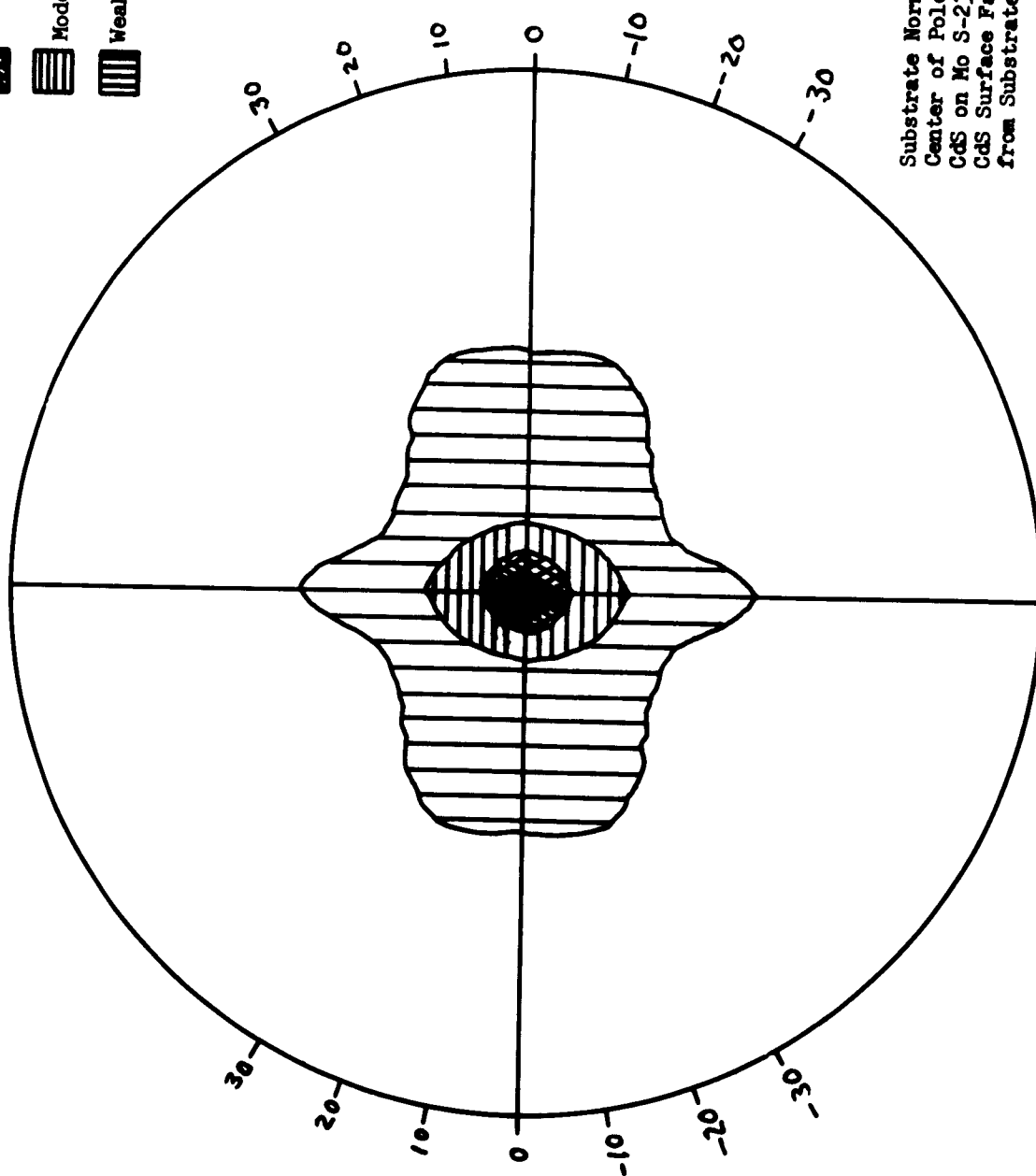
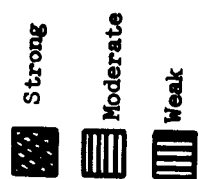


FIGURE 36
X-RAY DIFFRACTION PATTERN OF VACUUM DEPOSITED CdS FILM SHOWING PREFERRED
ORIENTATION OF GRAINS - BEAM PARALLEL TO PLANE OF FILM



Substrate Normal at
Center of Pole Figure,
CdS on Mo S-23,
CdS Surface Farthest
from Substrate

FIGURE 37
POLE FIGURE FOR (0002) PLANES OF VACUUM DEPOSITED CdS FILM ON MOLYBDENUM SUBSTRATE

REFERENCE LIST

1. F. A. Shirland, G. A. Wolff, and J. D. Nixon; "Research on Solar-Electrical Energy Conversion Employing Photovoltaic Properties of Semi-Conducting CdS", ASD-TDR-62-69 (January, 1962). Published by Aeronautical Systems Division, WPAFB, Ohio.
2. F. A. Shirland; "Photovoltaic Cadmium Sulfide", ARL Technical Report 60-293 (August, 1960). Published by Aeronautical Research Laboratories, WPAFB, Ohio.
3. D. A. Hammond and F. A. Shirland; "A Cadmium Sulfide Solar Energy Generator" WADC Technical Report 57-770 (December, 1957). (AD-151036).
4. General Electric Company, Luminescent Grade CdS, Code 113-3-291.
5. F. A. Shirland, G. A. Wolff and J. D. Nixon; "Fourth Quarterly Progress Report," Contract No. AF33(616)-7528, pgs. 46-49, July 20, 1961.
6. J. H. Gilles, and J. Van Cakenberghe; "Photoconductivity and Crystal Size in Evaporated Layers of CdS"; Nature 182, 862-863 (1958).
7. J. E. Starek, "Decorating Metals", U. S. Patent 2,081,121 (May 18, 1937).
8. R. O. Hull; "Apparatus and Process for the Study of Plating Solutions", U. S. Patent 2,149,344, (March 7, 1939).
9. "Proceedings of The Solar Working Group Conference, Vol. I., Radiation Damage to Semiconductor Solar Devices." Conference Held February 27 & 28, 1962 at the NASA Auditorium Federal Office Bldg. No. 6, Washington, D. C. Published by Power Information Center, University of Pennsylvania.
10. E. P. Warekois, M. C. Lavine, A. N. Mariana, and H. C. Gatos; J. Appl. Phys., 33, 690-6 (1962).

1. Solar cells
2. Energy conversion
3. Photovoltaic cells
4. Crystal growth
5. Solar energy conversion
- I. AFSC Project 8173.
- Task 817301
- II. Contract AF 33(616)-7528
- III. The Harshaw Chemical Co., Cleveland, Ohio
- IV. F. A. Shirland, et al.
- V. Avail fr CTS
- VI. In ASTIA collection

Aeronautical Systems Division, Dir/Aeromechanics, Flight Accessories Lab, Wright-Patterson AFB, Ohio. Rpt Nr ASD-TTR-62-69, Vol II. RESEARCH ON SOLAR-CONVERSION EMPLOYING CADMIUM SULFIDE. Final report, Dec 62, 63p. Incl illus., tables, 10 refs. Unclassified Report

Development of a thin film solar cell using vacuum evaporated layers of CdS was continued. Primary emphasis was on the front wall CdS film cell using molybdenum foil substrates. Efficiencies of large area (up to 9 in²) front wall cells have been increased to the range of 2 to 3%. The major factor in this increase was the reduction of sheet resistance by the use of a fine mesh metallic grid laminated to the barrier surface.

Improved vacuum evaporation techniques have made possible a reduction in CdS film thickness and in

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Some tests of CdS front wall film cells and arrays indicate that they should be stable in the high vacuum of space, and that they may be fairly resistant to radiation of the Van Allen types.

Research studies on the structure of CdS single crystals and polycrystalline films were continued with particular reference to grain growth, orientation and polarity effects, and etching and grain boundary studies. There have been indications of a correlation between crystallite orientation and photovoltaic response.

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