NASA CR 72159

FINAL REPORT

STUDY OF THIN FILM LARGE AREA PHOTOVOLTAIC SOLAR ENERGY CONVERTER

F. A. Shirland, J. R. Hietanen, and W. K. Bower

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-8502

December 30, 1966

ELECTRONIC RESEARCH DIVISION

CLEVITE CORPORATION

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SUMMARY

Design changes were introduced to remove causes of cell instability, decrease cell thickness and weight, increase reliability and decrease fabrication costs. These changes appear to have been successful, though only a few cells of the improved design have been tested so far on temperature cycling.

Instability of cell output on shelf storage was eliminated by cementing the grids to cell barriers with conductive epoxy resin. A transient degradation of output during elevated temperature exposure was eliminated by using a gold pigmented epoxy instead of a silver epoxy.

Degradation of cell output on exposure to humid ambients was eliminated by using a clear epoxy resin to attach the cover plastic to the cell in place of the hygroscopic nylon adhesive layer used previously.

Cell and array reliability was improved by using a full width integral extension of the conductive substrate as the negative lead of the cell, and a full width integral extension of the collector grid as the positive lead. Thus, cells can be interconnected in series by soldering, welding, cementing or otherwise making a broad area contact between adjacent cells. The thinness and flexibility of these leads permit the interconnection to be made behind the cells without sacrifice of active exposed area.

The thickness and weight of the cell were reduced while enhancing cell flexibility. This was accomplished by reducing the CdS film thickness, the thickness of the substrate and of the cover plastic, and eliminating the cement joint for lead attachment by going to integral leads. Maximum cell thickness was thus reduced to 0.004" while the weight of an average 55 cm^2 area cell, including leads, was reduced to 1.75 grams.

Major economies in cell fabrication were effected by using a copper collector grid made by a photo-chemical etching process in place of the earlier electroformed gold grid, by substituting copper foil for molybdenum for the metal substrate cell, and by revising cell processing so that the entire process is more amenable to mass production techniques.

These improvements were effected while increasing the rate of cell fabrication more than tenfold and maintaining an average cell efficiency of about 5%.

INTRODUCTION

This report summarizes a one year development program on the CdS thin film photovoltaic cell under Contract NAS 3-8502. This was a continuation of the program under Contract NAS 3-6461.[1] During the earlier contract period the frontwall plastic and metal substrate CdS film cell constructions were developed to the point where 4 to 6% conversion efficiencies could be obtained regularly for 3" x 3" size cells. Some efficiencies up to 8% were obtained.

During the present contract period work was directed toward eliminating causes of cell instability, continuing efforts to improve cell life under space environmental conditions, reducing the weight and cost of the CdS cell, and increasing the efficiency. It had been established earlier that the barrier of the CdS thin film cell as fabricated at Clevite was inherently stable and that the instabilities observed on many cells were due to failures of the collector grid contact or to shortcomings of the cell package.

Several possible cell design improvements had been investigated during the previous contract period. These included the use of alternate metal foils for cell substrates as substitutes for molybdenum, the incorporation of thinner CdS films and substrates for lighter weight more flexible cells, the introduction of etched metal grids to lower unit cell cost, and the use of leads that were integral extensions of the substrate and collector grid for increased cell reliability. Each of these changes in design was adopted as standard practice at the beginning of this contract. In addition, the pressure contact of the grid was eliminated in favor of cementing the grid with conductive epoxy.

Incorporating all these design changes into the standard fabrication process and evaluating their effect on cell performance and stability have been the major task of this year's effort. The changes have been successfully implemented and the necessary adjustments in processing procedures made to accommodate them. As a result, major gains have been effected toward the goal of a thin flexible large area solar cell having stable characteristics, low weight and cost, and greater reliability for space power applications.

STANDARD CELL DESIGN

A number of changes in the design of the standard CdS thin film solar cell evolved during the period of this contract. While some of these were conceived and investigated earlier they were proved-in during this period. These changes, of course, were not effected without difficulty. In many instances considerable adjustment of the processing conditions was necessary in order to achieve satisfactory results. These adjustments will be discussed in more detail in the following section on cell processing. In this section each of the major component parts of the present design cell are described with the changes from the earlier design indicated.

a. Substrate

1. Plastic Substrate

The plastic substrate is now 0.001" thick Kapton[2] film where it used to be 0.002" thick. Kapton is a polyimide resin capable of extended high temperature service and resistant to ultraviolet and high energy particle radiation. It is metallized on one surface with silver particles[3] dispersed in a polyimide matrix to a thickness of about 0.0003". This metallizing is very conductive having a sheet resistance of less than 0.04 ohms per square. It has a surface coating of zinc to provide a low resistance ohmic contact for the subsequently deposited CdS film.

2. Metal Substrate

The metal substrate is now 0.001" thick, 99.95% pure electrolytic copper foil where it used to be 0.002" thick molybdenum metal foil. It also has a surface coating of zinc, but this coating usually alloys with the copper substrate to form a brass surface layer.

b. CdS Film

There have been no changes in the design nor processing conditions of the CdS film in this period. The CdS layer is still a vacuum deposited polycrystalline film, typically 0.0008" thick. The grains are very fine and generally oriented with the [0001] axis perpendicular to the plane of the substrate. It is not purposely doped but gets its n-type semiconducting properties from a stoichiometric excess of cadmium. Its resistivity is on the order of 50 ohm-cm.

c. Barrier Layer

The barrier layer has also remained unchanged. It consists of a very thin layer, on the order of 0.5 microns thick, of what appears to be copper deficient Cu_2S.

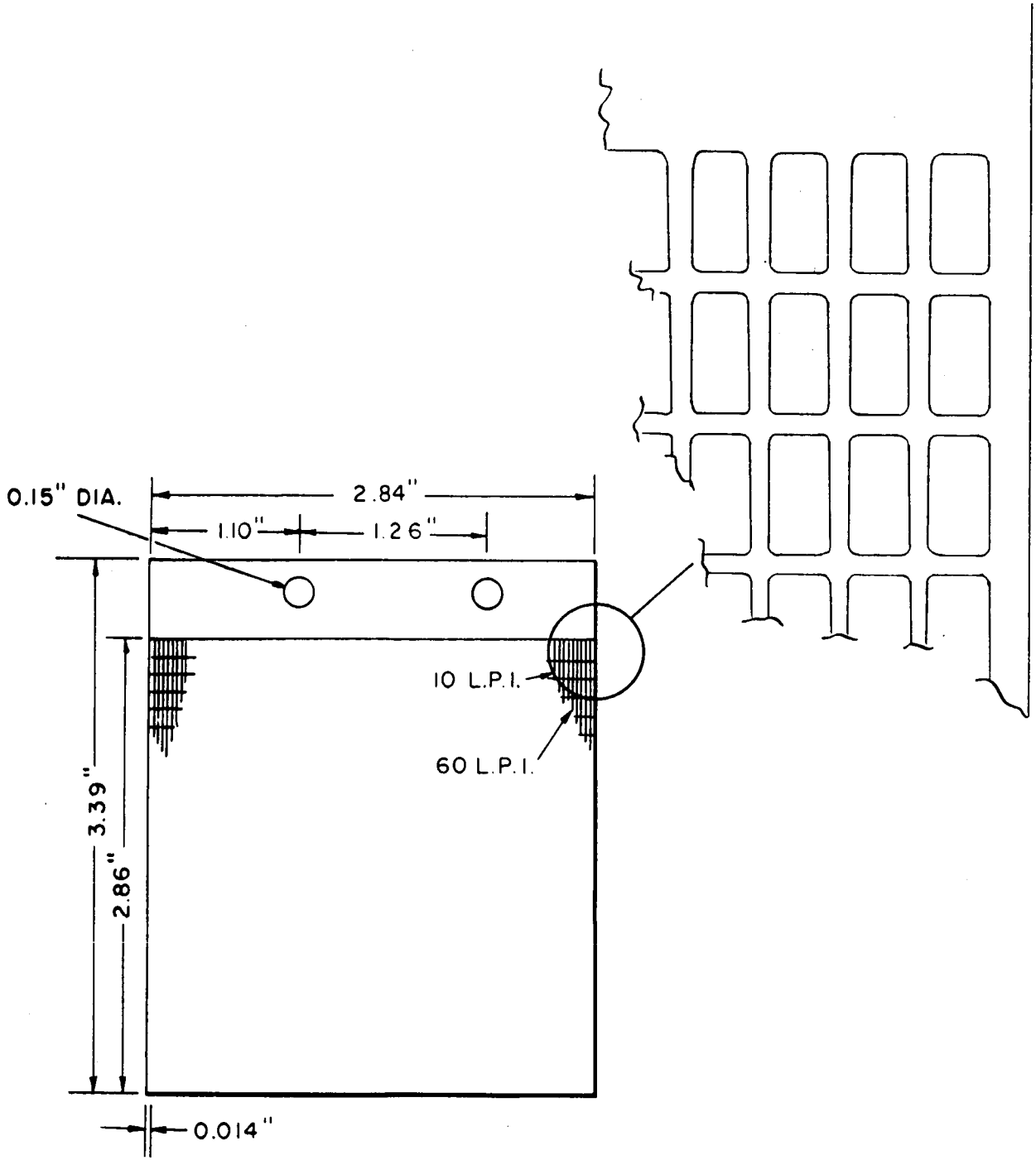
d. Collector Grid

A major change has been made in the collector grid. This used to be a fine electroformed gold metal mesh about 0.0002" thick with 60 wires per inch in each direction, and about 85% transmissive. It is now etched from 0.00045" thick rolled copper foil and then gold plated. It is 91% transmissive, having 60 wires per inch in one direction and 10 per inch in the other. The general design and dimensions are shown in Figure 1. While this design has by no means been optimized, it has evolved gradually over the last year or so and appears to be yielding reasonably satisfactory results. The main current carrying wires leading to the tab electrode are slightly tapered from 0.75 mils wide at the far end to 1.25 mils wide at the tab. There is a radius between these wires and the tab and also the first cross grid wire to help prevent breakage of the wires at the tab during processing.

e. Conductive Cement

The earlier design cell did not use this item at all but depended upon the lamination of the cover plastic to hold the collector grid in intimate electrical contact with the barrier layer. Investigations showed that a loosening of this pressure contact, probably due to cold flow of the laminating plastic, was the major cause of instability of CdS cell output on dry shelf storage.

At first a commercial conductive silver epoxy composition[4] was used between the copper grid and the barrier layer and this gave a major improvement over the pressure contact used earlier. However, a serious instability was discovered during thermal cycling tests at Lewis Research



NOTE: NOMINAL 0.001" LINE WIDTH

FIG. 1. DESIGN OF COLLECTOR GRID.

Center of NASA. Subsequent studies at Clevite found that this was associated with the kind of metal used to contact the barrier. Copper or silver in contact with the barrier caused a temporary degradation of cell output following high temperature exposure. The extent of the drop depended on the time and temperature of the exposure. However, gold did not cause this degradation and hence the copper grids were gold plated and a gold pigmented epoxy cement[5] was substituted for the silver epoxy.

f. Cover Plastic

The cover plastic is either Mylar[2] or Kapton, which is now 0.001" thick where it used to be 0.002" thick. Kapton is used where the cells are expected to be exposed to high energy particle radiation or to strong ultraviolet for extended periods. Otherwise, Mylar is preferred since there is a loss of up to 20% of the cell output due to the absorption of short wavelength light by the Kapton.

g. Cover Plastic Adhesive

The cover plastic earlier was laminated to the cell barrier using a Capran[6] adhesive layer. Capran is a polyamide resin (nylon) and is thermoplastic thus enabling the lamination to be accomplished quickly with heat and pressure. Unfortunately in many instances cold flow of the Capran adhesive must have occurred which permitted a loosening of the grid-barrier contact and a drop in cell output. Also, the Capran is strongly hygroscopic and not only loses its adhesive properties as it takes up moisture, but also causes degradation of cell output because of the moisture held in intimate contact with the cell barrier.

In this Contract a high temperature clear epoxy resin[7] has been used to cement the cover plastic to the cell barrier. This cement does not appear to exhibit cold flow.

h. Insulation Strip

A strip of Kapton or Mylar plastic, 0.0005" thick and about 1/8" wide, has been used to insulate between the positive lead and the edge of the cell. This is necessary because of the very close proximity of the positive lead and the n-type CdS (or conductive layer on the plastic substrate) at that edge of the cell. The insulation strip is attached with clear epoxy cement. Kapton insulation is preferred when a Mylar cover plastic is used, and vice versa, because the difference in color makes it easier to check for the presence and correct positioning of the insulation strip.

i. Integral Leads

The earlier design cells used separate gold plated silver foil leads attached to the metal substrate and to the collector grid for negative and positive leads respectively. The attachment was effected usually by conductive epoxy cement, though other methods were also

used. This design caused an appreciable bulge in the cells where the leads were attached and was an incipient source of unreliability since the leads were usually thin and narrow and hence subject to breakage, or the contact between the lead and the grid or substrate might fail. This type of failure would of course be catastrophic when a large number of cells were connected in a series string since the entire string would then be open circuited.

The use of an integral extension of the conductive substrate the full width of the cell for the negative lead and an integral extension of the collector grid, also the full width of the cell but extending out the opposite edge, for the positive lead was introduced in the present contract period. These eliminated the bulges associated with the earlier design, greatly decreased the possibility of cell failure from loss of contact, improved the ease of interconnecting cells in series strings, and eliminated several steps in processing the cells thus reducing fabrication cost and increasing the yield of good cells.

The positive lead tab is gold plated for tarnish resistance. The negative lead tab is first copper plated and then gold plated for increased solderability and for tarnish resistance.

Figure 2 shows in cross-section view the changes in design for the plastic substrate cell effected during this year's effort. The thickness is of course exaggerated relative to the cell length to illustrate the construction details. However, the difference in overall thickness and relative design reliability between the old and new constructions is readily apparent.

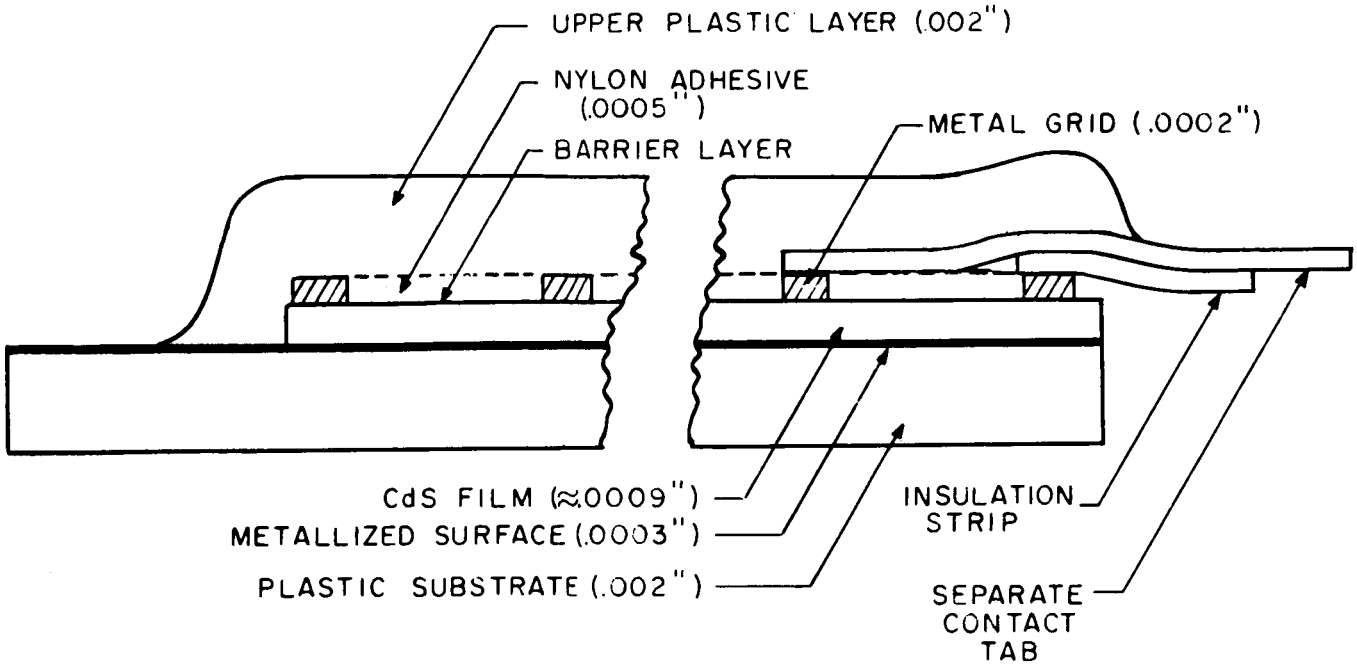
Figure 3 illustrates the design differences for the metal substrate cell.

STANDARD CELL PROCESSING

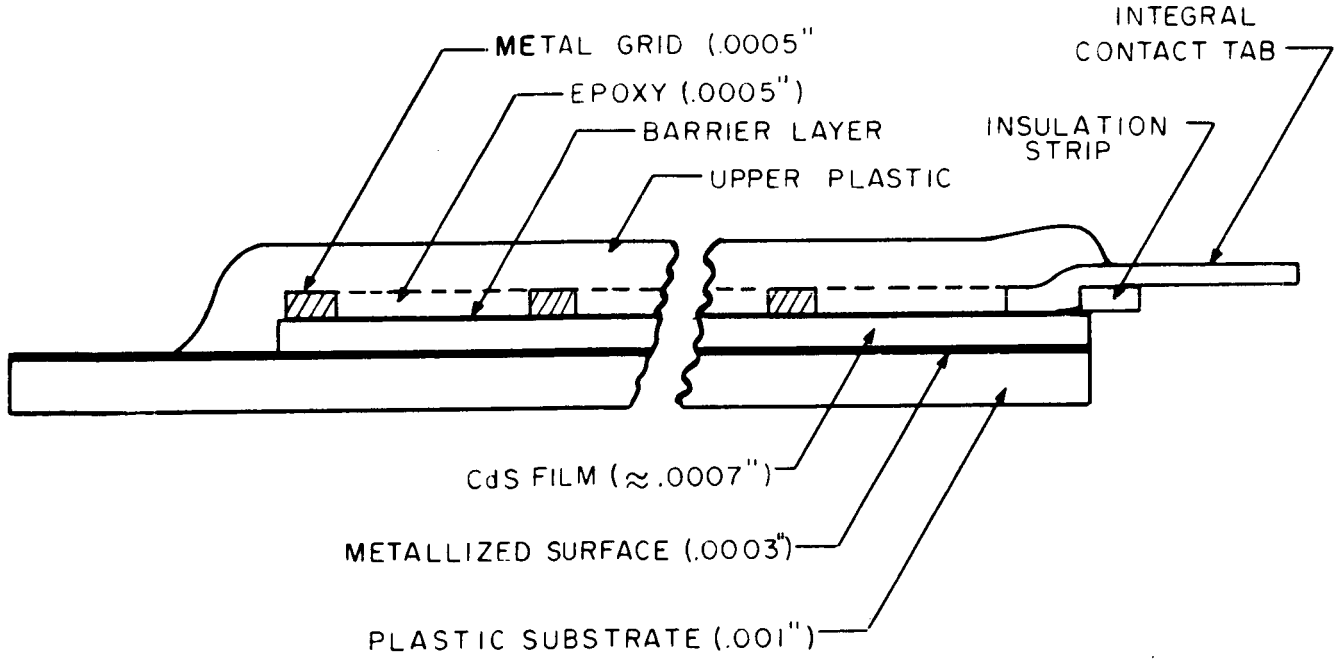
a. Substrate Preparation

1. Plastic Substrate

The development of a practical process for forming the conductive coating on the Kapton plastic substrate was one of the major problem areas encountered during this contract period. When the process was first evolved this was done by spraying multiple coatings of a silver Pyre-ML® mixture onto the plastic substrate, drying out the solvent, curing in place, scraping away dust particles and other imperfections and burnishing after each coat. The process was slow and painstaking and the yield was low since a single large dust particle could result in a large pinhole and, therefore, a scrap piece. Further, the adherence between the metallized layer and the Kapton substrate proved to be variable. This was also true with the adherence of the CdS film to the metallized substrate. A concerted effort was therefore made to develop a substrate preparation process which would eliminate



(a) EARLIER DESIGN



(b) PRESENT DESIGN

FIG. 2. OLD AND NEW DESIGN OF PLASTIC SUBSTRATE CELL. (ENLARGED CROSS-SECTION VIEWS)

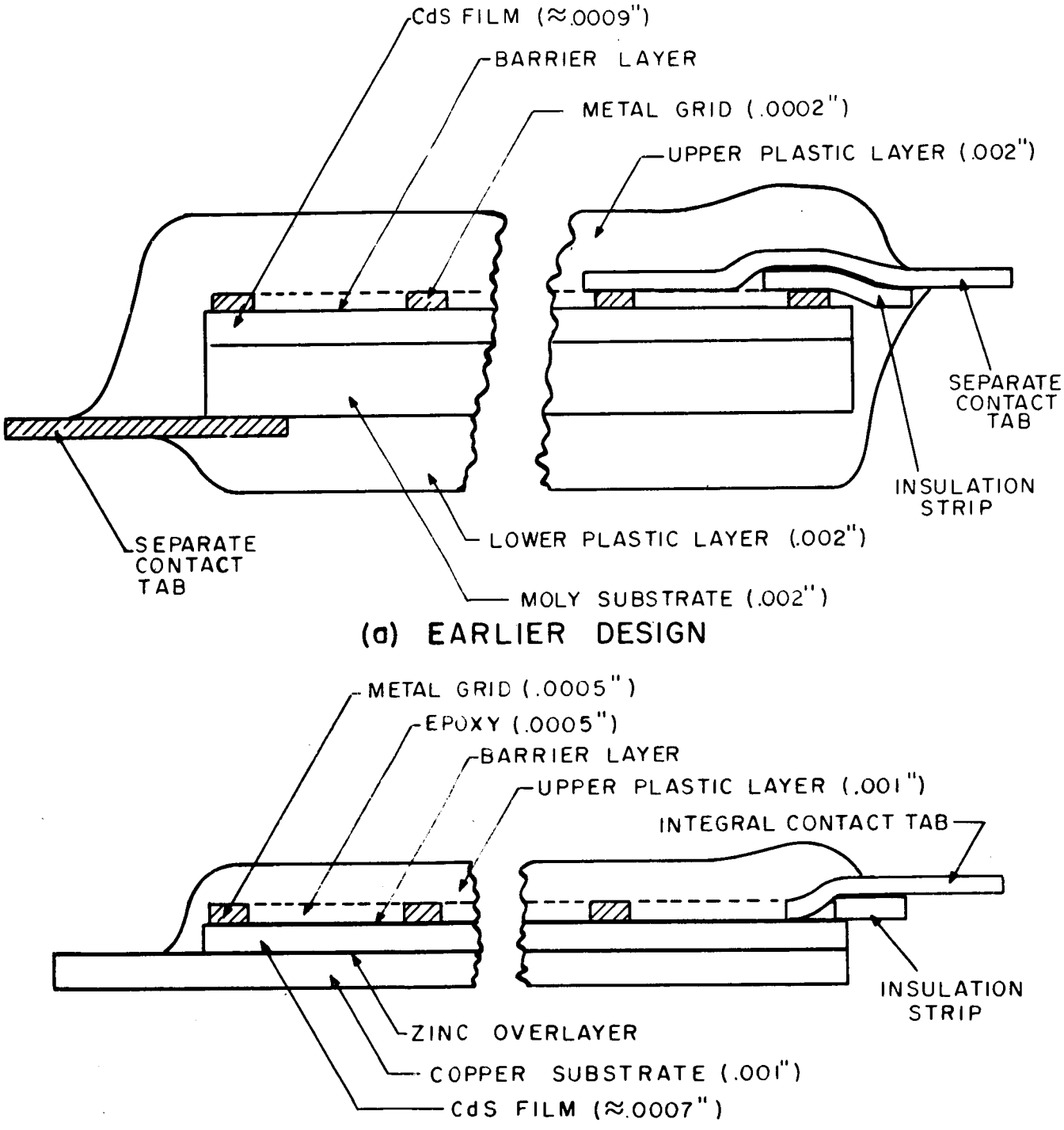


FIG. 3. OLD AND NEW DESIGN OF METAL SUBSTRATE CELL. (ENLARGED CROSS-SECTION VIEWS)

or, at least, minimize these difficulties and make the process more compatible with a volume production process.

Initial efforts centered around attempts to reduce the number of coats required to secure the needed conductance by increasing the ratio of the silver pigment used in the spray mixture. A number of spray mixtures were tried which resulted in layers of either too low a conductance or too poor an adherence. The most satisfactory mixture that could be found, that resulted in films with satisfactory adherence as well as conductance, consisted of a 1:2 weight ratio of silver pigment to Pyre-ML binder. Single spray layers of 0.0003" thickness with resistances of about 0.04 ohms per square were produced. This formula has been standardized for the plastic substrate cell.

Even with this pigment to binder ratio poor adherence of the component parts was experienced intermittently in the fabrication of cells. The adherence problem was broken down into several contributing factors, and dealt with separately.

First, the adhesion of the silver Pyre-ML coating to the Kapton substrate was improved by the use of a simple Kapton cleaning process and an improved drying and curing operation. The cleaning process consists of an N, N-Dimethyl Formamide scrubbing using a soft paper towel followed by a drying step in which the substrate is scrubbed with a second paper towel and a 5 minute air drying at room temperature. This method of substrate cleaning has helped to secure improved adherence. Much of the earlier adherence problem appears to have been due to incomplete removal of the solvent (N-N-Dimethyl Formamide) from the silver Pyre-ML layer prior to the curing of the Pyre-ML. When the curing step is started prior to complete removal of the solvents, a skin forms which traps residual solvents and leads to incipient blisters and areas of poor adhesion. This problem was alleviated by extending the drying period of the uncured Pyre-ML coating to 15 minutes at 150°C before the final cure of 30 minutes at 250°C. A few poorly adherent metallized layers are still being produced however. A visual inspection to catch these was introduced. This consists of observing the layer from the underside of the Kapton. Poorly adherent films are characterized by a mottled appearance when observed through the Kapton. This visual inspection step appears to have eliminated nearly all of the poorly adherent substrates from further processing.

A second area of poor adherence, that between the metallized layer and the CdS film, also received special attention. Several separate causes of poor adherence in this area have been considered. One cause results from the occasional poor zinc plating on the metallized layer. Careful attention to the plating bath composition, purity of materials, and plating conditions has resulted in a vastly improved control over this process. Systematic analysis of plating bath composition and periodic bath filtering and electrode cleaning have also helped in securing improved control over the process. Secondly, a glow discharge step has been introduced in the vacuum

evaporation process immediately prior to evaporation. Whether this results in removal of contaminated zinc from the surface of the zinc coating, or merely a removal of adsorbed gas atoms from the surface is not known. However, a number of controlled experiments using a glow discharge have shown a marked improvement in CdS film adhesion.

The coating thickness uniformity and texture have been and still are primarily a function of operator skill in spraying the silver Pyre-ML mixture onto the substrate and in controlling the spray mixture viscosity. Improved spraying equipment incorporating air filters and automatic solution mixing features has helped to yield more uniform coatings. A final burnishing process is still needed however to remove major agglomerates of silver particles which develop and dust or lint particles that settle from the atmosphere during the spraying or curing operations.

2. Metal Substrate

Two major areas of difficulty were encountered in the processing of copper substrate cells. First, the copper foil supplied showed a tendency to crack while being processed through grid contacting or cover plastic lamination. Second, the adherence of the CdS film to the substrate was at times marginal. Both these problems received attention but so far no completely satisfactory answer has been found for either.

The cracking was not observed on all cells processed. Initially, it appeared to be associated with the particular lot of copper foil used. Elongation tests of the various lots revealed a difference in per cent elongation before rupture varying from 2 or 3% up to 6 to 7%. Foil from lots having an elongation of less than 5% before rupture always cracked upon processing. An annealing step in which the foil was heated to the range of 350°C to 450°C appeared to alleviate much of the cracking and a specification requiring copper foil with elongations of greater than 5% was initiated. Some substrates were fabricated near the end of this contract period from a lot known to have a satisfactory elongation specification but which still showed a tendency to crack. It may be that the elongation varies from section to section of the lot or that 5 to 7% elongation before rupture is not by itself sufficient. This problem has not yet been completely resolved.

Some of the steps which led to improved adherence of the CdS to the plastic substrate were also taken for the copper substrate cell. Improved zinc plating bath controls and the use of a glow discharge immediately prior to CdS evaporation were introduced in the processing. The CdS film adherence however remained marginal.

A chromate stabilizing agent was found to be present on early lots of the as-supplied copper foil. This was suspected as a primary cause of poor adherence. Later batches of the copper substrate material contained no surface stabilizer however, yet film peeling was still somewhat evident. Hence, the earlier supposition that the stabilizing agent caused the poor CdS adherence to the copper substrate is now questionable.

Another approach was the study of the effect of zinc plating thickness on CdS film adherence. This was founded on the observation that while adherence to copper was marginal, the adherence to plastic substrates processed at the same time was satisfactory. The chief difference between the two cell constructions appeared to be the formation of a brass layer on the copper substrate while the zinc remained unalloyed into the silver of the plastic substrate. Various thicknesses of zinc were plated onto copper substrates to compare adherence with zinc layer thickness. There was an indication that the substrate plated for the longest period of time had the best adherence, but more recent work has not confirmed this.

A review of this problem area has led to the suspicion that the quality of the adherence has lately been more a function of the evaporation process than the substrate preparation process. Poor CdS film adherence has been observed without regard to differences in the methods of substrate preparation. Some literature[9, 10] suggests that one of the main reasons for peeling of thin films of such materials as SiO, ZnS, and CdS is the build up of excessive stress forces as a result of the parameters of the evaporation process. Good adherence in these films was obtained by balancing tensile and compressive forces in the films proper by the control of the evaporation parameters during film growth. Evaporation source temperatures and ultimate vacuum had a marked effect on the film adherence. Some CdS films grown on copper substrates in a vacua in the 10^{-6} Torr range had excellent adherence. Other films grown under poorer vacuum conditions have shown a typical poor adherence. Further efforts in this area are indicated.

b. CdS Film Evaporation

The standard CdS film evaporation process remained constant throughout this contract period. It was carried over essentially unchanged from the previous contract period except for minor changes in evaporation source spacing and substrate distance to accommodate the growth of uniform thickness films over a larger area.

The process for CdS film evaporation is the same for the copper and plastic substrate cells. A commercial luminescent grade of CdS powder[11] is pre-sintered in vacuum to 850°C and in argon to 1200°C in order to densify it and drive off high vapor pressure impurities. It is then ground to pass about a 42 mesh screen. No doping has been used for films evaporated in this period.

The densified CdS powder is charged into cylindrical tantalum evaporation sources which are heated to about 1050°C to 1100°C by passing an electric current through them. Vacua on the order to 10^{-5} to 10^{-6} Torr are used, and the substrates are preheated by radiation to 220°C. The open end of each evaporation source is closed with a finely perforated screen and a Fibre Frax[12] plug which prevents spattering of the substrate with ejected CdS particles. Deposition rates of 200 to 300A per second are normally employed and a total film thickness of 15 to 20 microns has given best results. Total

evaporation time is about 10 to 15 minutes. Approximately 10 minutes is usually taken to reach full evaporation rate, and the system is held at temperature for about 10 minutes after the evaporation is supposedly completed to ensure emptying of the sources.

c. Barrier Formation

The barrier process has remained essentially unchanged since its development in the middle of 1964. A change from a 1:1 $HCl:H_2O$ pre-etching solution to a 3:2 solution was introduced after it was determined that the stronger etchant produced higher output cells. Test variations of the time in the barrier solution are performed periodically to determine if the barrier being produced is optimized. No changes were deemed necessary on standard process cells throughout this contractual period.

A difficulty that had been experienced intermittently for many months early in this contract period was the precipitation of elemental copper onto the barrier surface during the barrier dipping process. This difficulty was manifested by the formation of a reddish cast layer on the surface of the formed barrier. This resulted in low cell efficiencies. At first it was thought that it might result from traces of zinc "showing through" a poorly grown CdS film. However, attempts to reduce the amount of zinc present and build up the thickness of the CdS layer so that the zinc would not "show through" did not alleviate the problem. It was discovered finally that the lacquer used to mask the edges of the cell during barrier dipping was not always completely dry. Residual solvent was being driven out of the lacquer when the cells were immersed in the hot CuCl solution, and this solvent would precipitate copper onto the surface of the cell. The problem was eliminated by using masking tape in place of lacquer for edge masking, though an oven drying step was found to be equally efficacious. The use of masking tape is more convenient as it is easier to remove afterwards.

d. Grid Contacting

The process of applying silver epoxy cement to the grids and then placing the grids against the cell barriers and curing the epoxy was evaluated under the previous contract. A good bond was effected without difficulty. This technique of grid attachment proved to be a major improvement over the pressure contact grid process where the Capran adhesive held the grid against the cell barriers. This improvement was manifested in greatly improved shelf stability. A major instability was discovered, however, during thermal cycling tests at Lewis Research Center (NASA). Tests in our laboratory showed that this instability was a result of the presence of the silver in the epoxy. This is discussed in more detail in the section on stability. The substitution of gold for the silver in the epoxy eliminated this fault. This technique of attaching grids to cell barriers using a gold filled epoxy has resulted in a fabrication process whereby the advantages of a good mechanical contact have been combined with good electrical cell outputs even under high temperature operating conditions. This grid contact has been used for the major portion of this contract.

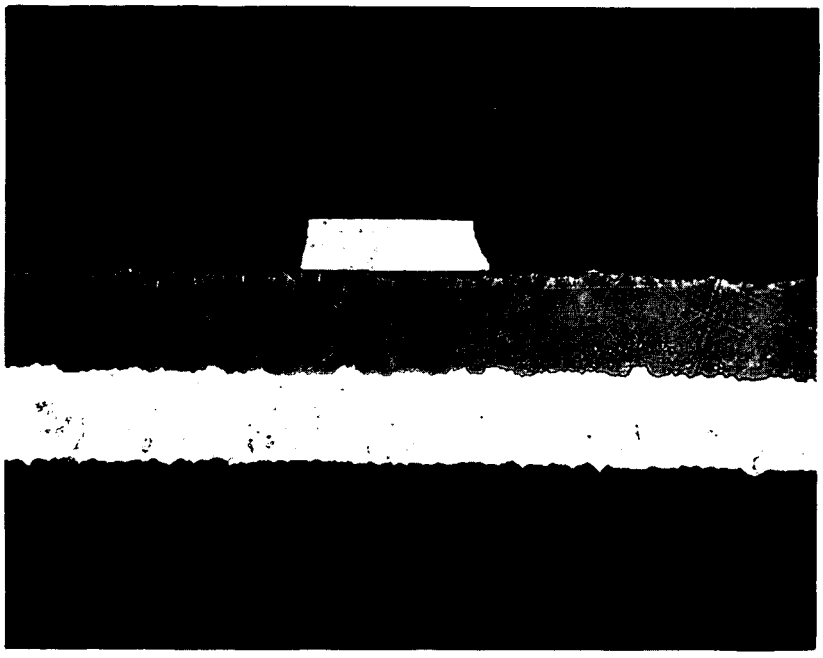
The introduction into the standard process of this method of grid contacting produced a number of processing difficulties which were successfully dealt with. These difficulties were generally manifested by low cell current and efficiency outputs and were attributed chiefly to incomplete electrical contact between the grids and the cell barriers.

Initially, a suitable commercial gold filled epoxy cement was not available so an attempt was made to synthesize one in our laboratory. Lower cell outputs than those obtained using the silver-epoxy cement or the pressure contact grid led to a thorough investigation of the process. The laboratory fabricated gold filled epoxy was initially suspected and certainly contributed but it was later discovered that a commercially obtained epoxy did not completely eliminate low output cells. A careful analysis was then made of how the epoxy resin behaves during the various cell processing steps from grid attachment through final lamination and heat treatment. For study purposes, cells were fabricated with the epoxy minus the gold powder in the grid application step of the process. These cells were fabricated under the microscope and prodded from time to time to determine what kind of bond was being effected between the grid and cell barrier. These observations revealed that the conditions normally used to cement the grids (as recommended by the manufacturer of the epoxy) were not sufficient to fully cure the epoxy. Though the room temperature bond strength was good, above 70°C the bond strength was poor and the subsequent application of the cover plastic and the conditions for curing the epoxy used to laminate the cover plastic would cause a softening of the grid adhesive. As a result, the grid would be pushed away from the barrier by the clear non-conducting epoxy used to laminate the cover plastic.

Increasing the time of cure of the grid adhesive (from 30 minutes at 190°C to 2 hours) was not sufficient to improve the bond so that the grid contact would not be injured during lamination. It was found that a 15 hour heat treatment in a vacuum oven at 130°C did cure the grid adhesive sufficiently that it would not loosen during the subsequent lamination step.

It is interesting to note that when the conductive pigment was left out of the cement used to attach the grids to the cells, cells with outputs from 6 to 8% were obtained if the epoxy cement was applied to the grid in a thin enough layer. About 0.0005" thickness was about optimum in this respect. More adhesive would give lower outputs and less adhesive would give a poor bond. The fact that any output is observed using this technique most likely lies in the uneven nature of the barrier. There are enough high spots on the barrier surface that push through the very thin epoxy layer to establish good electrical contact. This is illustrated in Figure 4. The chief disadvantage of this construction is the critical adhesive thickness tolerance required for good electrical contact.

This might be brought under control by careful control of epoxy cement thickness and curing conditions and would offer major savings over the use of the gold pigmented epoxy. However, it was



Cross-Section
View - 500X
Copper Substrate
Cell - 5.0% Eff.

PLATE 13790

FIGURE 4

GRID ATTACHED WITH NON-CONDUCTING EPOXY CEMENT

Fair contact established from high spots on barrier.

felt the positive electrical contact of the gold epoxy was a surer way of securing a stable grid contact at this time.

Figure 5 shows the poor contact which was obtained using a gold filled epoxy cement formulated in our own laboratory. It was difficult to incorporate enough gold pigment into the epoxy without making the cement too viscous to be spread out and transferred to the grid. It was applied therefore by thinning with solvent and dipping the grid in the thinned mixture and drying out the solvent. It is evident from the photomicrograph that there are not enough gold particles bridging the gap between the grid wire and the cell barrier. While this view shows only a small portion of the total grid contact area, it is typical of many such views of the same cell and on similar cells which were studied at the time. The cell efficiencies for this kind of grid contact were low, mostly less than 5%. This contacting method was therefore abandoned after several months when a commercial source of conductive gold epoxy cement was established.

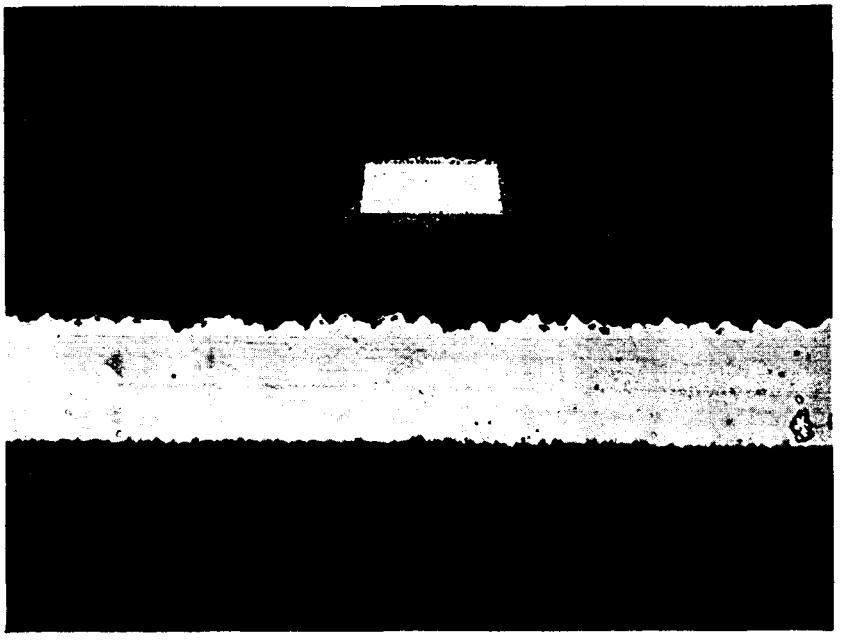
Figure 6 is an enlarged cross-section of a cell gridded utilizing a commercial gold filled epoxy. The conductive path is formed by the gold particles bridging the space between the grid and cell surface. Cell efficiencies for this type of package are typically in the 4 to 7% range with an average efficiency slightly over 5%. Cell efficiency is determined largely by the quality of the bond of the grid to the barrier surface and the completeness of coverage of the grid with the gold epoxy cement.

Continued improvement of the parameters for applying and curing the gold epoxy cement led to a gradual improvement in cell efficiency which became fully apparent only after the 12th month of the contract period. The finally evolved technique for applying the cement is to roll out a thin layer onto a sheet of teflon plastic using a squeegee or roller, and then to transfer this to the grid with a gentle yet evenly applied pressure. While this is still a manual process which is dependent on operator skill for success, it is amenable to automatic procedures. In the meantime, careful visual inspection of the process has given reasonably satisfactory results.

e. Cover Plastic Attachment

A clear epoxy resin was selected for initial trials as an alternate cement to the Capran because the epoxy is relatively non-hygroscopic, is transparent, can be used at moderately high and low extremes of temperature, and is noted for the strength and stability of its bond. This epoxy resin has been used throughout the latter part of this contract and proved to be a major factor in eliminating cell instability. It has generally been used with little difficulty.

Difficulties that have been encountered with the cover plastic attachment process have been associated with the inclusion of voids in the adhesive layer. These are areas at the front surface of the cell where there has either been an insufficient volume of epoxy to fill the space between the cover plastic and the cell barrier, or where gases



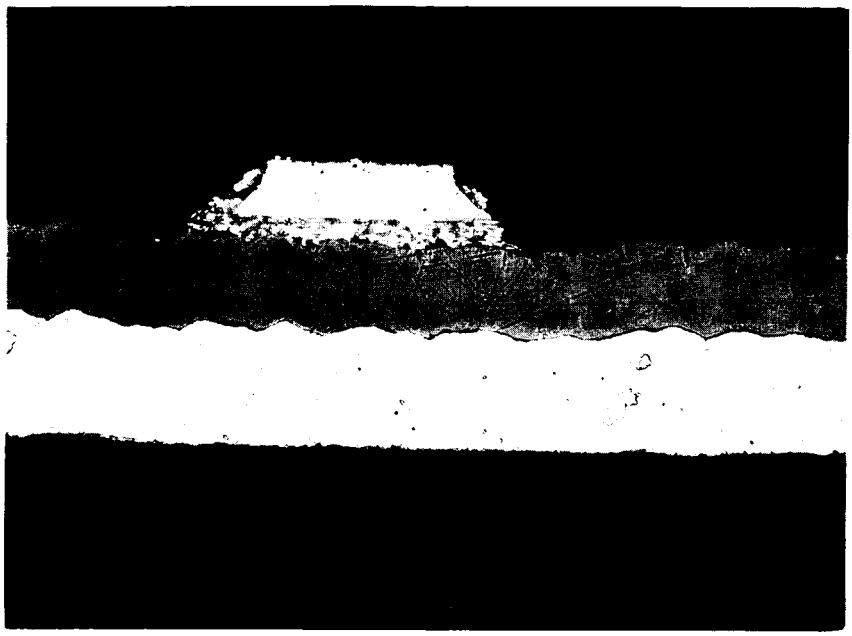
Cross-Section
View - 500X
Copper Substrate
Cell - 4.0% Eff.

PLATE 13832

FIGURE 5

GRID ATTACHED WITH GOLD FILLED EPOXY CEMENT

Poor Contact from Laboratory Formulated Cement



Cross-Section
View - 500X
Copper Substrate
Cell -5.6 % Eff.

PLATE 14184

FIGURE 6

GRID ATTACHED WITH GOLD FILLED EPOXY CEMENT

Good Contact from Commercial Cement

have been trapped between cell and cover plastic during the attachment process. These voids result in interfaces which impair the optical coupling between the cover plastic and the cell barrier and result in very high reflection losses. They probably also represent localized areas that would be subject to moisture penetration, oxidation or other chemical reaction. This effect is noticeably more severe when Kapton rather than Mylar is used for the cover plastic.

The solution of this problem came from careful control of the thickness of the epoxy adhesive used to attach the cover plastic, grid thickness, the thickness of the gold filled epoxy used to attach the grids to the cell, and from vacuum evacuation of trapped air during lamination. In early work, the epoxy had been applied by diluting with solvent and spraying onto the underside of the cover plastic with an air brush. Later an outside vendor[13] was able to provide epoxy coated cover plastics with tight control of the thickness parameter. The epoxy is applied to either Mylar or Kapton by roll coating. The key to eliminating voids in packaging has been to provide an epoxy layer of the same thickness as the grid plus gold epoxy thickness and to remove the gases from the lamination chamber before curing the cement. Tight controls of these factors have eliminated the void problem.

STANDARD CELL FABRICATION

A laboratory cell assembly line was operated for fabricating large area ($55cm^2$) cells over the entire period of the contract. This line served as a means of standardizing cell design and fabrication processes, demonstrating the evolving state-of-the-art, providing controls for experimental design or process variations, providing cells for stability and characterization tests, demonstration samples and samples for submission to the Contract Monitor.

a. Plastic Substrate Cells

The standard plastic substrate cells fabricated on the laboratory assembly line during this year are summarized in Table I. The changes in design or fabrication introduced during this period were as follows:

Month 1, 2 & 3	all cells contacted by cementing etched silver plated copper grids in place with conductive silver epoxy. Cover plastic attached with Capran adhesive.
End of Month 3	gold plated copper grids attached with laboratory formulated gold epoxy cement applied by thinning in solvent and dipping grids. Clear epoxy cement used for cover plastic attachment.
End of Month 4	masking tape used to mask edges of cells during barrier dipping in place of lacquer used previously. Copper precipitation problem solved.

TABLE I

STANDARD PROCESS LINE PLASTIC SUBSTRATE CELLS

Month	Total Cells	Scrap Cells	Efficiency Min. %	Efficiency Max. %	Efficiency Avg. %	Avg. Power/wt. W/lb.
1	7	5	5.4	6.4	5.9	77
2	11	5	3.1	5.5	4.3	53
3	7	4	3.9	4.1	4.0	57
4	5	0	3.7	4.2	4.0	65
5	73	33	3.0	5.4	3.5	58
6	54	28	3.3	5.4	4.0	68
7	62	4	3.7	5.9	4.8	90
8	59	3	4.0	6.0	4.6	87
9	40	7	3.7	5.7	4.8	95
10	56	12	4.1	5.9	4.9	88
11	60	19	4.3	5.4	4.9	80
12	62	29	4.1	5.9	5.0	86
Total	496	149	3.0	6.4	4.6	81

Note: All cells - 55 cm^2 area, encapsulated in Mylar Plastic. All efficiency readings are in equivalent Air Mass 1 Sunlight at 25°C.

7th, 8th and 9th Month readings all reduced 8% from actual measured values as a result of 8% calibration error.

Power/wt. calculated for Air Mass 0 on basis of 1.2 times the Air Mass 1 output.

End of Month 6	commercial gold epoxy cement became available, improved epoxy curing process introduced.
End of Month 7	improved substrate preparation process introduced.
End of Month 10	problem areas associated with faulty cover plastic attachment defined, roll coating of epoxy cement onto cover plastic proved-in.

Throughout the period of this contract there was a continuing effort to increase the rate of cell fabrication by improved tooling and fixturing and by revisions to cell processing. During the first few months less than 2 cells were produced each working day. This was increased to more than 20 cells per working day at the end of the period so that only a fraction of the total available time was needed to fabricate the required number of standard process cells.

As the production rate was increased and as cell quality improved, increasingly severe inspection limits were placed on the various fabrication steps and on the finished cells. Thus the monthly production and scrap figures presented in Table I do not fully reflect the steady improvement in cell quality that was actually experienced.

b. Copper Substrate Cells

Table II gives the results of laboratory fabrication of the standard process copper substrate cell. The changes and improvements factored into the standard process for this cell were as follows:

Month 1, 2 & 3	all cells contacted by cementing etched silver plated copper grids in place with conductive silver epoxy. Cover plastic attached with Capran adhesive.
End of Month 3	gold plated copper grids attached with laboratory formulated gold epoxy cement applied by thinning in solvent and dipping grids. Clear epoxy cement used for cover plastic attachment.
End of Month 4	many cracks appearing in the copper substrate - usually after barrier formation, during cure of the epoxy cement or during cell lamination.
Month 1, 2, 3 & 4	lacquer used to mask edges of cells during barrier operation. High incidence of copper precipitation observed on barriers.
End of Month 4	tape substituted for lacquer in masking edges of cells during barrier dipping.

TABLE II

STANDARD PROCESS LINE COPPER SUBSTRATE CELLS

Month	Total Cells	Scrap Cells	Efficiency Min. %	Efficiency Max. %	Efficiency Avg. %	Avg. Power/wt. W/lb.
1	16	0	3.2	6.1	5.0	42
2	11	1	3.9	6.2	4.9	45
3	13	1	3.9	6.6	5.2	43
4	69	5	3.0	6.3	4.8	47
5	24	5	3.2	5.4	4.2	42
Total	133	12	3.0	6.6	4.8	45

Note: All cells - 55 cm^2 - all encapsulated in Mylar Plastic.

All efficiency readings are in equivalent Air Mass 1 Sunlight at 25°C.

Power/wt. calculated for Air Mass 0 on basis of 1.2 times the Air Mass 1 output.

End of Month 5	copper substrate cell withdrawn from standard cell production due to excessive substrate cracking and marginal CdS adherence.

STABILITY

Development work on the preceding contract, as mentioned earlier, led to design revisions which were expected to give good cell stability. These design changes were placed in effect during this contract. The major task of this program was to evaluate the effect of these changes on cell stability and to isolate and eliminate any remaining weaknesses in cell design which would interfere with long term stable performance in space.

The initial work of this contract dealt with the investigation of cells having the grid held in place with a silver filled epoxy resin and the cover plastic held in place with Capran. Thermal cycling tests at NASA, Lewis Research Center, revealed a further instability which subsequent tests showed was associated with the silver. A conductive gold epoxy resin was substituted for the silver epoxy resin and this cause of instability was eliminated. Finally it was found that epoxy resin when used for attachment of the cover plastic made the cells practically unaffected by high humidity ambients. A clear epoxy resin was, therefore, substituted for the Capran adhesive for cover plastic attachment.

a. Effect of Conductive Silver Cement for Grid Attachment

The process of attaching grids with conductive silver epoxy cement was developed over a year ago as a possible means of getting around the problem of cells shorting on temperature cycling. Cells with the grids attached with conductive silver epoxy cement did not develop short circuits on temperature cycling, but they did fail in a different manner. They dropped steadily in output within a few hundred cycles, and then leveled off at about 1/3 to 1/4 of their initial output level. It appeared to be the open circuit voltage and fill factor that were affected rather than the short circuit current. When the cells were removed from temperature cycling tests, they recovered soon afterwards to their original output levels.

This effect was studied in more detail. A cell with a copper grid cemented in place with silver epoxy cement was heated at 110°C in nitrogen atmosphere. After 18 hours its OCV fell from 0.455 to 0.415 volts and its maximum conversion efficiency fell from 6.2% to 5.4%. Then it was heated for another 40 hours in vacuum at 110°C. The OCV fell further to 0.370 volts and the efficiency to 3.7%. It was then placed in a desiccator at room temperature. After 5-1/2 hours the cell had recovered to yield 0.435 volts OCV and 5.5% efficiency. Another cell with a gold grid held in pressure contact to the barrier was given the same treatment and was virtually unaffected.

The drop in output on temperature cycling appears to be a transient effect resulting from the heating of the cells, and is associated with the type of metal contacting the barrier. It seems to be the same

effect that makes it necessary to wait several hours after laminating cells with silver or copper grids in pressure contact before full output can be obtained. The cause of the effect is basically not understood, but it does not occur at all for gold contacts. Thus, the use of gold contacts as a means around this difficulty was evaluated.

b. Effect of Conductive Gold Cement for Grid Attachment

A number of cells were fabricated using a gold filled conductive epoxy cement for grid attachment in place of the silver epoxy cement. Also, to ensure that only gold contacts were made to the barriers, the grids were gold plated. The cells were given various elevated temperature treatments in the range of 100 to 150°C for periods of several days to several weeks. None of them showed the transient degradation effect that was experienced for the silver epoxy cemented grid cells.

There were however several complicating factors that made a direct comparison of gold vs silver cement difficult. First, a commercial gold filled epoxy cement with the required high temperature properties could not be located, and it was necessary to fabricate our own. Second, the gold epoxy mixture that was developed was a solvent borne type that dries to a tack-free consistency (i.e., a "B" stage) that permits handling before curing. Third, before many such direct comparisons had been attempted, it was found desirable to replace the Capran laminating adhesive with another epoxy cement, and this introduced other complications which are discussed in more detail below.

These complications were entirely a matter of developing practical fabrication processes for grid attachment and for cover plastic attachment. The advantages of using gold filled epoxy cement for grid attachment were quite clear at this point.

c. Effect of Clear Epoxy for Cover Plastic Attachment

It was found earlier that the Capran (nylon) plastic used to laminate the Mylar or Kapton cover plastic to the cell barriers is actually hygroscopic. It was thought that the use of a different but non-hygroscopic adhesive in place of the Capran might make the CdS thin film solar cell much less susceptible to degradation from high humidity ambients.

A clear epoxy resin[7] was selected for initial trials which could be used at moderately high and low extremes of temperature and which could be applied and dried tack-free to permit handling prior to curing.

The epoxy was mixed with its curing agent, thinned with solvent and sprayed onto Mylar cover plastic to a dry thickness of about 0.5 mils. It was dried in an oven at 70°C for 30 minutes to remove all traces of solvent. Curing of the epoxy was accomplished by heating at 190°C for 30 minutes.

Initial trial cells were fabricated with the epoxy laminating adhesive using copper grids in pressure contact, silver plated and gold

plated copper grids in pressure contact, and silver plated copper grids cemented with silver filled epoxy cement. Along with these tests, controls were run for each type of grid with the then standard Capran-Mylar lamination.

In all cases the cells with epoxy laminating adhesive gave lower output initially, but continued to climb for periods of several weeks and more. The Capran adhered cells however reached full output within the first day and then started to drop. It was evident that additional heat treatment was needed to bring the epoxy adhered cells to full output more rapidly. Different heating cycles were tried. Temperatures on the order of 80°C to 150°C for periods of about a day seemed to be adequate to bring the cells up to full output.

The epoxy resin was successful in yielding a better bonded cell package that is much less susceptible to degradation from humid atmospheres than the Capran adhesive used previously. This process was therefore standardized for all cells fabricated subsequently.

d. Stability Characterization

A number of stability tests have been carried out over the course of this contract. Major design and processing changes were introduced during the first seven months of the contract which resulted in appreciable improvements in cell stability. Hence, characterization of cell stability for the present design cell dates from the seventh month of the contract.

1. Dry Shelf Storage

Several cells of the finally evolved design were selected at random each month and placed on dry shelf storage test. This test consists of simple storage in a laboratory desiccator cabinet at room temperature. The cells were removed periodically and tested for output under standard test conditions - i.e., equivalent air mass 1 sunlight at 25°C.

The data available to date are presented in Table III. Unfortunately the earlier readings for this test, marked with an asterisk, were taken using a faulty thermopile to calibrate the light intensity. The defective thermopile was not discovered until several months of faulty readings had been taken, and the exact amount of the error could not be reconstructed. The readings involved have been lowered by 10% to partially compensate for the calibration error, but this is probably not enough and the error may not have been constant.

Discounting the earlier readings of questionable accuracy there appears to be no trend indicating cell output degradation on dry shelf storage for the 16 week period. There was some minor fluctuation between consecutive readings, and in order to minimize the effect of these more frequent readings were initiated for later cells during the first month of the test. Larger quantities of cells need to be tested over longer periods, but it does appear that the present design cell is stable on shelf storage.

TABLE III

DRY SHELF STORAGE TEST

Standard Plastic Substrate Cells - Stored in Desiccator at Room Temperature

Cell No.	% EFFICIENCY AFTER STORAGE TIME IN WEEKS: 0	1	2	3	4	8	12	16	20	24	28
D289D	4.9*						4.9*	4.8	4.8	4.9	4.8
D292D	4.7*						4.9*	4.6	4.6	4.9	4.9
D296B	4.5*						4.4*	4.3	4.2	4.3	4.3
D304A	4.8*						4.5*	4.5	4.5	4.5	4.5
D306D	4.9*						4.9*	4.8	4.8	4.9	4.9
D315A	5.2*						5.2*	5.0	5.0	5.2	5.3
D336D	4.2*					4.1*	4.0*	4.0	4.1	4.0	4.2
D344C	5.2*					4.9*	4.8	4.7	4.7	4.7	
D355C	5.7*					5.3*	5.2	5.3	5.4	5.4	
D364F	4.7*					4.2*	4.1	4.1	4.1	4.1	
D375C	4.4	4.4	4.3	4.4	4.3	4.4	4.1	4.4			
D381A	5.1	5.0	5.0	5.0	5.1	5.2	5.1	5.1			
D385B	5.0	5.0	4.9	5.2	5.2	5.1	5.1				
D386E	5.1	5.1	5.1	5.3	5.2	5.1	5.2				
D391B	4.7	5.0	4.8	5.1	5.0	5.2	5.0				
D395C	4.2	4.2	4.2	4.2	4.2	4.1	4.2				
D403B	4.6	4.7	4.8	4.7	4.7						
D410B	4.9	4.8	4.8	4.8	4.8						

* readings marked thus were lowered 10% below original recorded values to partially allow for subsequently discovered calibration error.

2. Moisture Test

Several cells of the final design were also placed on high humidity test each month. This test consists of storage in an air chamber where the relative humidity is controlled at 80%. The temperature was not controlled but is estimated to have averaged about 30°C.

The data are presented in Table IV. The same comments as made in the previous section apply to the accuracy of the earlier measurements made for this test; i.e. - those marked with an asterisk.

Again discounting the earlier readings of questionable accuracy, there is little or no indication of cell degradation on high humidity exposure. One cell, No. D294A, exhibited a definite drop of about 20% in output that cannot be explained by calibration error. Visual examination of this cell disclosed a high incidence of voids in the epoxy cover plastic adhesive and this could account for the drop since the voids represent local areas of no cover protection. There is insufficient information to be conclusive but it does appear that in general the present design cells exhibit less than 5% but probably more than 2% output degradation after 12 weeks of storage at 80% relative humidity at 30°C.

3. High Temperature Exposure

Randomly selected cells were placed on high temperature vacuum storage tests each month. This test was run at a temperature of 100°C. A commercial vacuum oven was used for the test with a two stage mechanical vacuum pump equipped with a liquid nitrogen cold trap which was filled manually. The vacua attained averaged about 10^{-4} Torr.

The cells were read initially and weekly for the first month and then at 4 week intervals thereafter. Tests were at air mass 1 equivalent sunlight at 25°C in each case. The data for the 100°C vacuum storage test are given in Table V.

As can be seen there is considerable variation between cells. Cell No. D357C dropped in output by 20% in the first 4 weeks and even more in the second 4 weeks, and to almost nothing in 16 weeks. Cell No. D407D dropped very little in the first 3 weeks and then plunged nearly 40% by the 4th week. There were 5 cells out of 12 which showed no drop in the first 12 weeks, and 1 cell out of 8 which showed no drop in 16 weeks.

This is a fairly severe test, and the interpretation is clouded by the uncertainty of the effect of residual oxygen on the cells at these times and temperatures. The indications are strong however that the cells are not intrinsically affected by moderately high temperatures for reasonable periods of time. That a few cells showed severe degradation is probably attributable to some fault in those particular cells. That some high output cells showed no degradation for 12 weeks (over 2000 hours) at 100°C is evidence that there is not an appreciable diffusion effect tending to wash out an impurity concentration gradient at the barrier.[14] This is in direct conflict with the prediction of Hill and Keramidas.

TABLE IV

HIGH HUMIDITY STORAGE TEST

Standard Plastic Substrate Cells - Stored in 80% R.H. at Room Temperature

Cell No.	% EFFICIENCY AFTER STORAGE TIME IN WEEKS: 0	1	2	3	4	8	12	16	20	24	28	32	36
D187B	5.5*									5.5*	5.2	5.3	5.3
D291A	4.6*					4.5*	4.6*	4.2	4.1	4.2	4.3		
D294A	4.3*					3.4*	3.2*	3.2	3.2	3.2	3.1		
D297C	4.6*					4.4*	4.3*	4.0	4.2	4.2	4.2		
D301A	4.6*					4.4*	4.3*	4.0	4.0	4.2	4.2		
D313C	4.4*				4.1*		4.1*	3.8	4.0	3.8	3.9		
D327A	2.8*				2.8*		3.0*	2.7	2.7	2.8	2.8		
D348A	4.8*			4.8*		4.8*	4.2	4.3	4.4	4.4			
D350F	4.8*			4.8*		4.8*	4.5	3.8	3.9	4.0			
D350C	4.3			4.3	4.3	4.4	4.2	4.3	4.4				
D357E	4.4			4.3	4.3	4.5	4.4	4.3	4.4				
D372A	4.5	4.4	4.4	4.3	4.3	4.3	4.3	4.3					
D378B	4.8	4.7	4.6	4.6	4.6	4.6	4.5	4.5					
D385F	5.1	5.1	4.9	5.2	5.2	5.0	5.0						
D401B	5.2	5.0	5.0	5.2	5.2	5.0	5.0	5.0					
D405A	4.8	4.5	4.5	4.5	4.5								
D411F	4.6	4.4	4.3	4.2	4.4								
D424B	4.5	4.5	4.4	4.4									
D424E	5.6	5.3	5.4	5.5									

* readings marked thus were lowered 10% below original recorded values to account for subsequently discovered calibration error.

TABLE V

HIGH TEMPERATURE STORAGE TEST - 100°C AT 10^{-4} TORR

Standard Plastic Substrate Cells

Cell No.	% EFFICIENCY AFTER STORAGE TIME IN WEEKS: 0	1	2	3	4	8	12	16	20
D349A	4.0		4.4	4.3	4.0	4.6	4.5	3.8	3.3
D357B	4.3		4.2	4.0	4.0	3.4	2.8	1.2	0.9
D357C	4.8		4.5	4.0	3.8	1.7		0.3	0.2
D363E	3.3		2.8	2.9	3.0	3.0	2.9	2.0	1.8
D369E	4.9	4.7	4.7	4.7	4.6	4.6	4.4	4.5	
D373C	4.1	4.1	4.1	4.1	3.9	3.9	3.6	3.8	
D377A	5.0	4.9	4.8	4.9	4.7	4.7	4.2	4.1	
D379E	5.1	5.3	5.2	5.3	5.2	5.2	5.0	5.1	
D385E	4.7	4.8	4.7	4.6	4.5	4.3	4.2		
D388F	4.6	5.1	4.9	5.1	5.0	4.8	4.9		
D392A	5.0	5.2	5.2	5.3	5.3	5.0	5.1		
D401F	4.5	4.7	4.7	4.7	4.7	4.6	4.7		
D403D	6.0	5.9	5.9	5.8	5.7	5.5			
D405C	5.6	5.7	5.6	5.6	5.6	5.5			
D407D	4.9	4.8	4.7	4.7	3.1	3.0			
D411D	5.0	5.0	4.9	4.5	4.4	4.2			
Avg.	4.74		4.71	4.66	4.47	4.25			

A group of the earlier design cells fabricated using the laboratory-made gold epoxy was placed on 150°C vacuum storage test. These showed severe degradation to about half of their initial values in 6 weeks, though a few cells did not reach the 50% output level until 18 weeks on test, and one cell that was originally 5.0% efficient is still 3.0% efficient after more than 7 months on this test. At 150°C temperature in a relatively poor vacuum, this is indeed a severe test.

4. Temperature Cycling

Preliminary temperature cycling tests have been performed on only 2 of the earliest of the present design cells. These were fabricated using the laboratory-made gold epoxy cement. The tests were conducted by the Energy Conversion Laboratory at the Lewis Research Center of NASA. These two cells experienced 4400 cycles between approx. -60°C and +60°C with no indication of any short circuits.

More extensive tests are being planned in the coming year using the latest design high efficiency cells and the more rigorous test conditions of the Boeing Company's temperature cycling facility. However, to date no CdS thin film solar cells constructed with collector grids attached by conductive epoxy cement have short circuited on temperature cycling.

OTHER DEVELOPMENT STUDIES

Investigations were carried out in all areas of cell fabrication in order to effect further design or process improvements. Some of these hold considerable promise for such improvement, but they have not as yet been carried to the point where the standard cell design or fabrication process could be changed.

a. Substrates

1. Chromium Undercoating

The use of chromium was evaluated in place of the zinc for an intermediate layer between the silver Pyre-ML substrate and the CdS film. Zinc was used because it gave an ohmic contact and it was convenient at the time when the process for the plastic substrate cell was first developed. However, zinc has a relatively low melting point and a high vapor pressure. This latter factor was suspected of contributing to poor CdS film adhesion.

Chromium was vacuum evaporated onto a number of silver Pyre-ML coated plastic substrates, and these were then processed into cells. Excellent CdS film adherence was obtained, but the CdS films were relatively dark in color and the cell efficiencies were low. It was suspected that the films were contaminated, possibly by extraneous impurities carried with the chromium raw material.

Therefore a high purity (99.999%+) chromium was tried, and this did eliminate the dark coloration experienced earlier. Approx. 30 cells were produced from films deposited on substrates with the higher

purity chromium coatings. Again these gave excellent I-V characteristic curves with high fill factors, but with relatively low currents and efficiencies. Table VI gives typical output data for a representative group of these cells formed on chromium undercoatings.

On the basis of film adherence and careful microscopic observation of CdS surface texture it was concluded that well structured CdS films had been secured. Therefore a number of efforts were made to modify the barrier formation conditions in hopes of raising the current and efficiency level. These efforts were not successful. In all cases the CdS films were deposited in the same vacuum chamber used to deposit the chromium undercoating. It is possible that chromium acts as a poison in CdS forming trapping centers at unfavorable levels, and that in the process of CdS evaporation chromium gets distributed throughout the bulk of the CdS film. Further investigations may be able to resolve this problem, or possibly to discover a way to capitalize on the advantages of chromium undercoatings without the disadvantages.

2. Evaporated Zinc Undercoating

At the time when considerable difficulty was experienced with the plating baths for electroplating zinc onto the silver Pyre-ML substrates, it was decided to try depositing the zinc by vacuum evaporation. It was reasoned that minor imperfections in the silver Pyre-ML coating might be covered if the zinc were evaporated, so that a more uniform surface would be presented for deposition of the CdS film. Earlier experiments along these lines were encouraging.

Subsequently it was seen that it would be advantageous from an economic standpoint if the zinc were deposited on the substrate in the same vacuum chamber and on the same pump down as used for depositing the CdS film. Of some 8 cells produced in this fashion the highest cell output obtained was 3.9% with an average of 3.3%. It is suspected that the presence of excess zinc in the CdS evaporation chamber contaminates the entire CdS film, possibly by overdoping, because of the high vapor pressure of zinc.

3. Brass Undercoating

When zinc is plated onto copper substrates, it alloys with the copper to form a brass layer. Since copper substrate cells have usually given about 10 to 15% more output than plastic substrate cells made at the same time it was suspected that the brass contact might be more advantageous in reducing series resistance. Therefore an attempt was made to reproduce the brass undercoating on the silver Pyre-ML coated plastic substrate. This was done by electroplating copper onto the silver Pyre-ML layer followed by a zinc plating and a short heating in vacuum.

Brass layers were formed satisfactorily in this manner and 8 CdS films were deposited onto them. All but one of these spalled so badly they could not be processed further. The one that did not spall

TABLE VI

EFFECT OF CHROMIUM COATING ON SUBSTRATE

Plastic Substrate Cells with Otherwise Standard Processing

Cell No.	OCV volts	SCC ma	Fill Factor	Efficiency %
A815C	.435	580	63.0	2.9
A815D	.435	565	64.5	2.9
A817B	.480	670	66.5	3.9
A818C	.455	640	62.0	3.3
A819A	.455	700	70.5	4.1
A819B	.445	680	67.0	3.7
A819C	.450	670	69.0	3.8
A819D	.455	670	68.5	3.8
A820A	.470	670	69.5	4.0
A820C	.470	675	69.0	4.0
A821D	.460	605	67.0	3.4
A822A	.450	540	65.5	2.9
A822D	.455	580	68.5	3.3
Avg.	.455	634	67.0	3.5

yielded a 4.7% efficient cell which was not better than obtained for the standard process cells made at the same time. The reasons for the poor CdS film adherence are not clear.

4. No Undercoating

Two cells were produced on silver Pyre-ML coated plastic substrates with no further coatings to determine what kind of a contact would be produced and what level of cell output could be obtained. The cell open circuit voltages were in the range of 0.2 volts, and the short circuit currents averaged 540 ma. These results validate the conclusion that silver does not make an ohmic low resistance contact to CdS and that a suitable intermediate layer is necessary.

5. Various Silver Pyre-ML Ratios

Some attention has been given to the relative proportions of silver pigment and Pyre-ML binder used to form the conductive coating of the Kapton plastic substrate. Higher proportions of Pyre-ML binder appear to yield more adherent coatings, but of course these are less conductive. Also, higher proportions of binder require more burnishing of the cured surface prior to zinc plating.

Initially a 1 to 1 ratio was used and, since the Pyre-ML contains 12% solids, this represented just over half the volume of the finished conductive layer being composed of silver. The actual resistance of an 0.0003" thick conductive layer then averaged about 0.028 ohms per square. In an attempt to secure more conductive coatings that would not require burnishing, experiments were run with pigment-to-binder ratios of 2:1 and 3:1. The resistance of the films did decrease, as shown in Table VII. However, the adhesion became very poor.

Because of the overriding requirement of very good adhesion between the Kapton substrate and its conductive coating, the pigment to binder ratio was lowered to 1:2 for most of the cells fabricated in the latter part of this contract. This yields a resistance for the substrate of about 0.04 ohms per square, which is high enough to have some limiting effect on the output of the very best cells. Now that other factors affecting the adhesion of the silver Pyre-ML layer have been brought under better control, the silver Pyre-ML ratio should be re-examined to see if a more favorable compromise between the factors of conductivity, thickness, adherence and need for burnishing can be reached.

6. Methods of Applying Silver Pyre-ML Coating

Alternate techniques of applying the silver Pyre-ML conductive layer to the Kapton substrate have been investigated. Various techniques evaluated include: electrostatic spraying, roller coating, and silk screening.

TABLE VII

EFFECT OF VARYING SILVER PYRE-ML RATIO

Ag/Pyre-ML (by wt)	Silver in Cured Film		Sheet Resistance of Film Actual	Adherence of Film to Kapton Substrate
	by wt.	by vol.		
1:2	81%	28%	.040 ohms/sq	excellent
1:1	89	53	.028	good
2:1	94	69	.010	poor
3:1	96	79	.007	poor
(1:0	100	100	.0025*)	

* calculated

NOTE: Pyre-ML varnish is 12% solids as received and used. Specific Gravity of Pyre-ML, when cured, assumed same as Kapton film = 1.42.

The electrostatic spray technique has shown some evidence of yielding an improved texture over the regular pressure spray method. The efficiency output of seven cells produced on electrostatically sprayed conductive layers varied from 4.8% to 5.2% as compared to a 5.1% average for three control cells produced on standard process substrates. Thus, the cell output is essentially equivalent to that of the standard process cell.

Roller coating by an outside vendor yielded films of better texture than obtained with any of the spray techniques. However, the coatings furnished have not been uniformly covered with the conductive pigment, and the conductivity of the substrates has not been as good.

The initial efforts with silk screening the conductive coating were discouraging. The consistency of the silver Pyre-ML mixture was not favorable for silk screening. Hence, these efforts were discontinued.

7. Thinner Substrates

The present standard plastic or copper substrate cells are approx. 0.004" in overall thickness. The substrate and the cover plastic are both 0.001", the CdS film is just under 0.001", and the collector grid is 0.00045" thick. There is a 0.0005" plastic insulator strip positioned under the grid where it crosses the edge of the cell to prevent shorting to the substrate, and at this point the cell is nominally 0.0040" thick. The epoxy adhesive used to hold these parts bonded together squeezes out to a very thin layer and does not normally affect cell thickness.

There has been little difficulty in going from 0.002" to 0.001" thicknesses for either the plastic or the copper substrates used in the cell fabrication process. A few preliminary tests have indicated that substrate thickness can be reduced further to about 0.0005" for both copper and plastic substrate cells but with some difficulty. Twelve cells were fabricated using 0.0005" thick Kapton as a substrate material. The physical handling of the thinner substrates and cells proved to be the major problem. The substrate extension tab in all cases was ripped during the grid attachment or cover plastic attachment stages, probably because the cells were clamped too tightly during these heating cycles. The efficiency of one cell was 4.4% which was similar to standard process cells measured at the same time. There was a marked decrease in the check cracking of the CdS film as compared to the standard process cell. Further work in this area could probably overcome the handling problems and yield cells with power-to-weight ratios of 175 watts per pound.

b. CdS Film Deposition - Thinner Films

Thinner CdS films are desirable in order to reduce the overall thickness and weight of the CdS thin film solar cell and to reduce cracking developed in the CdS films due to thermal mis-match between film and substrate. Present CdS film thicknesses average approx. 0.8

mils. The experience has been that when the thickness drops to 0.7 mils or below the shunt characteristics of the cells start to deteriorate, and occasionally cells will actually be shorted.

Careful microscopic examination of cross-sections of different cells suggest that the physical perfection of the CdS film is the major factor requiring thicker films. Therefore, attempts were made to deposit CdS films in the range of 0.4 to 0.5 mils using a higher substrate temperature during film growth and a slower evaporation rate in order to secure a higher degree of film perfection. Some promising results were obtained with this approach using molybdenum or copper foil substrates. However, in the present contract most of the work has been on the plastic substrate cell and two major problem areas were encountered when depositing thinner films on plastic substrates. First, the zinc underplating on the plastic substrates tended to re-evaporate from the substrate at the 350°C substrate temperature before the CdS film could deposit on the substrate. This resulted in very poor structured films which were completely unsatisfactory for high efficiency cells. Second, the utilization of CdS under these conditions was much poorer than had been experienced under the standard evaporation conditions and hence the films were much thinner than the desired 0.4 to 0.5 mil range even when the evaporation sources were completely filled with CdS.

In an effort to get around the latter difficulty, a semiclosed hot-wall system was constructed to operate at the 350°C substrate temperature. Most of the effort on this problem was spent trying to work out the process parameters for evaporating CdS films onto 350°C substrates with the use of the semiclosed hot-wall chamber. The results were not satisfactory. Most of the problem appeared to be associated with the deleterious effect of the zinc re-evaporating from the substrate. Further work along these lines was therefore postponed until an improved ohmic contact interlayer between the substrate and CdS film can be developed to replace the zinc.

c. Barrier Formation

1. Rinsing Variations

An attempt was made to determine whether a more thorough distilled water rinse between the pre-etch and the barrier dipping step or whether a mid-rinse in $CdCl_2$ solution would improve cell stability. A controlled experiment showed no difference in this respect between doubly rinsed films, singly rinsed and $CdCl_2$ dipped films, and standard processed films.

Another set of experiments was run with an ultrasonic distilled water rinsing of cell barriers between the pre-etch and the barrier dip. Cells processed this way gave low initial outputs (approx. 3% efficiency) and deteriorated steadily.

Post barrier rinse treatments in hot distilled water yielded results equivalent to those obtained when the barriers were rinsed in

the standard room temperature distilled water. No advantage was noted so this process was not investigated further.

2. Nonaqueous System

Water is known to be harmful to the barriers of CdS solar cells and to cause degradation. Water is present in the pre-etch, the barrier dipping solution and the post rinses used in the standard cell fabrication procedure. It has been theorized that it would be much easier to optimize the cell fabrication parameters if water was not present at all. Also, such cells might be more stable since it is probably very difficult if not impossible to remove all traces of water from the finished cells.

Previously some cells were fabricated using a nonaqueous barrier dipping solution, and no pre-etch or water rinses. These cells gave high open circuit voltages, outputs of 4.6 to 4.9%, and appeared to be more stable than regularly processed cells. Higher outputs were obtained when the HCl pre-etch was used, but this, of course, contained water and nullified the effect of the nonaqueous dip.

In this period further work was done with the nonaqueous barrier dip process using no pre-etch. As before, lower output cells were obtained. Also, there were indications that these cells were more stable on shelf storage. However, these experiments were run early in the year before evolution of the final more stable cell design. The instability of the pressure grid contact and other factors at that time made it difficult to isolate the effect of the nonaqueous barrier process in conclusive fashion.

There has not been time available in the later months of the year when the more stable cell process had been adopted to repeat these nonaqueous system experiments. It is planned to do further work along these lines in the follow-on program including the introduction of nonaqueous pre-etches and rinses as well.

3. Deionized Water Rinsing

A further variation tried in the barrier formation process was the substitution of deionized water for the distilled water normally used. The purpose here was to determine whether this would have any adverse effects on the cell performance. It would be more convenient and economical to use deionized rather than distilled water.

Twelve cells were fabricated using deionized water. These averaged 4.58% in efficiency as compared to 4.75% for a group of standard production control cells. The cells have been stable on shelf storage for 12 weeks, to date. The data are presented in Table VIII. Further, larger scale trials are indicated.

4. Evaporated Cu_2S Overlayers

The evaporation of Cu_2S onto cells with barriers was performed

TABLE VIII

EFFECT OF DEIONIZED WATER RINSING

Water Rinses	Cell No.	Cell Efficiency Initial	Cell Efficiency After 12 weeks on Shelf Storage
Distilled H_2O (Std process)	D385B	5.0	5.1
	D386E	5.1	5.2
	D391B	4.7	5.0
	D395C	4.2	4.2
	Average	4.75	4.88
Deionized H_2O	D399A	5.1	5.1
	D399B	4.8	5.0
	D399C	2.8	2.7
	D399D	4.2	4.4
	D399E	4.8	5.1
	D399F	4.5	4.6
	D400A	4.7	4.9
	D400B	4.8	5.0
	D400C	5.3	5.5
	D400D	5.0	5.0
	D400E	4.5	4.7
	D400F	4.4	4.5
	Average	4.58	4.71

to determine the possibility of reducing shorting by filling in pin holes with the evaporated Cu_2S. Also it was thought that this might improve the resistance to moisture degradation. Cu_2S layers of approx. 700A and 1500A thickness were evaporated onto cells that had been processed through the barrier formation step of the standard process and which had a high incidence of pin holes. Of the six cells processed, four were shorted, indicating that the technique was not successful in covering pin holes with Cu_2S. One of the remaining cells had a lower output (4.5%) as compared with the outputs of three control samples (5.0%). The 4.5% cell was put on humidity test along with a control sample. After two weeks neither showed any signs of deterioration. It appears that a simple evaporation of Cu_2S onto barriered cells has no observable beneficial value. It may, in fact, result in cell output reductions.

d. Grid Attachment

1. Electroplated Grids

Early design CdS thin film solar cells with electroformed metal mesh collector grids held in place by the Capran thermoplastic lamination of the cover plastic had a high incidence of catastrophic failures on vacuum thermal cycling tests.[15] These failures were caused by a short circuiting of a grid wire through the cell barrier to the CdS film or substrate below.

At the time, Clevite and Harshaw (who were the only suppliers of these cells) took different approaches to eliminate the failures. The method taken by this laboratory was to cement the grids to the cell barriers with conductive epoxy cement. At Harshaw the method was to apply the grid by electroplating in place. While both methods were beset with difficulties, each laboratory was able to work out the difficulties and to develop a process for making grid contacts that appeared to solve the original shorting problem.

During the last quarter of this contract, at the request of the Contract Monitor, an attempt was made to reproduce the Harshaw process for electroplating grids in place. The process specifications and materials specifications were obtained and several months were spent trying to form electroplated grids in place on the barriers of Clevite high efficiency cells. To date these efforts have not been successful.

The difficulties encountered were centered chiefly in obtaining a uniform pinhole free photo resist mask on the barriers of the cells. It was particularly hard to flow the photo resist smoothly and evenly over the cell surface. There was not available suitable spinning equipment to handle 3" x 3" size pieces. The very flexible plastic substrate cell readily curls at this stage of its processing and where the cell is not held down flat there is a tendency for a bead of photo resist to form in some places while thin areas occur in others.

As a result the photo resist masks applied tended to be on the

thin side and subject to pinholes which caused excessive amounts of gold to be plated on the surface of the cells due to leakage through the mask. More than 20 full sized cells were processed in this manner and all of these gave very low outputs. The highest output obtained was about 2.5% efficiency, but most were below 1%.

Further analysis of those low output cells disclosed that much of the reason for the low outputs was series resistance. This was traced to high lateral resistance of the grid wires which in turn was a result of the wires being too thin. Attempts to build up the thickness by longer plating times were thwarted by the problem of leakage through the mask.

There is no doubt that a more thorough approach to this problem with better equipment, and materials selected for the task, would be successful. However, unless the cemented metal grid process has an unexpected weakness there seems little reason for further work on the electroplated grid process. The cost advantage of the cemented grid plus the reliability feature of the integral lead seem to favor the cemented grid.

e. Cover Plastic Attachment

1. Effect on Transmission

There was some concern that the Mylar cover plastic-epoxy cement combination used to complete the packaging of the CdS thin film solar cell might not have good light transmission properties for all the photoeffective wavelengths. Curing of the epoxy cement is done at 190°C in a poor vacuum (approx. 10^{-2} Torr) in about a 30 minute period, followed by a 16 to 18 hour anneal at 130°C in a slightly better vacuum. Small amounts of oxygen at these temperatures could cause darkening of the plastic layers, and hence affect cell output.

This possibility was checked by exposing samples of epoxy coated and uncoated Mylar to the heat-time cycle commonly used for cell lamination in both air and vacuum and measuring their transmission. The transmission curves are shown in Figure 7.

Plain Mylar appears to be about 85% transmissive (reflection losses not corrected for) whether it is heated in air or in vacuum for the time and temperature used for lamination. There is a slight indication of minor absorptions in the blue for the case of heating in air, but a high degree of accuracy is not claimed for this measurement.

When coated with epoxy the transmission seemed to be decreased by nearly 5% when heated in vacuum and increased by about the same amount when heated in air. It is indeed difficult to explain these latter results. It may be that the transmission test procedure was faulty and that extra reflections or scattering effects occurred on these test specimens that would not occur with the better optical coupling of a well-laminated cell.

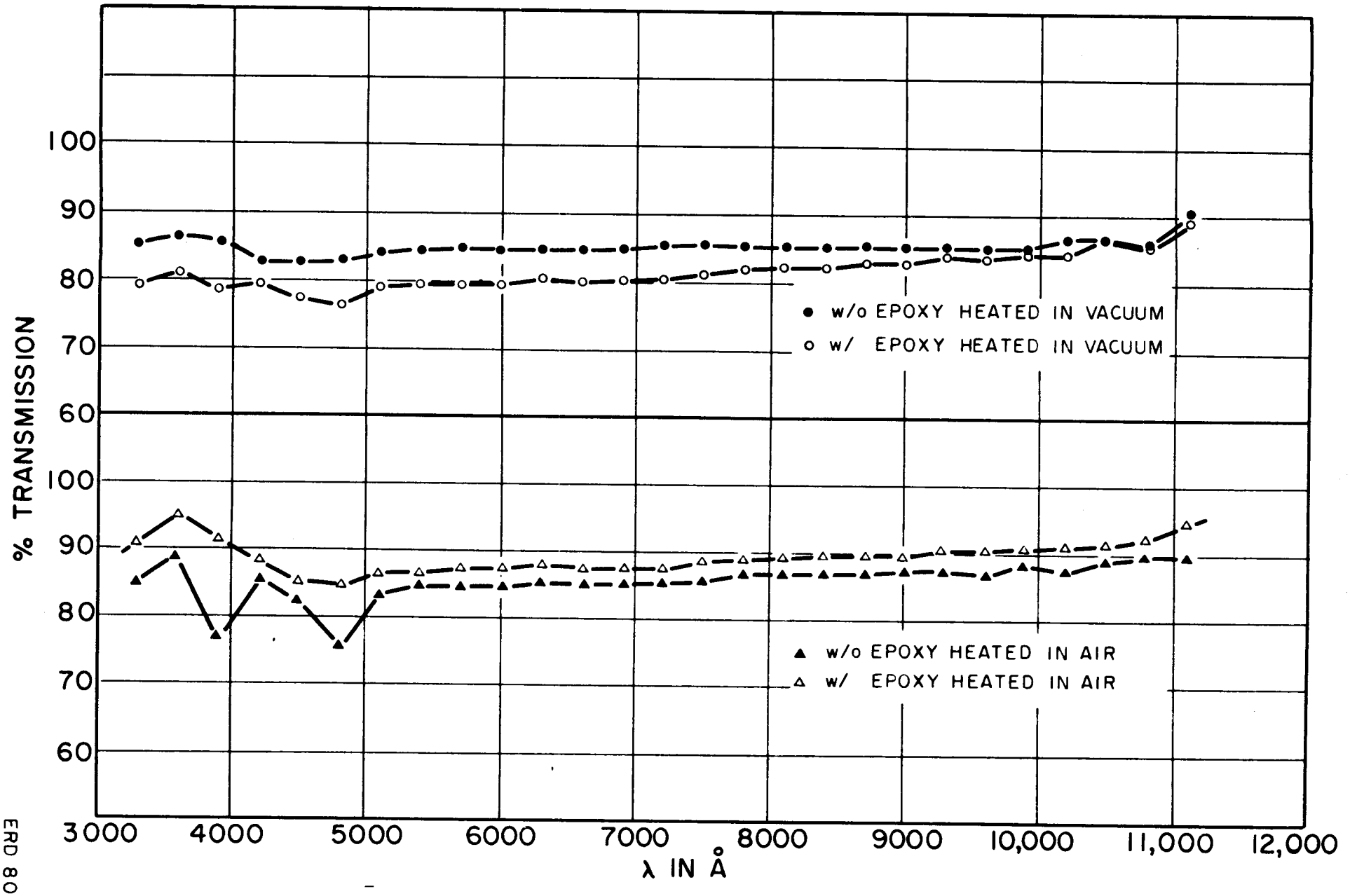


FIG. 7. TRANSMISSION OF VARIOUS HEATED MYLAR COVER PLASTICS.

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2. Effect on Spectral Response

Considering the difficulty of interpreting the results of the transmission measurements of the plastic alone, it was decided to measure the effect of the cover plastic on the spectral response of a cell. Therefore the spectral response of a cell was measured both before and after attachment of the cover plastic. Figure 8 shows the monochromatic response, and Figure 9 the response under white light bias conditions.

The monochromatic response is somewhat higher without the cover plastic. The response under white light bias was markedly higher without the cover plastic at the peak response point in the green and markedly lower in the infrared. These observations are also difficult to interpret, especially since the cell was 4.5% efficient prior to cover plastic attachment and 4.7% after. Usually there is an even greater difference which has been attributed partly to some anti-reflection aspects of the cover plastic and partly to additional cell forming occurring during the process of cover plastic attachment.

f. Cell Testing

Accurate yet convenient determination of cell output levels has still not been achieved in this laboratory as is evident from the shelf storage test data presented in this report. Reproduction in the laboratory of sunlight illumination conditions continues to have pitfalls, particularly for the CdS solar cell whose response has strong peaks in the blue and green portion of the spectrum.

The data presented in this report represent tests run with cell temperature held at 25°C ± 2°C under water filtered tungsten light, the intensity of which is adjusted (by varying the cell to light source distance) to give the same output as obtained in air mass 1 sunlight. As before, calibration of the absolute intensity of the tungsten light has been done by means of testing a large number (usually 50 or more) of cells in direct sunlight, extrapolating the output of each cell linearly to 100 mw/cm^2 conditions, reproducing that output for each cell in the tungsten light, measuring the absolute intensity of the tungsten light in each case, and averaging those values. Subsequent tests in the laboratory are run at that level of absolute tungsten illumination, and this is what is called "equivalent air mass 1 sunlight".

The water filter used is 2 inches thick deaerated distilled water to which 1 gram per liter $CuSO_4$ has been added. It is contained in a special frame made from 1/8" sheets of Corning 7740 IRR glass. The $CuSO_4$ water solution in the filter is replaced periodically, about once a week, as it deteriorates gradually in use. A different sunlight calibration is made for Kapton encapsulated cells than for Mylar encapsulated cells as these different plastic covers make radical differences in the absolute intensity of tungsten light needed to reproduce sunlight conditions. Further, a recalibration of the equivalence of sunlight and the laboratory tungsten light set-up is made regularly - once a each month, whenever possible.

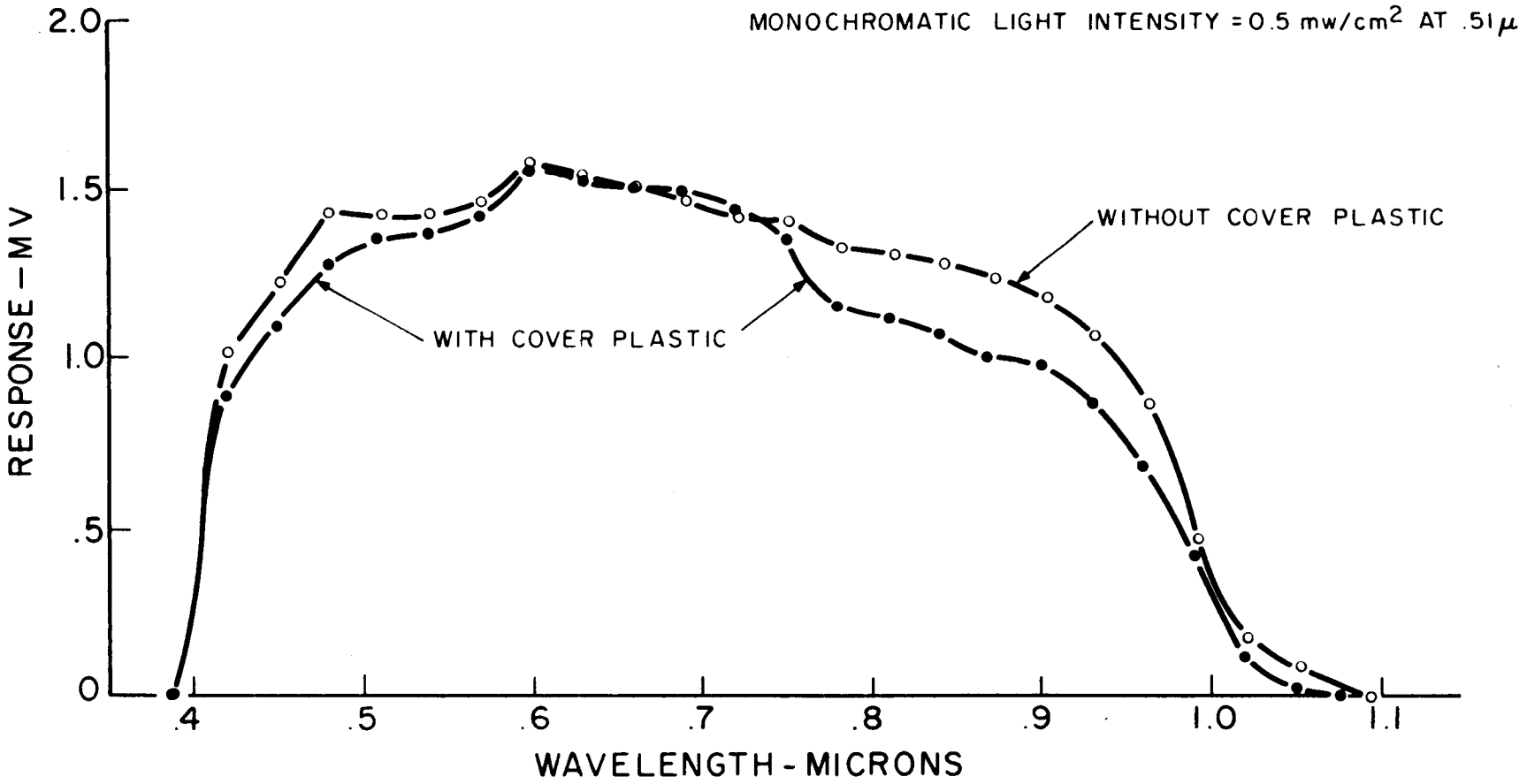

FIG. 8. EFFECT OF COVER PLASTIC ON MONOCHROMATIC SPECTRAL RESPONSE.

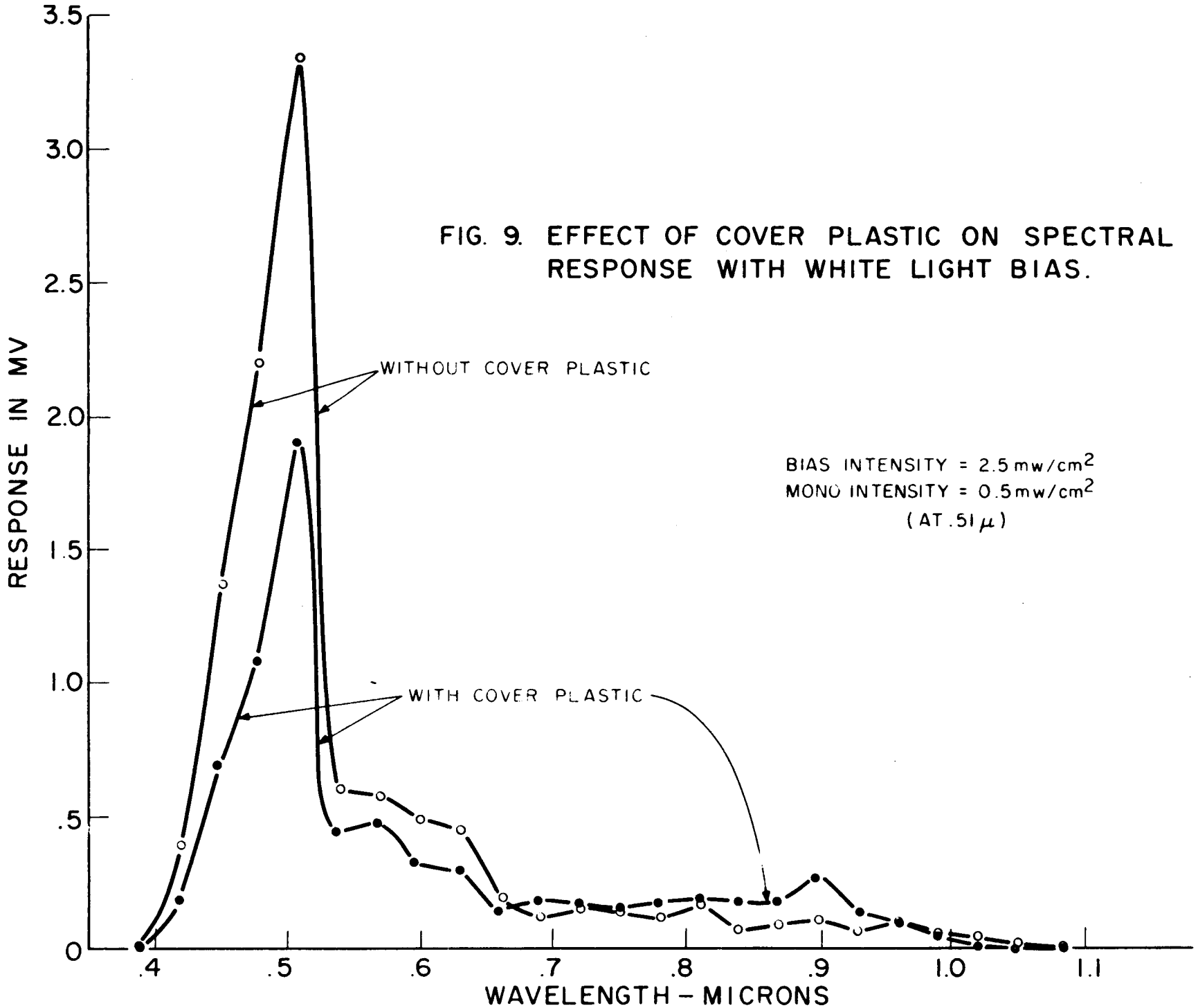

FIG. 9. EFFECT OF COVER PLASTIC ON SPECTRAL RESPONSE WITH WHITE LIGHT BIAS.

Even with these procedures and the use of 2 secondary standards - an Eppley thermopile and a standard silicon solar cell - difficulties have been encountered. In this period, both the thermopile used for measuring light intensity and the standard silicon cell used as a secondary check apparently went off calibration at about the same time and by about the same amount. As a result, all the data taken over about a three month period were erroneously high. The readings were probably more than 10% high, but probably less than 15% high, as nearly as can now be reconstructed.

After this experience an Eppley radiometer, cross-calibrated in direct sunlight with Eppley Laboratory's standard radiometer by Dr. A. J. Drummond, Director of Research of Eppley Laboratory, is being used as our primary standard of measurement of light intensity. This is backed up by the Eppley Thermopile which has been re-calibrated, another silicon standard cell, and a CdS thin film solar cell which has been stable for more than 2 years.

Even so, it is probable that any single reading of solar cell output made in our laboratory may be in error by as much as ±2%. For this reason, a number of measurements are usually made when higher accuracy is desired. For life tests, etc., it is planned to take more frequent readings in the future so that trends can be more accurately detected.

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2. "Kapton" and "Mylar" are registered trademarks for polyimide and polyester films obtained from E. I. duPont de Nemours Co., Wilmington, Delaware.

3. Grade MD 750 Silver Flake obtained from Metals Disintegrating Co., Elizabeth, New Jersey.

4. E-Solder #3012 obtained from Epoxy Products Inc., Irvington, New Jersey.

5. Gold-Epoxy #3205 obtained from Epoxy Products Inc., Irvington, New Jersey.

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7. Epoxy BP-242-4A and Curing Agent BP-242-2 obtained from Astro Chemical Co., Schenectady, New York.

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