Progress Report No. 8

MECHANISM OF THE PHOTOVOLTAIC EFFECT IN II-VI COMPOUNDS

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

January 1 - March 31, 1970

School of Engineering
Department of Materials Science
Stanford University
Stanford, California

Grant NGL-05-020-214 S-1

Principal Investigator
Richard H. Bube, Professor

Report Prepared By:

R.H.Bube
A.Fahrenbruch
P.F.Lindquist

Department of MATERIALS SCIENCE
STANFORD UNIVERSITY

Progress Report No. 8

MECHANISM OF THE PHOTOVOLTAIC EFFECT IN II-VI COMPOUNDS

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

January 1 - March 31, 1970

School of Engineering
Department of Materials Science
Stanford University
Stanford, California

Grant NGL-05-020-214 S-1

Principal Investigator
Richard H. Bube, Professor

Report Prepared By:

R.H.Bube
A.Fahrenbruch
P.F.Lindquist

CONTENTS

ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

ABSTRACT, CONCLUSIONS AND RECOMMENDATIONS

A correlation has been made between the extensive series of measurements on non-heat-treated and heat-treated Cu_2S-CdS cells. The results demonstrate that trapped charge in the interface region, manifested by photocapacitance measurements, is responsible for the enhancement and quenching effects observed in the photoresponse of heat-treated Cu_2S-CdS heterojunctions. This trapped charge also affects the photoresponse of non-heat-treated junctions, but to a lesser extent. There can be no question but that this trapped charge is a vital factor in the photovoltaic performance of the Cu_2S-CdS cell. Whereas before heat treatment the dependence of short-circuit photocurrent on photocapacitance (trapped charge) is linear, the dependence after heat treatment is exponential; these are the kinds of dependences to be expected from a small spike in the conduction band at the interface. Complete details will be provided in Progress Report No. 9, the Ph.D. Thesis of Peter F. Lindquist.

Properties of Cu-CdS cells prepared by vacuum evaporation of Cu have been investigated. Dependence of properties on etching of the surface is noted, as well as marked differences between A- and B-face CdS surfaces used for Cu evaporation.

Future work includes a correlation between the ratio of cupric to cuprous sulfide and the photovoltaic properties of the junction, as well as investigations of surface treatment, nature of bulk CdS conductivity, and the phenomena involved in heat treatment.

I. INTRODUCTION

The discussions of the last two Progress Reports have dealt mainly with the properties of non-heat-treated cells. The effects of trapped charge at the interface of such non-heat-treated Cu_2S-CdS heterojunctions was extensively studied by photocapacitance techniques

When such a junction is cooled to about 100°K and illuminated with bandgap light, a large increase in the junction capacitance is observed. After photoexcitation a significant capacitance increment, which can be as much as 50 percent of the capacitance before illumination, remains indefinitely.

This photocapacitance increment can be quenched by (a) heating, (b) applying forward bias in the dark, or (c) illuminating with photons with energy between 1.2 and 1.8 eV. The photocapacitance data are consistent with a model in which holes are trapped in deep levels near the interface and decrease the width of the depletion layer.

At 105°K the short-circuit photocurrent measured after establishing the photocapacitance exceeds the photocurrent with zero photocapacitance by a factor of three over the entire response range. Thus the effect is small but noticeable in the non-heat-treated cell.

In the present report we summarize some of the behavior of such a cell as it is progressively heat-treated. What is presented in this report is only a portion of the results obtained. The next Progress Report (No. 9) will consist of the complete PhD Thesis of Peter F. Lindquist, in which all of these details will be included and discussed.

The present report also describes some of our initial results on Cu-CdS junctions prepared by evaporation of Cu metal.

II. EFFECT OF HEAT TREATMENT

Previous results have demonstrated that Cu_2S-CdS single crystal cells with relatively high photovoltaic efficiency can be produced without heat treatment and that trapping of charge at the interface, revealed by photocapacitance measurements, plays a major role in determining the electrical and photovoltaic properties of the heterojunction. In order to relate these results directly to the properties of commercial thin-film Cu_2S-CdS cells and to our previous investigation of the heat-treated Cu_2S-CdS system, one sample was given a series of 2 minute heat treatments in air. The I-V characteristics, capacitance-voltage curves, spectral response and photocapacitance behavior were measured after each heat treatment. The sample chosen was 2-B(P+E)-1, for which extensive data had been previously obtained. The heat-treatment temperatures were 100°C, 150°C and 200°C.

The main characteristicts of the results can be summarized as follows:

1. Light-generated I-V curves show a steady decrease in short-circuit current and a slight decrease in open-circuit voltage with heat treatment.

2. The anomalous cross-over of light and dark I-V curves is brought about by heat treatment.

3. The dark current at low forward and reverse bias was increased significantly after the 100°C and 200°C heat treatment, but was much lower after the intermediate heat treatment at 150°C. The reason for this behavior is not clear.

4. With heat treatment the value of capacitance at zero bias decreases and the intercept of the $1/C^2$ vs. V plot increases with increasing heat treatment. These effects can be interpreted as the result of a widening intrinsic intermediate layer in the space-charge region.

5. Heat treatment reduces the short-circuit current at all wavelengths, but particularly at longer wavelengths, as has been frequently observed previously. Transient effects in the measurement of the short-circuit current (associated with enhancement and quenching effects) begin to appear in the curves measured after 150° and 200°C heat treatments. Similar effects are observed in the spectral response of the photovoltage.

6. Figure 1 illustrates the effect of photocapacitance on the spectral response of the short-circuit current at 105°K after the 200°C heat treatment. It is evident that the presence of the photocapacitance in this heat-treated sample has a profound effect on the short-circuit photocurrent, increasing it by two orders of magnitude to nearly its value at 300°K *before* heat treatment.

7. Figure 2 gives another representation of the effect of photocapacitance on photocurrent after heat treatment. The sample was photoexcited with various intensities of 0.7 micron light at 105°K, and the initial value of photocurrent (corresponding to the particular value of photocapacitance) was recorded. Whereas before heat treatment the dependence of photocurrent on photocapacitance was linear, the dependence after heat treatment is exponential. These are the kinds of dependences to be expected from a small spike in the conduction band.

8. The optical quenching of photocapacitance in the heat-treated sample (200°C) was measured at 105°K. The shape of the spectrum is qualitatively the same as that reported previously for the non-heat-treated sample.

These results demonstrate that trapped charge in the interface region, manifested by photocapacitance measurements, is responsible for the enhancement and quenching effects observed in the photoresponse of heat-treated Cu_2S-CdS heterojunctions. This trapped charge also

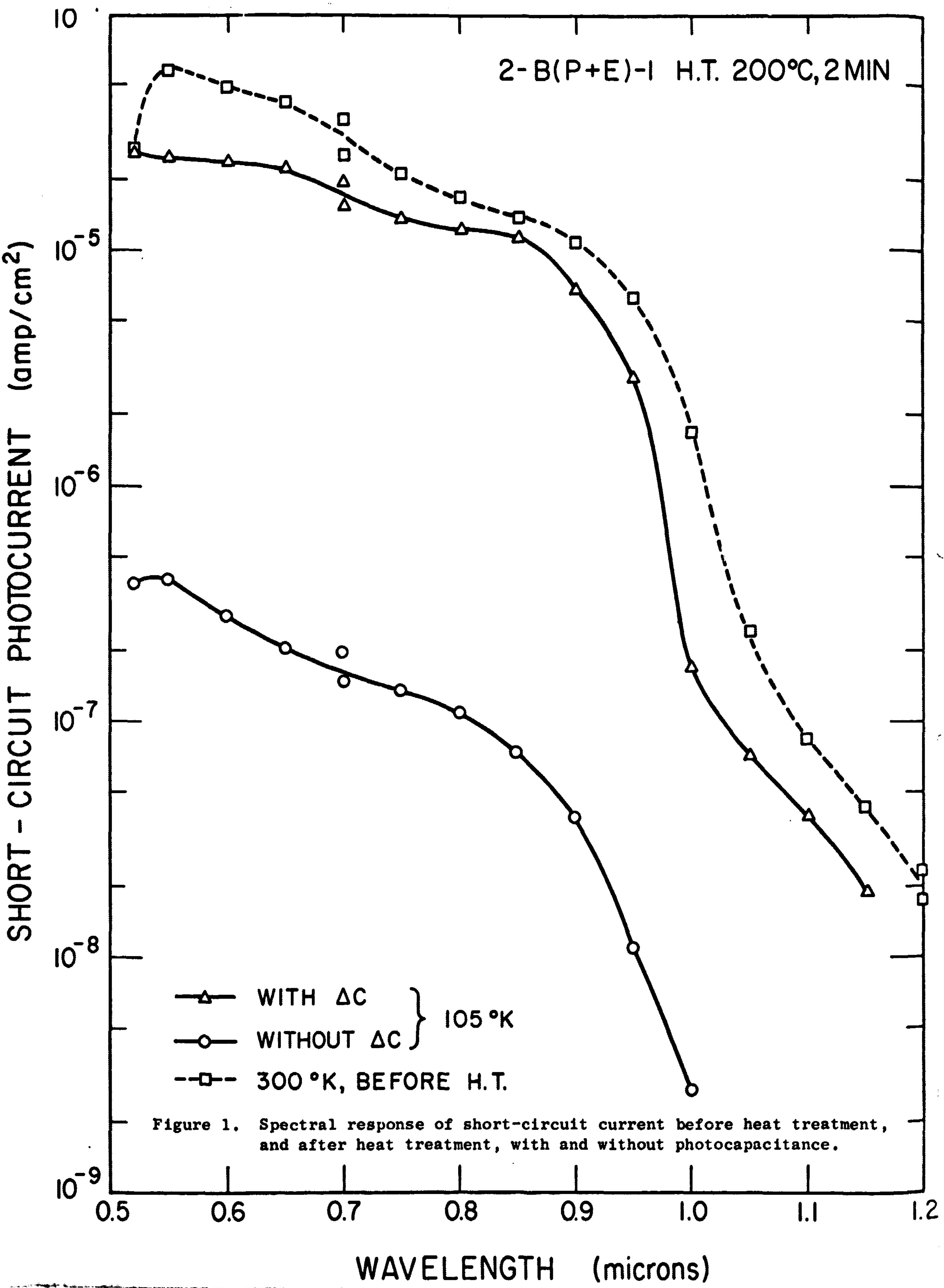


Figure 1. Spectral response of short-circuit current before heat treatment, and after heat treatment, with and without photocapacitance.

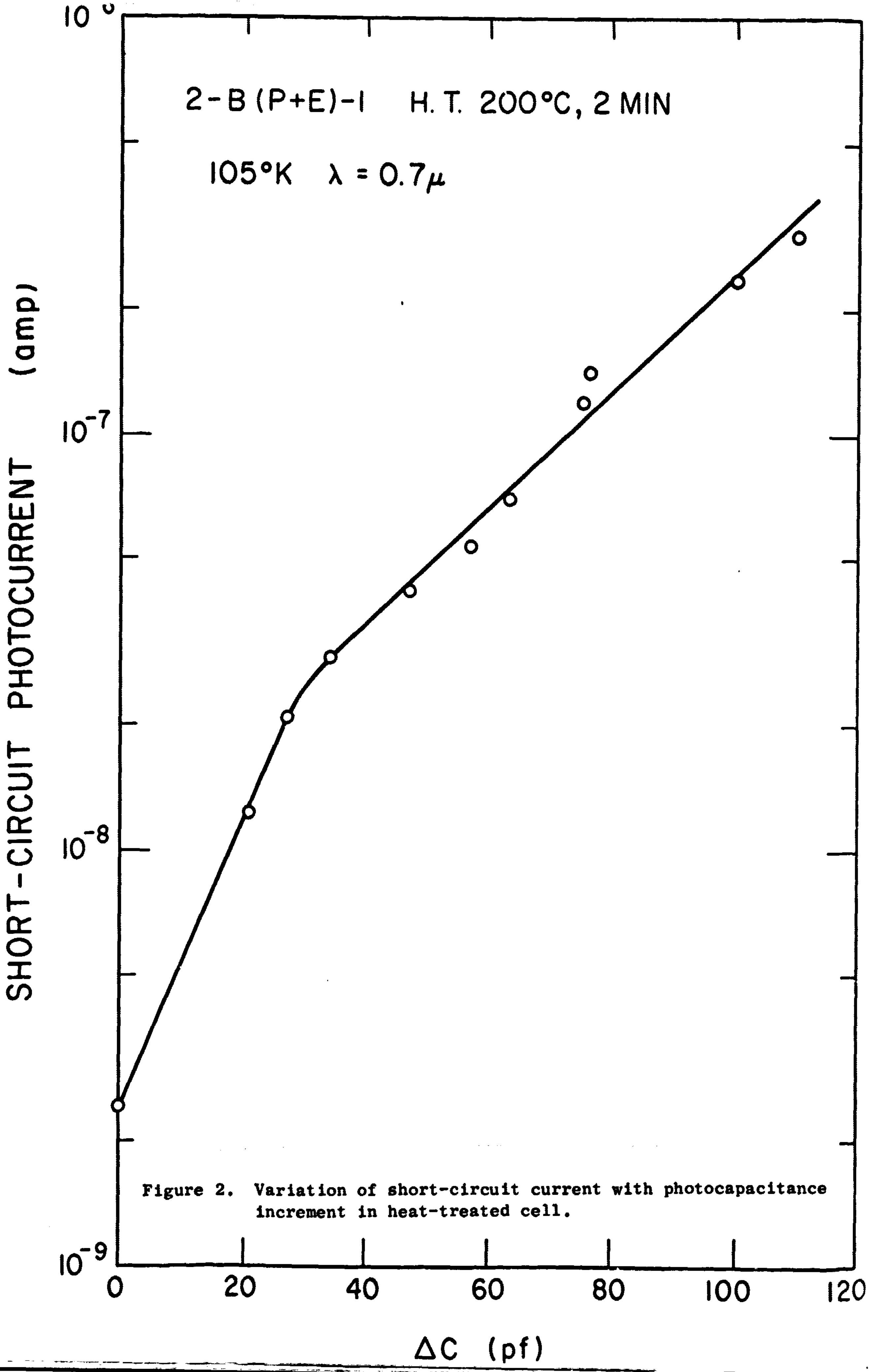


Figure 2. Variation of short-circuit current with photocapacitance increment in heat-treated cell.

affects the photoresponse of non-heat-treated junctions, but to a lesser extent. There can be no question but that this trapped charge is a vital factor in the photovoltaic performance of the Cu_2S-CdS cell.

III. Cu-CdS CELLS

To determine the effect of different modes of junction preparation on the total photovoltaic properties of the resulting heterojunction, experiments have been done on Cu-CdS cells made by the vacuum evaporation of Cu onto single crystal CdS. Simhony, Williams and Willis (J.Appl. Phys. 39, 152 (1968)) investigated the electrical behavior of Cu-diffused insulating layers in CdS. They measured layer thickness by making capacitance measurements after various heat treatments, and obtained values between 1 and 10 microns. C-V dependence characteristic of a Schottky-like barrier was found only in non-heat-treated samples.

Our investigation is directed toward the study of thinner layers of insulating material such as is characteristic of the temperature and time in dipping and heat treatment of Cu_2S-CdS cells. Cells with rather different characteristics depending on the initial treatment have been prepared; these can be separated into three major categories.

1. Cells with only partial diode behavior in the dark result when the CdS surface is etched least. These cells are highly photoconductive but show no photovoltaic response.

2. Cells with good diode behavior but little or no photovoltaic response show small photoconductive response compared to (1). Their major response to white light is found in an increase in reverse photocurrent.

3. Cells with good diode behavior and appreciable photovoltaic response (short-circuit current at least 2.5 ma/cm^2) are better for evaporation on the B-face samples, which have a rougher surface after

etching than A-face samples.

Samples for evaporation are prepared by polishing and etching in the same way as used for Cu_2S-CdS dipped cells. After water-rinsing and air-drying they are coated with 0.2-1.0 micron of 99.99+ percent Cu at about 10^{-5} Torr. Leads are attached to the Cu layer with silver-paint; ohmic indium contact is made to the CdS. The estimated temperature during evaporation does not exceed 100°C; the period of evaporation is about 30 seconds.

Dark forward I-V characteristics for two cells are shown in Figure 3. F-13, a Type 2 cell, shows $I \propto V^3$ over five orders of magnitude of the current at room temperature. This cell shows only a small variation of capacitance with bias voltage. F-21, a Type 3 cell, shows a more complicated dependence of I on V, which more nearly approximates the $\ln I \propto V$ behavior found in good Cu_2S-CdS cells; capacitance is strongly dependent on bias voltage for this cell.

Typical I-V characteristics of Type 1, 2, and 3 cells are given in Figure 4.

Figure 5 illustrates a significant difference between A-face and B-face Cu-CdS cells. The A-face cells show much higher resistance in the dark and strong cross-over in the light; the B-face cells show no cross-over. This difference may be related to the different surface produced by etching A- and B-faces, as mentioned above.

IV. FUTURE WORK

Since measurements are incomplete at this time, data on evaporated Cu-CdS cells will be reported and interpreted in a later report. These cells will also be heat-treated to determine the change in their properties as the depletion width in the CdS increases.

Principal areas of interest for future work are the following.

1. Compositon of the Cu_xS layer formed by the dipping and the

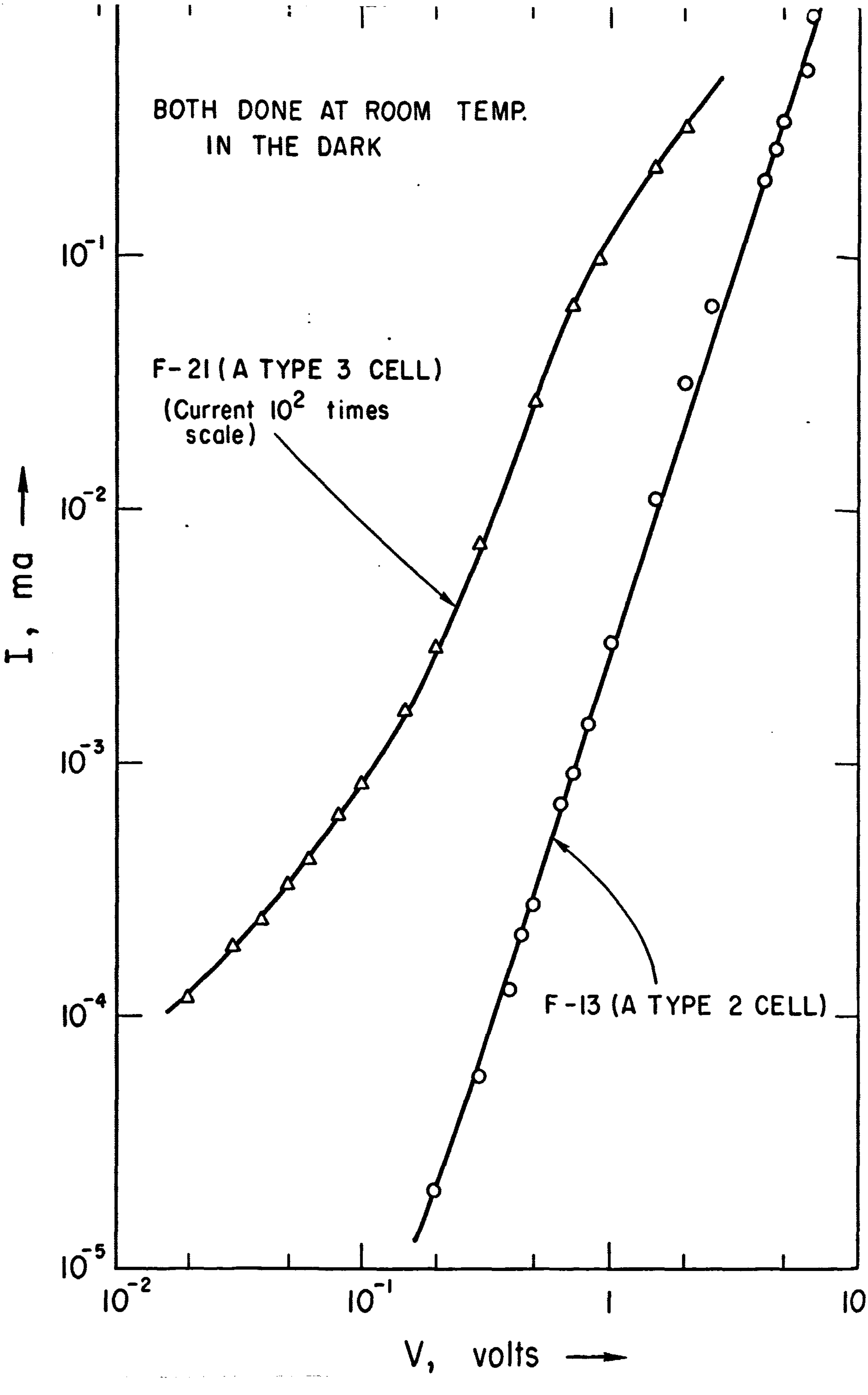
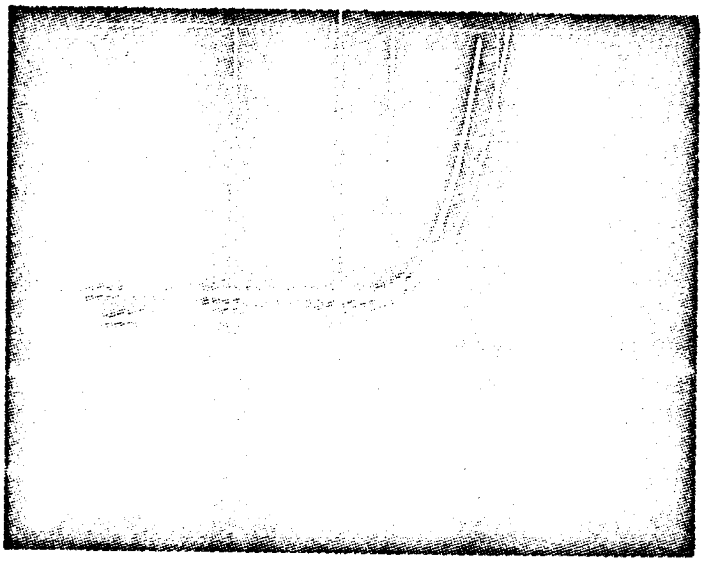


Figure 3. Details of I-V characteristics of a Type 2 and a Type 3 evaporated Cu-CdS cell.

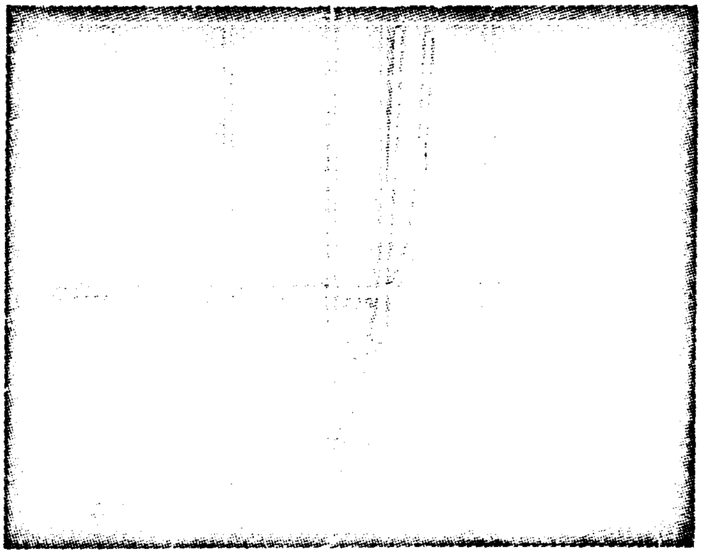
Type 1

(F-10)



Type 2

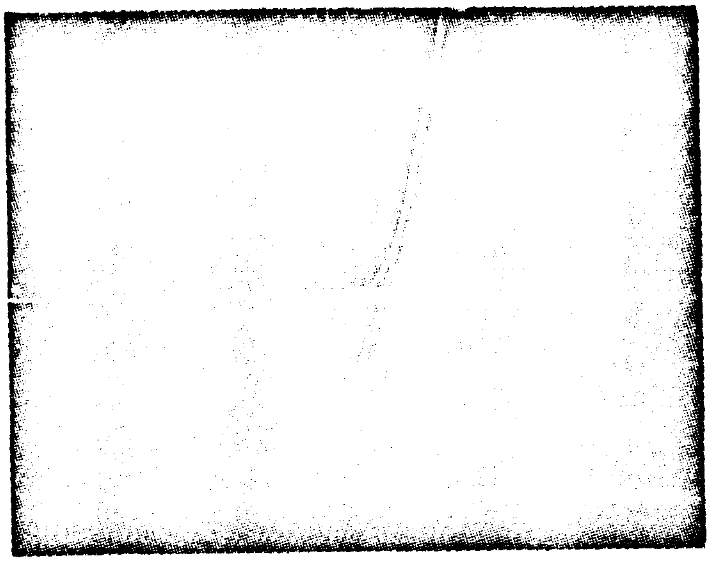
(F-17)



Type 3

(F-21)

Figure 4. Characteristic I-V curves in light and dark, for Type 1, 2, and 3 Cu-CdS cells. Scale: 0.2 V/div; 0.05 ma/div.



B-Face

(F-22)

A-Face

(F-23)

Figure 5. Characteristic I-V curves in light and dark, for A-face and B-face evaporated Cu-CdS cells. Scale: 0.2 V/div.; 0.05 ma/div.

correlation with the photovoltaic properties of the heterojunction formed. A variety of chemical and optical methods are being considered for the determination of the Cu^{+}/Cu^{++} ratio in the dipping solution as well as of the value of x in the Cu_xS-CdS cells.

2. The effect of surface treatment of the CdS on the photovoltaic properties of the heterojunction formed. Distinctions between chemical and physical effects on the surface will be sought.

3. The effect of the source of conductivity in the CdS on the photovoltaic properties of the heterojunction formed. Measurements to date have been made with non-stoichiometric high-conductivity CdS crystals. A crystal of CdS with In impurity is currently being grown. Properties of Cu_2S-CdS junctions formed on CdS crystals with a pre-diffused thin insulating Cu-rich layer may also be investigated.

4. Phenomena involved in heat treatment. Further detailed investigation of the nature of the phenomena involved in heat treatment is planned.