



NASA CR-54996

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

THIRD QUARTERLY REPORT

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

RESEARCH & DEVELOPMENT

IN

CdS PHOTOVOLTAIC CELLS

BY

J. C. Schaefer, E. R. Hill, T. A. Griffin

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

December 29, 1965 to March 29, 1966

CONTRACT NAS-7631

N66 30542

FACILITY FORM 602

(ACCESSION NUMBER)

34

(PAGES)

CR-54996

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

03

(CATEGORY)

THE HARSHAW CHEMICAL CO.

N O T I C E

This report was prepared as an account of Government sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA), nor any person acting on behalf of NASA:

- A.) Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B.) Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with NASA, or his employment with such contractor.

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Attention: AFSS-A
Washington, D. C. 20546

THIRD QUARTERLY REPORT
RESEARCH AND DEVELOPMENT
IN
CdS PHOTOVOLTAIC CELLS

by

J. C. Schaefer, E. R. Hill, T. A. Griffin

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

December 29, 1965 to March 29, 1966

Contract NAS 3-7631

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Space Power Systems Division
Clifford Swartz

Harshaw Chemical Company
Crystal-Solid State Division
1945 E. 97th Street
Cleveland 6, Ohio

FOREWORD

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

Project direction has been provided by Mr. J. C. Schaefer with Mr. E. R. Hill and Mr. T. A. Griffin acting as principal investigators for the research and development work respectively. The following Harshaw personnel have contributed to this program: B. Keramidas, R. J. Humrick, R. W. Olmsted, D. J. Krus, W. W. Baldauf, N. E. Heyerdahl, P. J. Marn, and Dr. N. K. Pope of the Royal Military College of Canada served as consultant.

Table of Contents

	<u>Page</u>
Model Research	1
Cu ₂ S Formation and Diffusion	1
Closed Space Vapor Transport	4
Film Control	4
Film Adherence	6
Cell Efficiencies	8
Grids	9
Grid Transmission	9
Electroplated Copper	10
Compression Bonded	10
Moisture Barrier Coatings	12
Pilot Line	14
Testing	14
Interface Materials	16
Procedure	16
Appendix - Calculations on Diffusion	19

Abstract

Further studies of the barrier formation mechanism are reported with respect to 1) rate of Cu_2S formation and 2) diffusion of the Cu_2S in CdS . An increase of maximum cell efficiency to 5.8% is reported. Preliminary results on an alternate, simplified, gridding technique are given.

Summary

N 66-30542

Barrier formation studies were made on the 1) rate of Cu_2S formation and 2) diffusion of the Cu_2S in CdS . The rate of Cu_2S formation is in proportion to the Cu^+ ion solution concentration. Theoretical and experimental curves based on the increase of Cu_2S mass per unit times show good agreement. The diffusion of Cu_2S in CdS appears constant at approximately 10^{-9}cm^2 per second.

Several cells were produced and delivered under provisions of the contract with efficiencies in the range of 5% to 6%. The maximum value was 5.8%. The average cell efficiency has not kept pace with this improvement.

The electroplated grid technique continues to provide reliable cell units. An alternate pressure-temperature technique has been used to attach the grids. Preliminary results show that it may provide a high reliability cell unit. This is based on a 600 thermal cycle test.

The vapor transport film formation technique reveals good control of film properties. An adherence to substrate problem prevents any large advance in this area.

Arthur

Introduction

The CdS thin film, flexible, solar cell continues to improve in both areas of fabrication and solar energy conversion. The cells being studied and fabricated on the present contract are constructed on a metallic substrate which also serves as the n-collector. The CdS is deposited on the substrate by either evaporation or vapor transport. The barrier is formed at the surface of the CdS film by immersion in a cuprous chloride solution. The barrier is contacted by a metallic grid which is attached by 1) a softened plastic (nylon) during encapsulation, 2) an electroplated grid applied before encapsulation, or 3) a pressure contact before encapsulation. All methods permit total encapsulation in sheet plastic. Methods 2 and 3 do not require complete encapsulation but do permit open faced cells without any encapsulation.

The CdS model has recently been developed to the point at which it can be used to describe certain cell features. Data during this quarter shows that the rate of formation of the Cu_2S barrier is proportional to the cuprous ion concentration in the bath. It also shows that the diffusion of the Cu_2S in the CdS is constant. A coefficient of $D = 10^{-9}\text{cm}^2/\text{sec}$ has been determined. It should be possible to predict the immersion necessary for maximum cell output.

The electroplated grid provides a high reliability cell. The grid attachment by means of encapsulation provides the highest initial cell output, but lacks reliability. The new pressure technique may be an alternate to the electroplated grid.

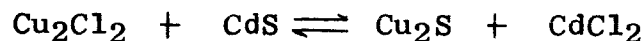
Vapor transport provides close control of variables but to no avail because of an adherence problem. Evaporation of CdS is the best method at present for forming the film.

The best cell to date has been 5.8% for a cell with an electroformed grid and 4.7% for the stable electroplated grid type.

Model Research

Cu₂S Formation and Diffusion

To study the nature of the junction in the CdS cell, one of the first steps is to determine the nature of the Cu₂S layer. This layer is chemically formed in an aqueous Cu₂Cl₂ solution. By the nature of this process, one expects two major features to be apparent. First, that the chemical reaction in the solution is governed only by the concentration of the active agent in the liquid and the surface concentration of the reaction product on the CdS film. Secondly, the distribution of Cu₂S in the bulk CdS is governed by physical diffusion as a result of concentration gradients. This can all be stated analytically in the following equations. First, the chemical reaction in the solution is:



Next, since the reaction concerns two components, its rate is proportional to the product of their concentration

$$\frac{d}{dt} [\text{Cu}_2\text{S concentration}] = \alpha [\text{Cu}_2\text{Cl}_2 \text{ concentration}] [\text{CdS concentration}]$$

where α = proportionality constant which may be
temperature dependent

Finally, in the bulk, the diffusion equation holds, and treating this as a one-dimensional problem,

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

where,

C = concentration of the diffusing specie,

D = diffusion constant of specie, which is temperature dependent, and

x = diffusion depth.

If the following notation is adopted:

where,

C = concentration of Cu_2S ,

C_0 = bulk concentration of CdS , and

C_L = concentration of Cu_2Cl_2 in liquid
is taken to be a constant,

then,

$$\frac{d}{dt} C(x=0, t) = \alpha C_L \left[C_0 - C(x=0, t) \right]$$

$$\text{or } C(0, t) = C_0 (1 - e^{-\alpha C_L t})$$

The diffusion equation is then solved using this as a boundary condition for $x = 0$; and $C(x, 0) = 0$ for all x .

The solution for the boundary conditions is rather involved, and the details are shown in the appendix. This solution gives an expression for $C(x, t)$. In the present device, determination of the profile of the Cu_2S in the CdS film is difficult. An easier technique is to determine the total amount of Cu_2S incorporated in the film. This is represented as:

$$M(t) = \int_0^{\infty} C(x, t) dx$$

The technique for measurement of this quantity is as follows. A CdS film of known area is weighed. It is then chemiplated for a known length of time to form the Cu₂S layer. It is then etched in a water solution of KCN to remove the Cu₂S and the water soluble reaction products. It is then dried and weighed again. The difference between the two weights represents the amount of CdS which entered into the reaction and produced Cu₂S. Thus, it is proportional to the mass of Cu₂S formed. The analytic expression for the integral is formidable, and so we look only at the asymptotic expressions for long and short immersion times. In these cases, the integrals can be evaluated easily. The results are:

$$M(t) = At^{3/2} \text{ for short times}$$

where

$$A = \frac{8C_0 D^{5/2}}{\lambda \sqrt{\pi}}$$

and

$$M(t) = \frac{2C_0 D}{\sqrt{\pi}} t^{1/2} \text{ for long times}$$

Then if one plots M as a function of time on log paper, the behavior should be as shown in Figure 1. The experiment was performed using 1 inch square films on molybdenum and a solution at 85°C. The results are shown in Figure 2. The noise level which is determined by the sensitivity of the balance obscures the short time behavior for this area of film. The long time dependence does show up, however, and from this, we can calculate the diffusion constant using

the bulk density of CdS for C_0 . This produces

$$D \simeq 10^{-9} \text{cm}^2/\text{sec.}$$

This number seems to be somewhat high, but can be verified by more extensive measurements. A check can also be made by determining junction capacitances as a function of immersion time and doping level in the bulk CdS film.

Closed Space Vapor Transport

A large number of CdS films were made by the closed space vapor transport method to investigate the degree of control obtained over film resistivity, mobility, and carrier concentration. The control is good. Adherence to various substrates was checked and final cell efficiency was noted. The degree of control over film properties is considered to be good.

Film Control

When a substrate is put in place over the CdS container, a piece of pyrex glass is positioned in juxtaposition. The CdS is deposited on the face of both materials at the same time. The CdS on glass is then used as the sample for the Hall measurements. It has been found that by changing the dopant level, the resistivity, mobility, and carrier concentration can be controlled easily and reproducibly from run to run. Table I shows a sampling of Hall data for films

doped with 0.05 wt. % indium sulfide. It was desired to control the film thicknesses between 15 and 20 microns. One film exceeded the range by one micron.

Table I
VT Film Characteristics

<u>Resistivity</u> (ohm-cm)	<u>Mobility</u> (cm ² -v-sec)	<u>Carrier Conc.</u> (cm ⁻³)	<u>Thickness</u> (microns)
1.44	2.13	2.04 x 10 ¹⁸	19
4.14	1.17	1.29 x 10 ¹⁸	18
4.86	0.67	1.91 x 10 ¹⁸	14
1.38	1.56	2.91 x 10 ¹⁸	21
4.41	1.0	1.4 x 10 ¹⁸	15
2.47	1.43	1.77 x 10 ¹⁸	15
3.35	1.36	1.37 x 10 ¹⁸	16

Good control of film properties is evident.

Runs made later from a batch of similar composition gave the following results:

<u>Resistivity</u>	<u>Mobility</u>	<u>Carrier Conc.</u>	<u>Thickness</u>
5.0	0.92	1.4 x 10 ¹⁸	15
2.3	1.7	1.4 x 10 ¹⁸	16
4.85	0.82	1.6 x 10 ¹⁸	15.5

These data show that certain film properties can be predicted and produced.

The following data were obtained on high resistivity films. Data on the mobilities or carrier concentrations were not obtainable.

<u>Resistivity</u> <u>(ohm-cm)</u>	<u>Thickness</u> <u>(microns)</u>
5.1×10^3	19
8.4×10^3	16
4.4×10^3	14
2.9×10^3	13
4×10^3	16
2.6×10^3	19

Therefore, it can be seen that the vapor transport procedure can provide films with controlled properties within a factor of four.

Film Adherence

Film adherence to the molybdenum has not been satisfactory since the rate of deposition and film thickness have been increased. With film thicknesses approaching 30 microns, the substrate cannot be bent more than 30 degrees or the film will crack and lift off. The problem is not apparent if the thickness is kept between 15 and 20 microns.

Since these films are essentially free of pin holes, the thinner film is sufficient for plating without fear of shorting through.

Experiments were conducted to determine whether this procedure was more amenable to metal substrates other than molybdenum. The metals and alloys investigated are as follows:

1. Pure Copper CdS attacked this substrate quite violently resulting in a flaky, black, non-adherent film. The substrate itself had holes in some areas.
2. 1010 Steel Resulting film was a non-adherent material that fell back into the boat. It was noted that the steel substrate lost weight during the run. It is also thought that the hexagonal crystallites in the film that formed were not CdS but FeS.
3. Invar The film had very poor adhesion and was quite brittle.
4. Copper Coated Molybdenum Resulting film was dark gray, very brittle with poor adherence to substrate.
5. Titanium Film was dark and somewhat glossy with very good adherence. This seemed to be useful, however, after further investigation, it was found to chip off as very small particles if the substrate was bent from its rest position.

6. Brass

The entire film separated from the substrate as one sheet. The film was approximately 4 mil thick with crystals 50 microns across.

Although only two runs were made with the metals, the titanium at present is the only metal of this group other than molybdenum that has possibilities.

Cell Efficiencies

A large number of films were made in an attempt to increase film thickness while decreasing the total transport time. Success was attained, but most of the cells produced were unsatisfactory. It is believed that the vapor transported films require a modified plating procedure. The highest efficiency to date has been 3.58%. Recent cells, after heating and testing, show a double diode I-V curve. After further heating, this characteristic generally disappeared but the cells have had rather low efficiencies of about 2%. Upon further investigation, a purple coloration was noted between the molybdenum and the CdS film. The presence of oxygen in the bell jar was suspected causing formation of an oxide of molybdenum and causing the double diode results.

The coloration was greatly reduced by flushing the bell jar with argon and burning Ti strips prior to each run. Therefore, it must be stated that contrary to earlier reports, air is not a suitable ambient gas.

It is also believed that the CdS powder becomes contaminated in contact with the tantalum boat. In trying to eliminate this possibility, a quartz insert has been fabricated and will be incorporated into the system.

Solution of the adherence problem will permit a certain degree of tailoring of the film and cell to the properties desired.

Grids

A breakthrough was accomplished this quarter with the production of electroplated grid cells with efficiencies above 4%. The maximum efficiency was 4.7% (NASA value). The efficiency increase is due to a shortened post-plating heat treatment and to recent advances in barrier formation.

Grid Transmission

The transmission of the Harshaw electroplated and the Buckbee-Mears electroformed grids were determined by 1) a microscope measurement of physical surface dimensions, and 2) by direct measurement of optical transmission. The transmission of the electroplated grid was found to be 82%; that of the best electroformed grid is 87%.

The electroformed mesh has served as a master for producing the necessary photographic masks. These masks were made approximately two years ago when the transmission of the Buckbee-Mears mesh was about 85%. This, along with unavoidable "errors" in the photoresist process, accounts for the lower

transmission of the electroplated grid. New photographic masks are being made from Buckbee-Mears mesh of the highest transmission.

Electroplated Copper

It is possible to electroplate copper grids onto the cell barrier from the cuprous chloride barrier chemiplating solution. Since only the area to be gridded is exposed, the solution should not be injurious to the cell, and the initial copper layer should prevent further barrier formation. A Hull cell^(1,2,3) was used to determine the optimum plating conditions of 10 ma/cm² at 25°C. Cells gridded by this method consistently produced low open circuit voltages. This is a direct confirmation of the results obtained with other copper plating solutions.

Compression Bonded

Experiments that began under a Harshaw-funded project have been continued under this contract. Initial results were quite favorable and the simplicity of the procedure warranted the continuing investigation.

One of the early cells (Number 45-1) that had a gold grid applied in this manner was submitted to NASA for thermal-cycling tests. As of the 30th of March, the cell was essentially unchanged after 600 cycles. This cell was 3" x 3" in size with the grid exposed (no face covering) and a plastic frame on the front and back. The grid material

was Buckbee-Mears Corporation electroformed gold mesh. Metal meshes other than gold were found to be unsatisfactory in the initial work.

Later development produced cells Numbers 147-2 and 175-2 which are distinguished by their copper grids. The grids are of the electroformed type and were treated before being applied to the surface of the cells.

Cell Number 147-2 was a 3 x 3 inch cell which also was of an exposed grid configuration with a picture frame of plastic on the front and back.

This cell was tested at NASA as being 4.0% efficient. Number 175-2 was a 3 x 3 inch cell with the compression bonded, treated, copper grid. The cell was laminated with Mylar-Nylon on the face and a picture frame plastic back. The efficiency of this cell as tested at NASA was 4.11%.

These cells are excellent indications that the compression bonding of the grid to the barrier surface without application of an epoxy or adhesive may be quite satisfactory.

Experiments were conducted with other metallic mesh materials resulting in mediocre or poor results. In several instances, the adhesion to the barrier surface was found to be excellent, but the electrical properties of the cell were so severely damaged that the cell was considered scrap. Several nickel and silver mesh grids were bonded using the same method. The silver grid was only fair in adhesion while the nickel would not adhere at all.

The transmission of the gold or treated copper mesh, when applied to the barrier surface is reduced to about 80% from the normal 85% due to a spreading of the grid lines during processing. This loss in active cell area has not been taken into account for cell efficiency calculations.

Copper and gold mesh of higher initial transmission has been ordered to permit fabrication of cells with increased light transmission and cell output in spite of the inherent spreading of the grid lines.

Moisture-Barrier Coatings

Four groups of two cells each were dip coated with numerous moisture-barrier materials. Cells C1 and C2 were coated with Aero seal (a product of the American Standard Company), cells C3 and C4 with Dow Corning #901, cells C5 and C6 with Vernon-Benshoff Acrylic, and Cells C7 and C8 with a polyester. Cells C9 and C10 were uncoated. The cells were placed in a 98% relative humidity environment. Table II shows that no coating provided complete protection. However, cells C7 and C8 (polyester coating) after 16 hours had 0% and 11% degradation as compared to 84% and 93% for C9 and C10 (uncoated) respectively. Additional work on the polyester coating is necessary to determine optimum curing time and temperature.

Table II
Dip Coatings for Moisture Protection
98% Relative Humidity Test

<u>Cell No.</u>	<u>Coating</u>	<u>Time in Environment (Hrs.)</u>	<u>Power (mw)</u>
C1	Aeroseal	0	6.8
		16	4.7
		40	3.5
C2	Aeroseal	0	11.0
		16	9.3
		40	4.7
C3	DC 901	0	15.9
		16	9.7
		40	7.7
C4	DC 901	0	6.8
		16	2.4
		40	1.1
C5	Acrylic	0	9.4
		16	2.2
		40	1.0
C6	Acrylic	0	9.0
		16	2.4
		40	1.2
C7	Polyester	0	12.6
		16	12.6
		110	9.4
		160	8.8
		200	8.8
		300	8.7
		400	8.6
C8	Polyester	0	13.1
		16	11.6
		40	11.4
		140	9.7
		200	7.7
C9	Uncoated	0	7.8
		16	1.3
C10	Uncoated	0	8.5
		16	0.5

Pilot Line

During this quarter, about 150 cells were fabricated on the pilot line. The highest efficiency measured for a 3" x 3" cell was 5.4% and 5.8% for 1" x 1". The average was slightly over 3%. The current density of the cells has been steadily increasing due to better barrier formation techniques. However, the efficiencies of the cells are not increasing as rapidly as the current since there has been a drop in voltage.

The cause of the lower voltages is not evident. The CdS source material being used as standard material is known as Harshaw Soft Sinter. This is CdS powder that has been sintered into a soft cake rather than a hard cake. It has been shown spectrographically that the soft sinter contains less impurities, particularly Al_2O_3 , than the hard sinter.

Testing

During this quarter, it was discovered that a significant portion of the cells' efficiencies was not being realized as a result of testing methods.

The spectral response of the present CdS cells are not the same as previous cells, and so the previous standard (G.E. light meter and RFL-2 tungsten lamp) is no longer suitable.

It was also evident that it is not correct to measure cells in 80 mw sunlight and then scale up the efficiencies by 20%. The missing light in 80 mw sunlight does not contribute significantly to cell operation.

A new test setup has been devised in order to gain better control in measuring cell performance, and a testing method consistent with that used by the contracting agency.

The test equipment incorporates a new light source patterned after that used at Lewis Laboratory, NASA.

(Figure 3). The lamps are four 650 watt G.E. sun guns. The G.E. lamps containing bromine were compared to the Sylvania lamps which employ iodine. The two types of lamps were found to provide identical results. The G.E. lamps were selected because of their convenient size and shorter filaments. These filaments are closer to being a point source.

The second important part of the light source is the filter. It consists of an aluminum frame, and two 1/4" plate glass windows. The 12" x 12" windows are 2" apart. The space between the windows is completely filled with 0.1% copper sulfate solution.

The base of the test rack seen in the figure contains a vacuum hold down and water cooling coils.

The intensity and uniformity of the light is adjusted by moving the lamps rather than changing the filament voltage. The course adjustment is made by moving the sun guns up, down, or to either side. The bulbs in each gun can be moved a short distance in relation to the reflector to provide a fine adjustment.

The standard cell used is a CdS cell provided by NASA. The CdS cell has been checked against other cells measured in sunlight. A silicon cell is also used for calibration purposes.

The I-V data is usually taken from the oscilloscope display, but it can also be recorded on an x-y plotter.

Tests will be conducted at this laboratory to compare the results of this light source with actual sunlight.

This light source has been adopted as a simulated supply to facilitate the accumulation of meaningful test data from various laboratories by means of an uniform testing procedure.

Interface Materials

During this quarter, several substrates with sputtered silver interfaces were processed on the pilot line. These cells do not show a great superiority to those on molybdenum. However, there seems to be a tendency to higher currents, on the silver substrates. More will be processed to help clarify the picture.

Procedure

An up-dating in procedure was accomplished at the end of this quarter. The best cell fabrication methods were incorporated in the pilot line. This will facilitate delivery of the cells still to be made and delivered on the contract.

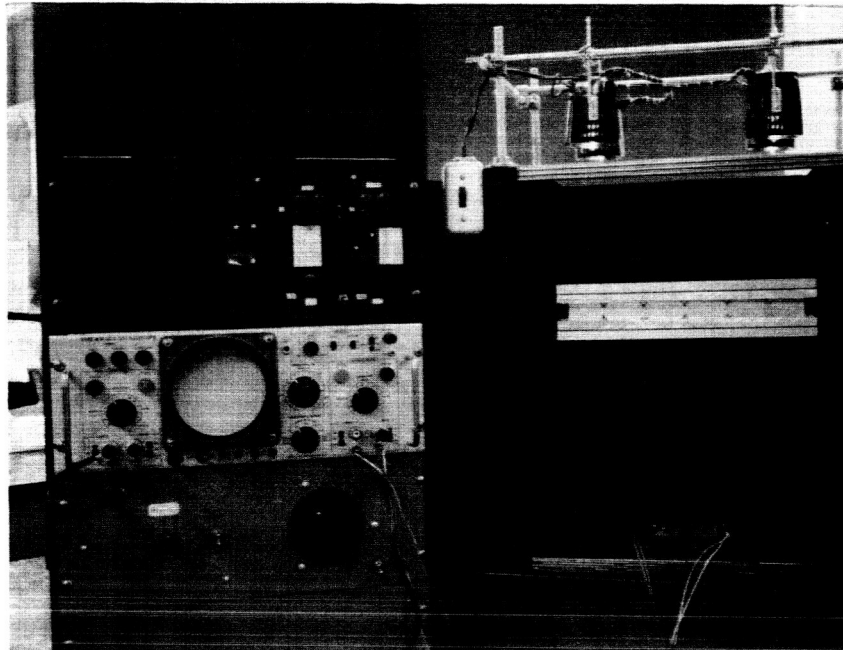


Figure 3
Simulation Solar Test Facility

References

- (1) F. H. MacIntyre and R. O. Hull, Am. Electroplaters' Soc., Proceedings (1943).
- (2) R. O. Hull, Am. Electroplaters' Soc. Proceedings (1939).
- (3) Ibid., (1943).

Appendix - Calculations on Diffusion

The diffusion equation to be solved is,

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad (1)$$

D = diffusion constant

x = distance from surface into the CdS film

The boundary conditions are

$$C = 0 \text{ at } t = 0$$

and

$$C = C_0(1 - e^{-\lambda t}) \text{ at } x = 0$$

C_0 = bulk density of Cu_2S

$\lambda = \alpha C_0 C_L$, the reaction constant at the CdS film surface

We call

$$C_0(1 - e^{-\lambda t}) = F(t) \quad (2)$$

Then the general solution to (1) is, from Carslaw and Jager (1)

$$C(x, t) = \int_0^t F(\lambda) \frac{\partial}{\partial t} G(x, t - \lambda) d\lambda \quad (3)$$

where

$$G(x, t - \lambda) = \frac{2}{\pi} \frac{\int_x^\infty e^{-z^2} dz}{2 D(t - \lambda)}$$

Letting

$$u = \frac{x}{2\sqrt{D(t-\lambda)}}$$

and substituting for $\frac{\partial G}{\partial t}$, we find

$$\begin{aligned} C(x,t) &= \frac{2}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^{\infty} F\left(t - \frac{x^2}{4Du^2}\right) e^{-u^2} du \\ &= \frac{2C_0}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^{\infty} \left(1 - e^{-\frac{\lambda x^2}{4Du^2} - \lambda t}\right) e^{-u^2} du \end{aligned}$$

The solution to this is

$$\begin{aligned} C(x,t) = C_0 \left\{ \operatorname{erfc} \frac{x}{2\sqrt{Dt}} - \frac{1}{2} e^{-\lambda t} \left[e^{ix\sqrt{\frac{D}{\lambda}}} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} - i\sqrt{\lambda t} \right\} \right. \right. \\ \left. \left. + e^{-ix\sqrt{\frac{D}{\lambda}}} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} + i\sqrt{\lambda t} \right\} \right] \right\} \end{aligned}$$

The error function for complex argument is

$$\operatorname{erf}(a+ib) = \operatorname{erf} a + \frac{2}{\sqrt{\pi}} \int_0^b e^{-y^2} (\sin 2ay + i \cos 2ay) dy$$

Thus, if $a = 0$

$$\operatorname{erf}(ib) = \frac{2i}{\sqrt{\pi}} \int_0^b e^{-y^2} dy = \operatorname{erf}(-ib)$$

We are interested in two asymptotic cases, (a) for short times, and (b) for long times.

For short times, (a)

$$\sqrt{\lambda}t \ll 2 \sqrt{Dt}$$

And then,

$$C(x,t) \simeq C_0 \left[\operatorname{erfc} \frac{x}{2 \sqrt{Dt}} \right] (1 - e^{-\lambda t} \cos x \sqrt{\frac{D}{\lambda}})$$

$$e^{-\lambda t} \simeq 1, \text{ giving}$$

$$C(x,t) \simeq C_0 \left[\operatorname{erfc} \frac{x}{2 \sqrt{Dt}} \right] (1 - \cos x \sqrt{\frac{D}{\lambda}})$$

Expanding the cosine term,

$$C(x,t) \simeq C_0 \left[\operatorname{erfc} \frac{x}{2 \sqrt{Dt}} \right] \left[\frac{x^2}{2} \frac{(D)}{(\lambda)} - \frac{x^4}{24} \frac{(D)^2}{(\lambda)^2} + \dots \right]$$

Keeping only the quadratic term

$$C(x,t) \simeq \frac{C_0 D}{2 \lambda} x^2 \operatorname{erfc} \frac{x}{2 \sqrt{Dt}} = \frac{C_0 D}{\lambda \lambda} x^2 \int_{\frac{x}{2 \sqrt{Dt}}}^{\infty} e^{-z^2} dz$$

The total amount of diffusant is,

$$M(t) = \int_0^{\infty} C(x,t) dx \simeq \frac{C_0 D}{\lambda \lambda} \int_0^{\infty} x^2 dx \int_{\frac{x}{2 \sqrt{Dt}}}^{\infty} e^{-z^2} dz$$

Letting $\frac{x}{2 \sqrt{Dt}} = y$

$$M(t) \simeq \frac{8C_0 D(Dt)^{3/2}}{\lambda \sqrt{\pi}} \int_0^\infty y^2 dy \int_y^\infty e^{-u^2} du$$

The integral is a number and consequently

$$M(t) = At^{3/2} \text{ for short times. } A = \text{constant.}$$

$$\text{For long times } \sqrt{\lambda t} \gg \frac{x}{2\sqrt{Dt}}$$

Then

$$C(x,t) = C_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}} = \frac{2C_0}{\sqrt{\pi}} \int_{\frac{x}{2\sqrt{Dt}}}^\infty e^{-z^2} dz$$

Again, the total amount of diffusant entering the surface is

$$M(t) = \int_0^\infty C(x,t) dx = \frac{2C_0}{\sqrt{\pi}} \int_0^\infty dx \int_{\frac{x}{2\sqrt{Dt}}}^\infty e^{-z^2} dz$$

$$\text{Again, with } y = \frac{x}{2\sqrt{Dt}}$$

$$\begin{aligned} M(t) &= \frac{4C_0 \sqrt{Dt}}{\sqrt{\pi}} \int_0^\infty dy \int_y^\infty e^{-z^2} dz \\ &= \frac{2C_0 \sqrt{Dt}}{\sqrt{\pi}} \end{aligned}$$

$$\text{So, } M(t) = Bt^{1/2} \text{ for long times}$$

where, $B = \text{constant}$

N66-30542

THE HARSHAW CHEMICAL COMPANY

1945 EAST 97TH STREET
CLEVELAND, OHIO 44106
AREA CODE 216
721-8300

Please insert the attached figures in your
copy of the Third Quarterly Report,
"RESEARCH AND DEVELOPMENT IN CdS PHOTOVOLTAIC CELLS",
identified as NASA CR-54996.

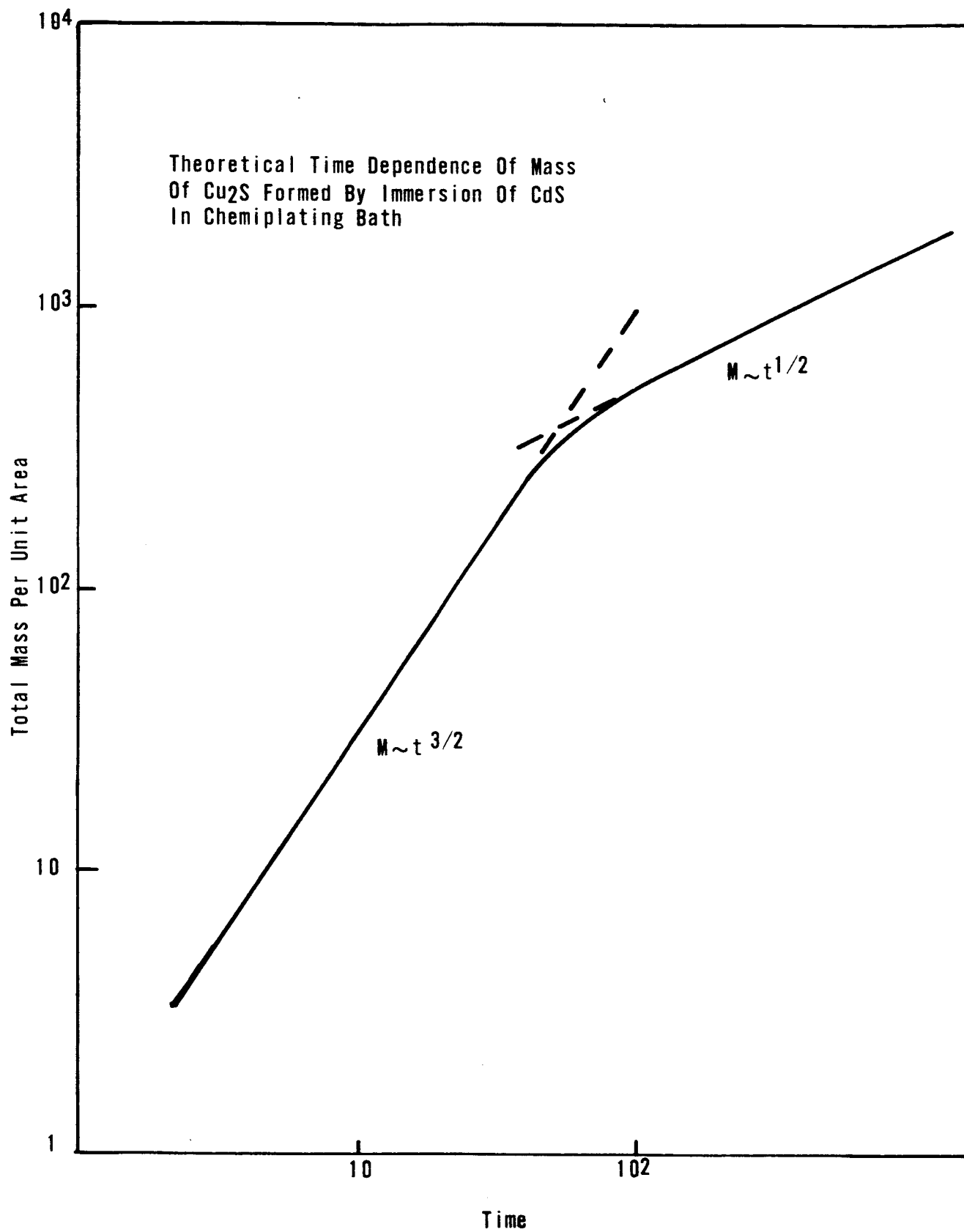


Figure 1 Theoretical Mass vs Time Curve For Cu_2S Formation

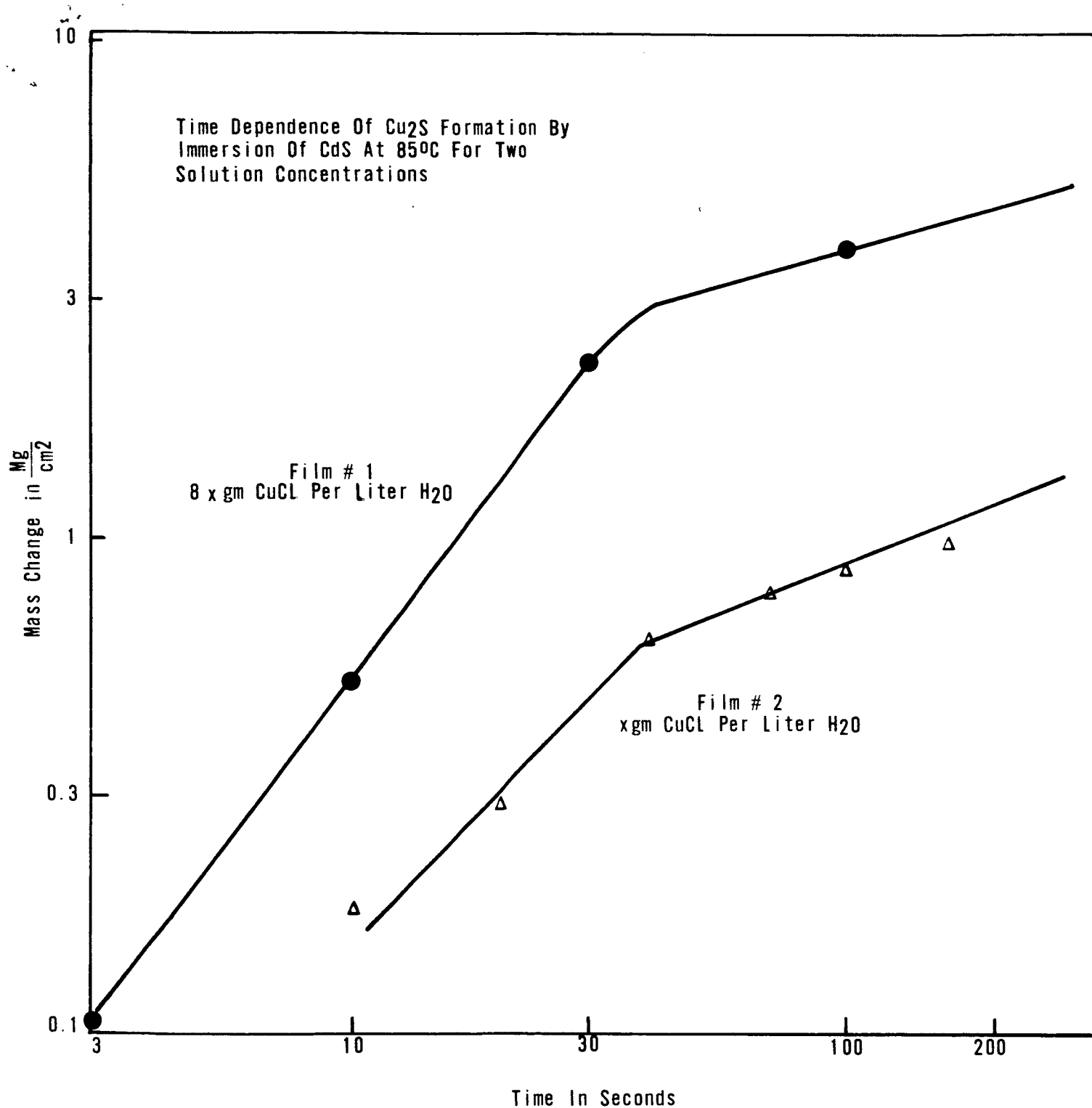


Figure 2 Experimental Mass vs Time Curve For Cu_2S Formation

THE HARSHAW CHEMICAL COMPANY
CONTRACT NAS3-7631
DISTRIBUTION LIST

QUARTERLY AND FINAL REPORTS

National Aeronautics and Space Administration
Washington, D.C. 20546

Attention: Arvin H. Smith/RNW (2)
H. B. Finger/RP
Millie Ruda/AFSS-LD

National Aeronautics and Space Administration
Scientific and Technical Information Facility
P.O. Box 5700

Bethesda, Maryland 20546
Attention: NASA Representative (5 + 1 Reproducible)

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland 20771

Attention: W. R. Cherry
M. Schach
B. Mermelstein, Code 672
J. W. Callaghan, Code 621
Librarian
P. H. Fang, Code 633

National Aeronautics and Space Administration
Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135

Attention: John E. Dilley, M.S. 500-309
B. Lubarsky, M.S. 500-201
H. Shumaker, M.S. 500-201
R. L. Cummings, M.S. 500-201
C. K. Swartz, M.S. 500-201 (3 + 1 Reproducible)
N. D. Sanders, M.S. 302-1
A. E. Potter, M.S. 302-1 (3)
C. S. Corcoran, M.S. 500-201
V. F. Hlavin, M.S. 3-14 (Final Only)
George Mandel, M.S. 5-1 (2)
Report Control Office
Technology Utilization Office,
M.S. 3-19
Office of Reliability & Quality
Assurance, M.S. 500-203

National Aeronautics & Space Administration
Langley Research Center
Langley Station
Hampton, Virginia 23365
Attention: W. C. Hulton
E. Rind

National Aeronautics & Space Administration
Electronic Research Center
Power Conditioning & Distribution Lab.
575 Technology Square
Cambridge, Massachusetts 02139

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103
Attention: John V. Goldsmith
Don W. Ritchie

Institute for Defense Analysis
Connecticut Avenue, N.W.
Washington, D.C. 20546
Attention: R. Hamilton

Advanced Research Projects Agency
Department of Defense, Pentagon
Washington, D.C. 20546
Attention: Dr. C. Yost

Naval Research Laboratory
Department of the Navy
Washington, D.C. 20546
Attention: E. Broncato, Code 6464
M. Wotaw, Code 5170
Dr. V. Linnenbom, Code 7450
Dr. C. Klick, Code 6440

U.S. Army Signal Research and Development
Laboratory
Fort Monmouth, New Jersey
Attention: Power Sources Branch

Air Force Cambridge Research Center
Air Research and Development Command
United States Air Force
Laurence G. Hanscom Field
Bedford, Massachusetts
Attention: Col. G. de Giacomo

Air Force Ballistic Missile Division
Air Force Unit Post Office
Los Angeles 45, California
Attention: Col. L. Norman, SSEM
Lt. Col. G. Austin, SSZAS
Lt. Col. A. Bush, SSZME
Capt. A. Johnson, SSZDT
Capt. W. Hoover, SSTRE

Office of the Chief of Engineers
Technical Development Branch
Washington, D.C.
Attention: James E. Melcoln/ENGMC-ED

Aeronautical Research Laboratories
Office of Aerospace Research, USAF
Wright-Patterson Air Force Base
Dayton, Ohio
Attention: Mr. D. C. Reynoles, ARX
Chief, Solid State Physics,
Research Lab.

Aeronautical Systems Division
Air Force Systems Command
United States Air Force
Wright-Patterson Air Force Base, Ohio
Attention: P. R. Betheand
Mrs. E. Tarrants/WWRNEM-1

Flight Vehicle Power Branch
Air Force Aero Propulsion Laboratory
Wright-Patterson Air Force Base, Ohio
Attention: Joe Wise/Code APIP-2

Flight Accessories Aeronautics Systems Division
Wright-Patterson Air Force Base
Dayton, Ohio
Attention: James L. Matice, ASRCM-22

Aerospace Corporation
P.O. Box 95085
Los Angeles 45, California
Attention: Dr. G. Hove
Dr. F. Mozer
V. J. Porfune
Dr. I. Spiro
Technical Library Documents
Group

Battelle Memorial Institute
505 King Avenue
Columbus, Ohio
Attention: L. W. Aukerman
R. E. Bowman
T. Shielladay

Bell and Howell Research Center
360 Sierre Madre Villa
Pasadena, California
Attention: Alan G. Richards

Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey
Attention: W. L. Brown
U. B. Thomas

Clevite Corporation
Electronic Research Division
540 East 105th Street
Cleveland, Ohio 44108
Attention: Fred A. Shirland
Dr. Hans Jaffe

The Eagle-Picher Company
Chemical and Material Division
Miami Research Laboratories
200 Ninth Avenue, N.E.
Miami, Oklahoma
Attention: John R. Musgrave

Energy Conversion, Incorporated
336 Main Street
Cambridge 42, Massachusetts
Attention: G. J. McCaul

General Electric Company
Electric Components Division
316 East Ninth Street
Owensboro, Kentucky
Attention: F. D. Dyer, Jr.

Heliotek Corporation
12500 Gladstone Avenue
Sylmar, California
Attention: Eugene Ralph

Hughes Aircraft Company
Aerospace Group, R & D Division
Culver City, California
Attention: C. A. Escoffery

International Rectifier Corporation
239 Kansas Street
El Segundo, California
Attention: Irwin Rubin

Leesona Moos Laboratories
90-28 VanWyck Expressway
Jamaica 18, New York
Attention: Stanley Wallack

Lockheed Missile and Space Division
3251 Hanover Street
Palo Alto, California
Attention: D. Marks, Dept. 5230

Material Research Corporation
Orangeburg, New York 10962
Attention: Vernon E. Adler

Martin Company
Orlando, Florida
Attention: W. A. Headley, Jr.

National Cash Register Company
Physical Research Department
Dayton 9, Ohio
Attention: R. R. Chamberlin

North American Aviation, Incorporated
Autometics Division
Anaheim, California
Attention: R. R. August

Perkin-Elmer Company
Optical Coating Section
Norwalk, Connecticut
Attention: Jim Peardsley

Philco Corporation
Blue Bell, Pennsylvania
Attention: Mr. A. E. Mace

Physics Technology Laboratories, Inc.
7841 El Cajon Boulevard
La Mesa, California
Attention: W. E. Richards

RCA Laboratories
Radio Corporation of America
Princeton, New Jersey
Attention: P. Rappaport

Ryan Aeronautical Company
Lindbergh Field
San Diego, California 92112
Attention: K. D. Hawkins

Sandia Corporation
Albuquerque, New Mexico
Attention: F. Smits

Sylvania Electronic Products, Incorporated
Electron Tube Division
Emporium, Pennsylvania
Attention: Georgiana Larrabee, Librarian

Tyco Laboratories, Inc.
Bear Hill
Waltham 54, Massachusetts
Attention: A. I. Mlavsky

Union Carbide Corporation
Parma Research Center
Technical Information Services
P.O. Box 6116
Cleveland, Ohio 44101

Solid-State Electronics Laboratory
Stanford Electronics Laboratories
Stanford University
Stanford, California
Attention: Prof. G. L. Pearson

Westinghouse Electric Corporation
Research and Development Laboratories
Churchill Borough, Pennsylvania
Attention: H. G. Chang

Westinghouse Electric Corporation
Semiconductor Division
Youngwood, Pennsylvania
Attention: Don Gunther

Massachusetts Institute of Technology
Security Records Office
Room 14-0641
Cambridge 39, Massachusetts