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Technical Summary Report No. 2

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

TECHNOLOGY CENTER

INVESTIGATION OF SINGLE ENERGY GAP SOLAR CELL MATERIAL

Contract No. DA36-039 SC-87381

Robert J. Robinson

U. S. Army Signal Research and Development Laboratory
Ft. Monmouth, New Jersey

25 years of research

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ARMOUR RESEARCH FOUNDATION
of
Illinois Institute of Technology
Technology Center
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Periodic Report No. 4
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Covering the period of January 1, 1961 to June 30, 1961

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ABSTRACT

The principal purpose of this program is to develop a single crystal cadmium telluride solar cell which has better high temperature characteristics than can be expected from silicon. The emphasis on the first year', program was on crystal growth, while in the second year the emphasis at first was on obtaining zone leveled CdTe, and then shifted to stressing the development of the fabrication procedures necessary to make a complete solar cell: these include slicing, lapping, polishing, chemical etching, junction formation, electroding and mounting on a crystal holder. Current emphasis on the program is on forming p-type layers on n-type zone leveled CdTe by vapor diffusion in the recently acquired multiple zone fabrication furnace. Low temperature diffusion fabrication studies have been emphasized and it is shown that shallow and deep junctions can be formed at 500° C. Electrical, thermal and optical studies of the n-type base material, and spectral response curves of the completed solar cells are included. Combined optical transmission and spectral response curves show that the absorption coefficient versus wavelength has a slope similar to silicon rather than to GaAs or InP which is favorable. The good collection efficiency of silicon is thought to be associated with the lack of very strong surface absorption over much of the wavelength region of interest. Low temperature fabrication is shown to be possible and is advanced as an argument for CdTe since less fabrication disorder is expected compared to high temperature fabrication. However, the room temperature conversion efficiencies of current CdTe solar cells are still low compared to silicon, but the still early state of the art of CdTe is stressed. Preliminary high temperature photovoltaic experiments tend to confirm the use of CdTe compared to silicon. Future work is outlined.

INVESTIGATION OF SINGLE ENERGY GAP SOLAR CELL MATERIAL

I. INTRODUCTION

This is the Fourth Periodic (Semi-Annual Technical Summary) Report for a program on the Investigation of Single Energy Gap Solar Cell Material, and the second period report under the new contract Number DA36-039SC-87381. It covers the work done from January 1, 1961 to June 30, 1961, which means from the third to the eighth month inclusively on the second year's contract. The principal aim of this program is to develop a solar cell with better high temperature characteristics than can be expected from silicon; the solar cell material chosen for this purpose is cadmium telluride.

The original choice of cadmium telluride as a high temperature solar converter was based on a) its favorable band gap, b) the knowledge that p-n junctions could be formed, and c) the fact that it could be grown from the melt. It was recognized that the state of the art, from a semiconductor viewpoint, was in its very early stages. This disadvantage, however, was considered to be outweighed by the inherent advantage of cadmium telluride for high temperature applications, but this disadvantage did determine the nature of the research program. Essentially, then, the program has been devoted to raising the state of the art of cadmium telluride as a useful semiconductor for device applications; specifically, for solar cell application.

The most recent work on this program has been devoted to fabricating p-n junction solar cells. A p-type layer has been formed by vapor diffusion on n-type material and electrodes have been attached to form solar cells. The n-type material is obtained by zone leveling indium into the sample following the process of controlled atmosphere zone refining of CdTe. The solar conversion efficiencies of these cells are low compared to silicon at room temperature but the many step developmental process involved in starting with elemental cadmium and elemental tellurium and ending up with a completely fabricated solar cell is still in its early stages. CdTe is a useful high temperature solar cell material, based upon the following experimental observations in this laboratory:

1) The absorption coefficient versus wavelength in CdTe resembles Si rather than GaAs or InP which indicates less dependence upon the surface for absorption in CdTe than in the above Group III-Group V compounds.

2) Comparatively low temperatures are needed for fabrication of p-n junctions by vapor diffusion; this results in less disordering of starting material during junction formation.

The starting material is elemental cadmium and elemental tellurium and the program objective is to fabricate a CdTe solar cell. This involves several developmental steps as listed below.

A) Preparation of polycrystalline CdTe from the elements

B) Zone refining of polycrystalline CdTe in a controlled atmosphere furnace

C) Zone leveling of the CdTe boule

D) Slicing, lapping and polishing

E) Chemical etching

F) P-N junction formation by chemical methods or by diffusion in the multiple zone furnace

G) Preparation of contacts to the N and P side

H) Mounting on crystal holder to complete fabrication of the cell

I) Evaluation of the electrical, optical, and thermal properties of the bulk material, and of the completed cell; (special emphasis has been given to the spectral response of the photovoltage of completed cells).

During the first year of this program, the work was principally devoted to crystal growth studies. Two different crystal growth methods were used: the Bridgman technique and the controlled atmosphere technique. Chronologically, the Bridgman technique was used first but useful, homogeneous single crystal material was not obtained. The simplicity of the technique was appealing, but the results were not impressive so that concurrent with the above experiments a controlled atmosphere system was developed. This led to zone refined CdTe boules which were much more homogeneous. Periodic Report No. 3, the first periodic report on the second year's program, discusses the controlled atmosphere technique and some early experiments on the zone refined material. Since parts A and B of the many step developmental process have been covered in previous reports, this report will treat parts C to I inclusively.

As our work has progressed and as the CdTe material has improved, it is becoming clear that CdTe will become a very suitable material for solar cell fabrication. In addition, we feel that CdTe will also prove valuable for other semiconductor devices, especially those devices whose use militates ambient temperatures in the 200° C range, temperatures above which silicon and germanium are useful.

II. ZONE LEVELED CADMIUM TELLURIDE

Zone leveling of CdTe is carried out in the apparatus used for zone refining in a controlled atmosphere, which was described in the previous summary report, Periodic Report No. 3. Currently the procedure being followed is to use the center three-fifths portion of the zone refined boule for the zone leveling process. The first two zone leveled boules which were made were doped with indium to make n-type CdTe. Indium, 0.05 percent by weight, was added to one side of the zone refined boule and the leveling was accomplished by making ten passes back and forth over the system. The overall resistivities of the zone leveled boules after removing ten percent from the ends were 0.046 and 0.048 ohm-cms, respectively. By using a probe technique the variation in resistivity was measured and the results for zone leveled boule No. 1 are shown in Figure 1.

By probing the different sides of the boule, it was found that the variations in resistivity were approximately only functions of the boule length. That is, the resistivity was nearly the same around the boule at any given point along the length. Based upon mobility measurements made by deNoble in CdTe-In for approximately the same dopant concentration, the concentration of electrons is calculated to be between 4 and 6 x 10^{17}. Resistivity versus temperature measurements made between 77° K and 473° K temperatures showed that the sample was saturated at room temperature. Therefore, the concentration of indium atoms is calculated to be between 4 and 6 x 10^{17}.

The method of preparation and the bulk electrical properties of these two particular boules are being described since sliced wafers from these boules were the starting materials for the p-n junction solar cells that were fabricated, evaluated and discussed in this report. The conductivities of these zone leveled

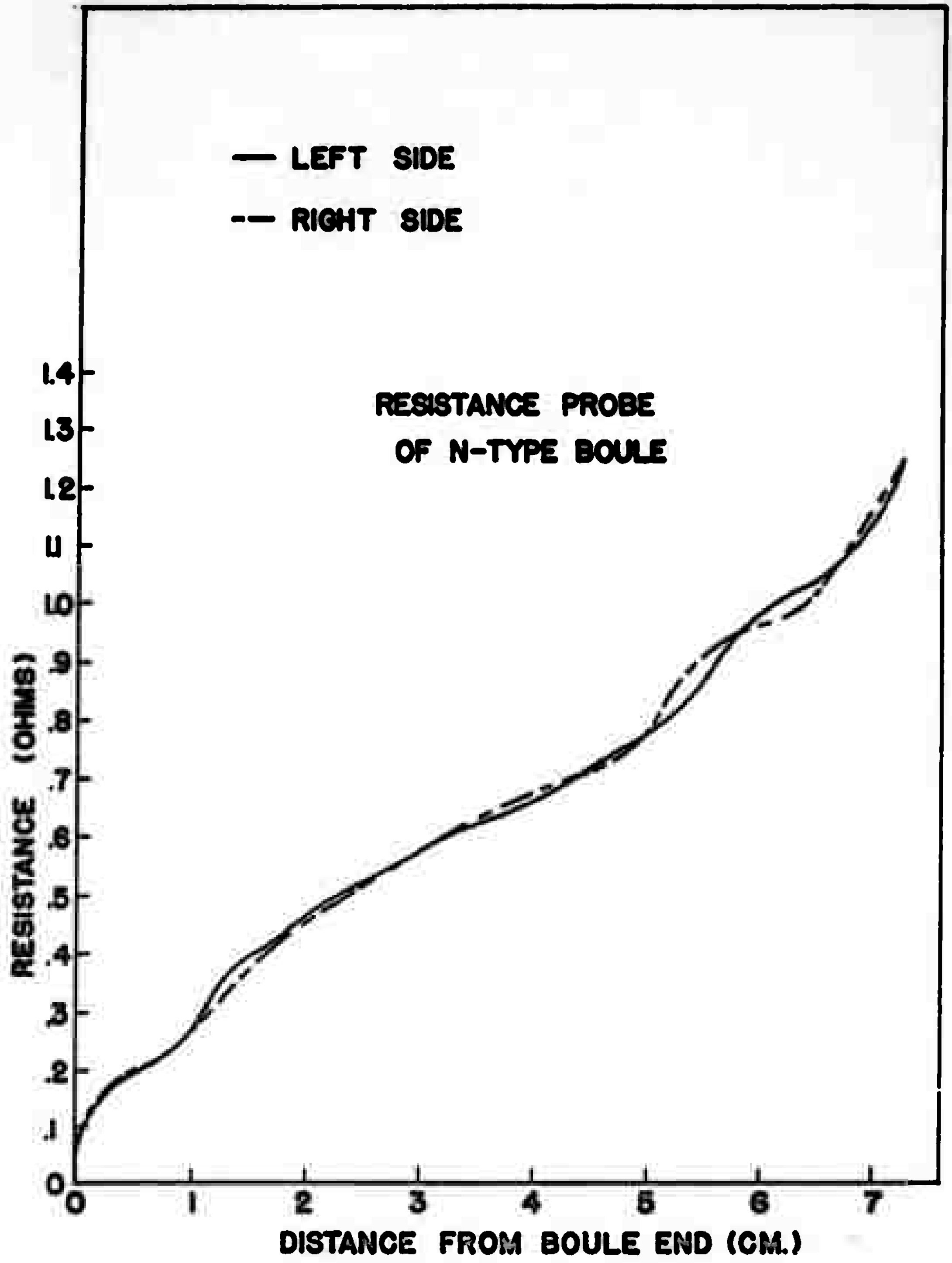

Fig. 1 - RESISTANCE PROBE OF N-TYPE BOULE

boules are approximately fifty times higher than the base conductivities for silicon solar cells. It is believed that the low efficiencies of current CdTe cells is partly associated with this very high conductivity, since the efficiency of silicon solar cells is lowered by starting with such a high base conductivity. One boule is available which was more lightly doped with indium but fabrication and evaluation work has not as yet been completed, while other boules are in various stages of preparation.

III. SLICING, LAPPING AND POLISHING

An early problem encountered with CdTe is that of cutting, lapping and polishing. Our early results indicated that CdTe is very brittle and difficult to cut. After some effort, however, it appears that this problem has been surmounted in this last reporting period. It has been found that CdTe boules can be sliced using 1800 mesh Red Diamond powder 9-OS-30 from Hyprex Diamond Company. Currently a copper-bronze wheel is used for slicing with this diamond powder while the boule is fixed to a die by shellac. Comparatively, it is found that CdTe cuts a little easier than indium antimonide, but it appears to be slightly more fragile. It has been observed that the ease of slicing through the outer surface of the boule varies from sample to sample of the zone leveled material but that the surface which was closest to the boat during the leveling process slices easiest.

Lapping of the sample following the slicing operation is done on a Lapmaster 12 and it is found that the material laps easily and well. Polishing to date has been done by hand with a diamond paste. It should be pointed out that the relationship between lapping and polishing and the process of obtaining optimum efficiency in the solar cell has yet to be determined, and additional effort in this direction will be required. The important point to be made here, however, is that these operations can now be carried out and that a solution has been found to a problem of the sort which constantly plague research and development programs.

IV. CHEMICAL ETCHING

The chemical etching materials being used for removing disorder layers due to polishing or for general surface clean up were not developed on this program, but the techniques involved in using them were necessarily developed. Currently, the chemical etching process is as follows:

1) The CdTe sample in a palladium holder is dipped into a nitric acid solution - usually a 50 percent concentrated nitric acid, 50 percent distilled water - for a short time. This time is determined by the thickness to be removed. Cadmium is removed leaving a black surface which is due presumably to tellurium or a tellurium oxide. It appears to date that for best results one should minimize the bubbling which occurs shortly after putting the CdTe into the nitric acid solution. If necessary, repeated short time dipping should be practiced.

2) The tellurium or tellurium compound is removed in a sodium dithionite ($Na_2S_2O_4$) plus 10 percent sodium hydroxide solution in distilled water. The solution is heated to a temperature in the region of 70 degrees centigrade before the cadmium telluride is immersed. Examples of non-uniform etching have been observed,

and it is possible that techniques can be developed for "dressing" junctions. So far, however, chemical etching has only been used to clean and/or to remove a thin layer on the surface.

Another chemical treatment is being used for the purpose of removing chemically deposided gold contacts. This is standard and consists of immersing the gold electroded CdTe into a boiling solution of potassium cyanide-potassium hydroxide in distilled water.

V. CHEMICAL JUNCTIONS

A chemical junction is a p-n junction formed by a chemical reaction on the surface of an n-type sample of CdTe. This process has been described in previous reports in which chemical Junctions were formed on zone refined CdTe. This has been extended to the growth of junctions on the n-type material which was obtained from the zone leveling procedure. A dilute solution of gold chloride in distilled water is spread over the surface and is either allowed to dry or is removed by capillary action after a short time. Experiments have been carried out with this technique where the time ranges between thirty seconds and five minutes. Contact to the chemical junction is made by using a very small drop of concentrated gold chloride solution which is allowed to dry. Presumably, a p-type layer is formed by substituting gold for cadmium in the CdTe. The photovoltage that one obtains with this cell for a given radiation intensity is a sensitive function of the gold chloride solution concentration, and the efficiencies of these cells are not high. While the n-type base material has a conductivity which is apparently too large for optimum efficiency better cells have been made by the vapor diffusion technique using this same base material. The spectral response of one of these chemical junction cells is shown in Section XI.

VI. MULTIPLE ZONE FURNACE FOR VAPOR DIFFUSION STUDIES

The most recent junction formation studies on this program have been concerned with vapor diffusion of a p-type layer on an n-type base material. The particular experiments and evaluation studies are discussed in more detail in Sections X and XI.

The problem of fabricating junctions on a compound semiconductor such as CdTe at high temperatures is complicated by the necessity of maintaining stoichiometry. If one adds to this the desire to have versatility in fabrication procedures, which is especially useful when the state of the art of the material involved is still in its early stages, then the fabrication furnace and accessory equipment have an important function in achieving a useful compound semiconductor solar cell. Because of this, the multiple zone furnace being used will be discussed in some detail.

A multiple zone furnace was purchased by Armour Research Foundation and is currently being used on this program. This furnace consists of a three zone high temperature tube furnace combined with a three zone low temperature tube furnace, (See Figure 2). The maximum safe working temperature on the larger furnace is 1427° C and is 1000° C on the smaller. The furnaces use West indicating control pyrometers with saturable reactors and have the advantage of being a constant seek rathern than on-off temperature controller. Some of the accessory equipment being used with this furnace was discussed in the previous reports and can be seen in Figures 3 and 4. Modifications have been made in the accessory equipment to suit the new multiple zone furnace. For example, the thin quartz tubes to which the boats or sample holders are fixed were too thin for the long furnace and larger diameter tubing has been substituted. If desired the tubes can be used as a gas inlet, for example, to carry or force the diffusant vapor over the CdTe sample. To minimize contamination at the beginning and end of a run, the boats can be completely pulled out of the furnance (Figure 4) while the CdTe sample is still under an inert or other ambient.

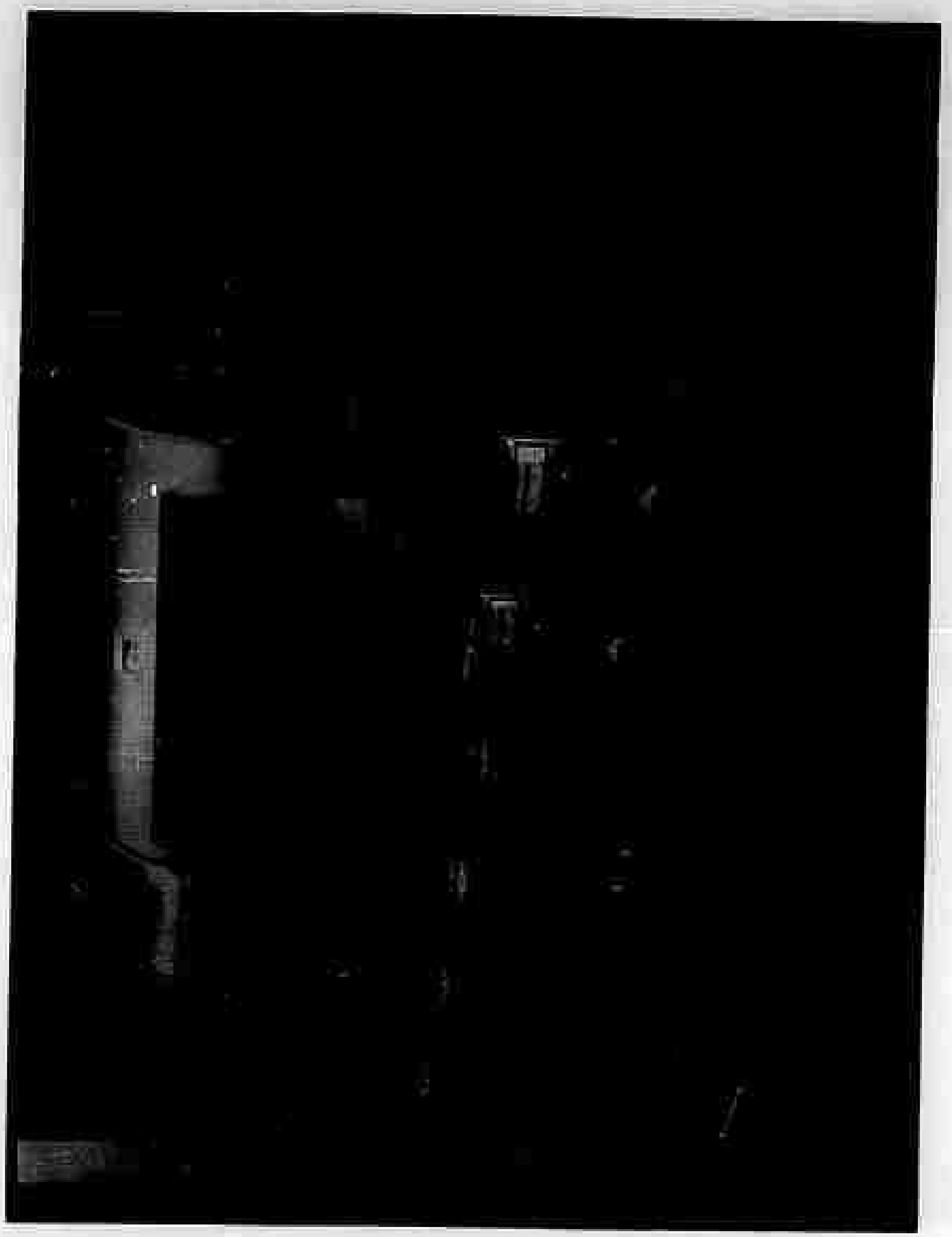

Fig. 2 - MULTIPLE ZONE FABRICATION FURNACE

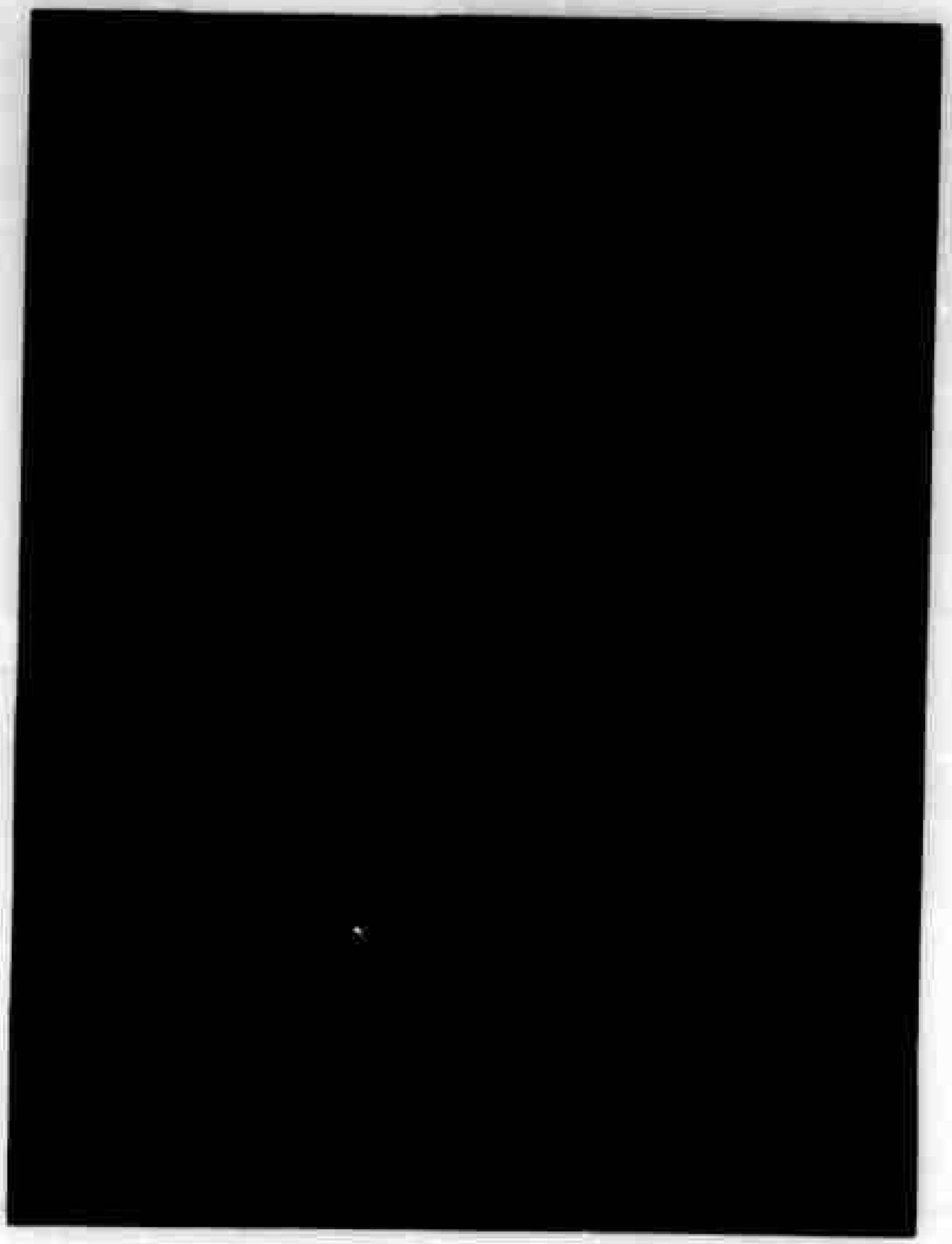

Fig. 3 - FURNACE WITH ACCESSORY EQUIPMENT

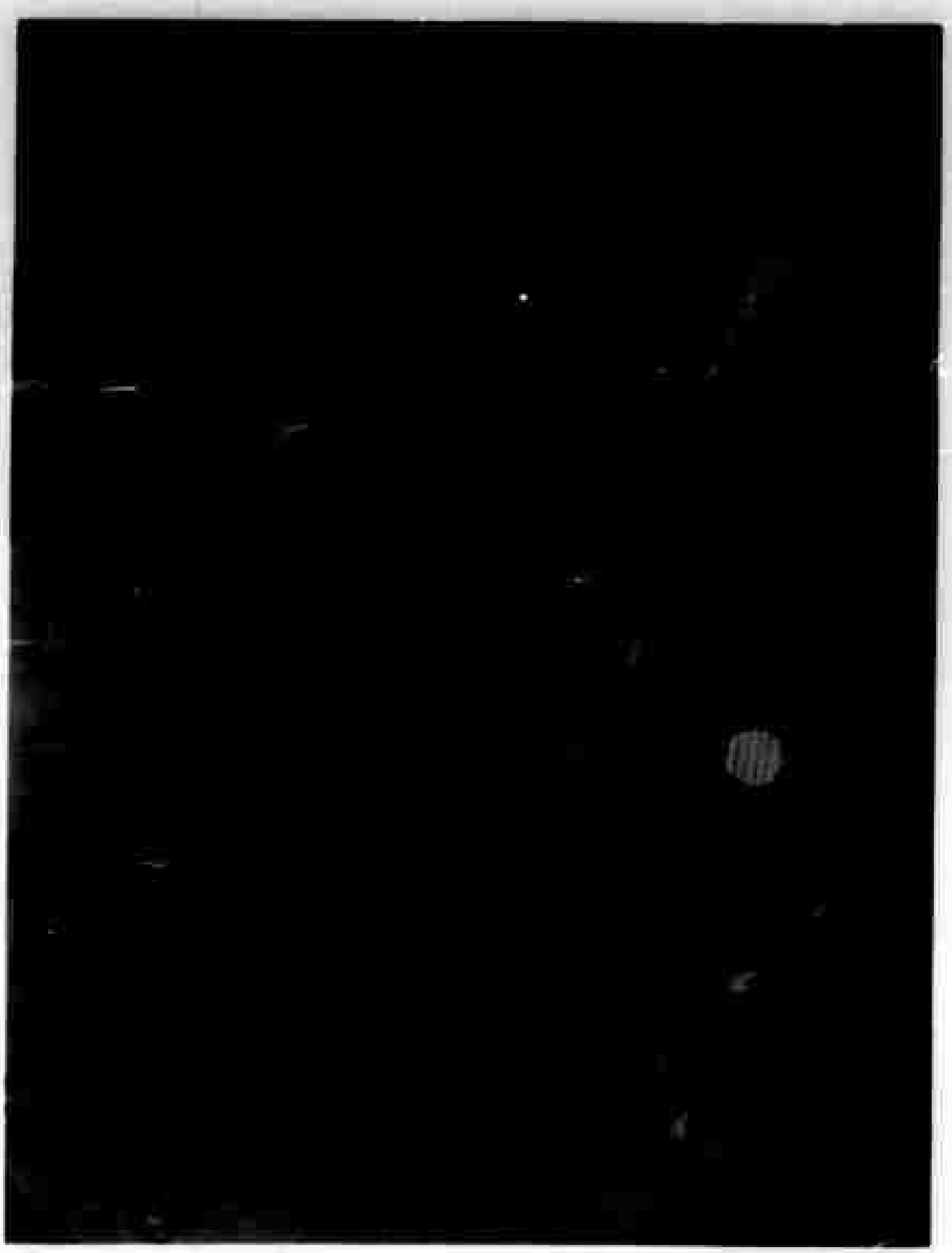

Fig. 4- T-TUBE ARRANGEMENT FOR REMOVING SAMPLE FROM FURNACE WHILE UNDER CONTROLLED ATMOSPHERE

The T arrangements shown in Figurg 3 are available for each end of the furnace so that a total of four boats can be used on any given run. To maintain stoichiometry elemental cadmium is heated at one temperature to allow a given atmosphere of cadmium over the heated CdTe sample while the diffusant can be maintained if needed at a third temperature. With the four boat arrangement, double diffusion experiments on compound semiconductors are currently possible.

Fabrication experiments utilizing this furnace were only started within the last two months since the furnace itself was only obtained within that time. Considering time for set up and calibration, the fabrication studies to obtain a good high temperature solar cells are still preliminary, and the inherent versatility of the furnace has not been exploited as yet.

VII. ELECTRICAL CONTACTS TO THE N AND P SIDES

The problem of putting ohmic or nearly ohmic contacts on the n and p sides of cadmium telluride is briefly summarized here, but the principal discussion in this section concerns the nature and type of electrical contact used in the CdTe solar cells that have been fabricated, and which are described in this report. A soldered contact using indium on n-type CdTe has previously been shown to be ohmic using electrical noise measurements as a tool. Since this is probably the most sensitive test for an ohmic contact, indium is currently being used on n-type CdTe to minimize contact resistance losses.

While indium melts at temperatures below 200° C, fabricated cells have been measured at temperatures above this figure. This has been possible since there is a positive pressure on the CdTe holding it to the crystal holder. The indium acts as both a cement and good electrical contact and to date no high temperature contact problems have been noted.

Silver and gold have been found to give nearly ohmic contacts to p-type cadmium telluride. Careful electrical noise measurements have not as yet been made to determine how closely these contacts approach true ohmic behavior. Current indications, however, are that these are low impedance contacts. Contacts to the p-side layer in the solar cells described in this report were made by using a small drop of a concentrated solution of gold chloride. This leads to a gold contact on the surface to which a lead can be attached. In order to minimize contact resistance a thin gold stripe contact to the p-side can be made with this technique, and this procedure will be followed as refinements in the fabrication methods are developed.

VIII. CONSTRUCTION OF SOLAR CELLS

The experimental cells made to date have been mounted on one-half inch diameter crystal holders. Contact to the crystal holder base is made to the indium contact on the n-side of the CdTe. This is done by heating the crystal holder with a soldering gun to the temperature at whicn indium melts. A positive pressure is maintained on the gold contact to the p-side of the CdTe with a soft material during the heating of the crystal holder. After cooling, a piece of nichrome wire is spot welded to an electrode on the crystal holder, and it is mounted in such a way that it exerts a strong spring pressure contact to the gold electrode on the p-side. A few experiments have been made to test this construction by dropping the completed cell from the laboratory bench and the contacts held. The particular method of mounting the cells is based upon two considerations: 1) ease in carrying out temperature versus photovoltage experiments, and 2) immediate availability of a few different types of crystal holders.

IX. ELECTRICAL, THERMAL AND OPTICAL PROPERTIES OF THE N-TYPE CdTe BASE MATERIAL

This section summarizes the results of measurements on the n-type base material used in making CdTe solar cells. The measurements were not extensive and the experiments were designed to help in evaluating the potential of CdTe and in evaluating the CdTe solar cells which were concurrently being fabricated.

As noted in Section II, the overall resistivities of the first two zone leveled boules were 0.046 ohm-cm and 0.048 ohm-cm respectively at room temperature. These measurements were made after removing ten percent from the ends. A slice from this ten percent part which was taken at the opposite end from the initial indium charge was found to have a resistivity of 10 ohm-cm at room temperature. Resistivity versus temperature studies of this slice and representative slices from the lower resistivity boules were made from 77° K to 473° K. This study was made to determine the stability of the material, the approximate depth of the indium defect level in electron volts below the conduction band, and the approximate position of the Fermi level. The variation of the saturation temperature with room temperature resistivity and indium concentration was also studied. The variation in saturation temperature might be expected to arise due to defect wave function overlap broadening of the energy level into a narrow band. Representative curves are shown in Figure 5 for the 0.046 ohm-cm and the 10 ohm-cm material.

The approximate Fermi levels were calculated from the resistivity, and the approximate values of the mobility and effective mass of the electron found in deNobel's work. From the effective mass one can calculate the density of states in the first kT region of the conduction band, and with the number of

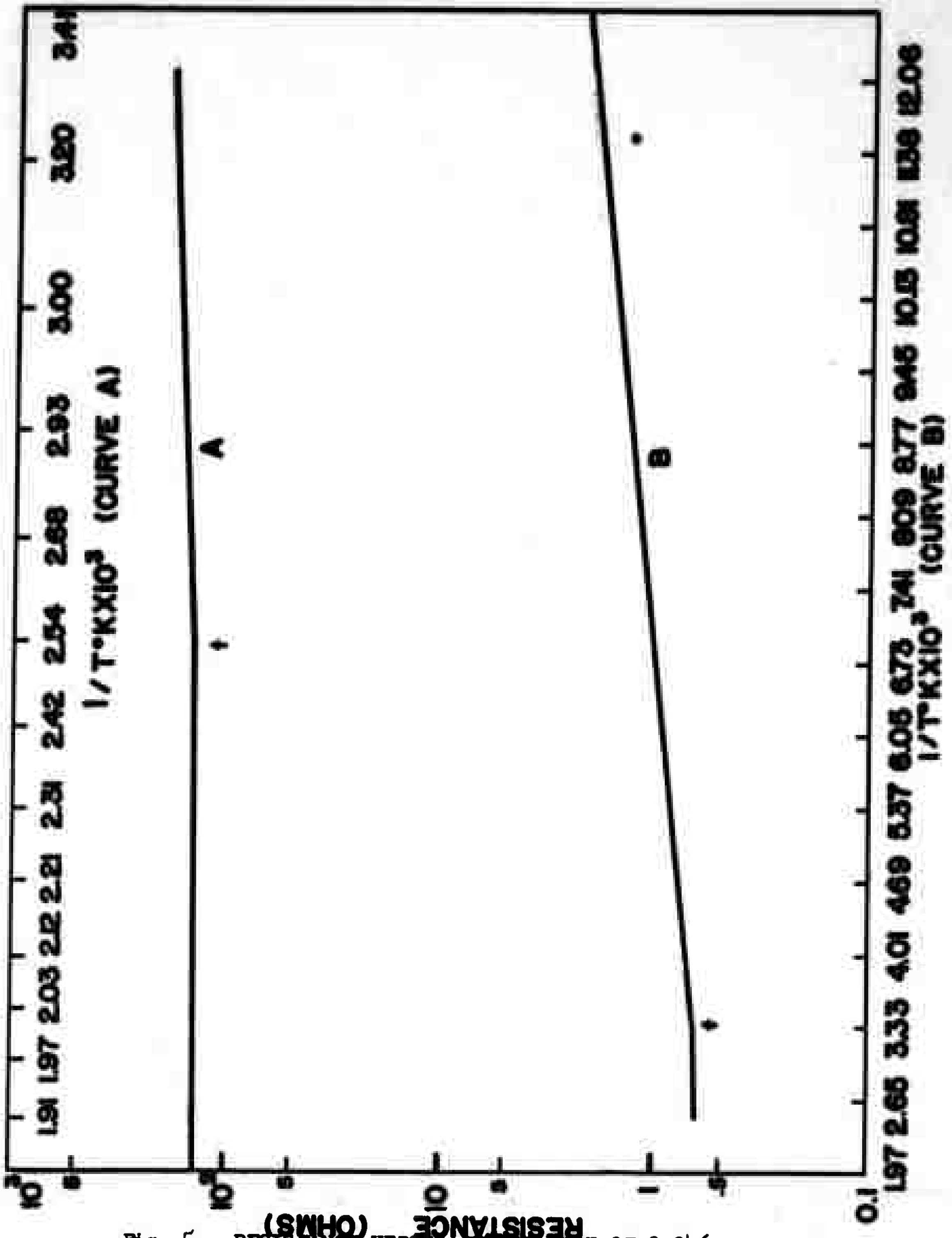

Fig. 5 - RESISTANCE VERSUS TEMPERATURE OF 0.046
AND 10 OHM-CM N-TYPE CdTe

occupied states one can calculate the Fermi level from the Fermi-Dirac distribution function and the slope of the curves of Figure 5. From the onset of saturation where the curves level off one can calculate, to a good approximation, the density of indium atoms from the number of conduction band electrons assuming all the levels have been emptied. A new distribution function for holes is set up and knowing the density of defect atoms one can calculate the approximate depth of the defect level below the conduction band. The calculated value for the 10 ohm-cm material was 0.03 electron volts, while for the 0.046 ohm-cm material the approximate depth was found to be 0.011 electron volts.

It is the measurement of the optical properties of the n-type CdTe which is of particular importance in this section. Figure 6 shows the transmission characteristics of a polished sample, and two things are of interest on this curve. One is that the absorption coefficient versus wavelength has a much gentler slope than the Group III-Group V compounds such as GaAs or InP. Secondly, the transmission characteristics of the CdTe is getting better as better material is made. The material which was available last year could not be used to determine the gentle slope of CdTe using the Cary spectrophotometer since the lack of homogeneity gave rise to too much internal scattering, with the result that the details in the absorption region were lost. The transmission of the recent material is greater than 40 percent in the pass region, which is a good indication that uniform material is becoming available for fabrication purposes.

The importance of the gentle slope in the absorption versus wavelength is that the surface assumes a less important aspect in the photovoltaic response. This means a more favorable collection efficiency considering the problem of low surface lifetimes. Kleinman[1] makes a strong argument that the gentle slope

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[1] D. A. Kleinman, Considerations of the Solar Battery to be published Bell Technical Journal.

of silicon has an important and favorable bearing on the collection efficiency compared to the steep slopes of GaAs or InP. The fact therefore that CdTe has a slope which resembles silicon rather than GaAs or InP is an important point in its favor. The Number 1 following the initial drop shows the approximate curve for GaAs or InP, and the vertical lines are an indication of the experimental error in the short wavelength region.

X. DIFFUSION JUNCTION FORMATION

The starting materials for this operation are polished slices of CdTe which have been lightly etched and dried just prior to being inserted in the furnace. In addition to the samples, powdered or small pieces of CdTe are placed in the sample boat but not in direct contact with the samples. Cadmium metal is placed in a different boat which is heated to a temperature lower than that of the CdTe samples to maintain the correct cadmium pressure for stoichiometry. The cadmium vapors are blown over the CdTe by means of an inlet gas, Argon, which is forced over the cadmium. The CdTe is placed between the inlet and outlet of the gas. A third boat for the dopant can be used but in the experiments to date, the dopant has either been at the sample or the cadmium temperature.

Previous preliminary work on diffusing indium, cadmium and silver indicated that comparatively low temperature fabrication would be possible. Since the starting material was n-type, an acceptor was needed to form the p-n junction. A low melting point, easily handled material which fits this category is silver. In seven of the eight experiments which have been made to date, silver has been used as the acceptor to form the p-type layer. In the eighth experiment excess cadmium was used. Since so little is known about forming p-n junctions by diffusion in CdTe, the experiments were set up as a survey of possible temperature and time conditions. The fabrication temperatures (the CdTe sample temperature) varied over a range between 500° C and 700° C, and the cadmium temperature varied between 300° C and 500° C. The fabrication times were either one hour or two hours. These are comparatively long times for diffusion, but they are part of the pattern emphasizing low temperature fabrication.

A complicating factor and one which helped determine the long fabrication times was the high conductivity of the starting material, approximately 0.047 ohm-cm. As pointed out previously this is about fifty times the conductivity of the base material in silicon solar cells. The result of this is that a large concentration of silver would be necessary in the CdTe just to compensate the n-type material. In fact, the only low forward resistance cells (as determined from the diode characteristics) which have been prepared were formed at 700° C. However, the efficiencies of these two cells were very low, and the open circuit output voltages were only 0.1 volt under 0.6 volt conditions for silicon. The low efficiency appeared to be partly due to reflection losses since the cells had a slightly metallic sheen. However, both cells had a well defined exponential current versus voltage relationship in the forward region up to the point where non-junction impedance was important. In this ohmic region, an approximate value of 10 ohms for the internal resistance was obtained, which is still high compared to the internal resistance of silicon solar cells. From the exponential behavior of the current under low applied voltages it was possible to calculate an α value of 1.4 in the expression

(see Figure 7)

$$I = I_s' \left(e^{\frac{eV}{\alpha KT}} - 1 \right)$$

where I_s' is a complicated expression for saturation current covering the ideal minority carrier diffusion current (much too small for this case) plus the generation and recombination currents in the space charge region of the junction which could well be a complicated function of the voltage. The complexity of the p-n junction in CdTe can be appreciated by considering that the current from a single defect level in the space charge region derived from the Shockley-Read equations for low forward bias should be dominated by and proportional to a term of the form

$$I \propto e^{\frac{eV}{2KT}}$$

However, the well defined exponential curve in CdTe for low forward bias is very definitely not of this form ($\alpha = 1.4$, not 2).

It is examples of this sort which show why the analytical evaluations on this program have been minimal; the accumulated data is small and the nature of the p-n junctions is complex. To date the effort has been directed to accumulating data, and making only rough calculations to give the program a direction. The "soft" reverse characteristic of this cell, referring to Figure 7 again, is obvious and while this is more extreme than for the low temperature fabrication cells, it does appear that leakage currents are important. It appears that the cells which have been made to date have not been sufficiently cleaned and etched, and further, it is believed that this may account for part of the low efficiency. However, there is a complicating factor. The very

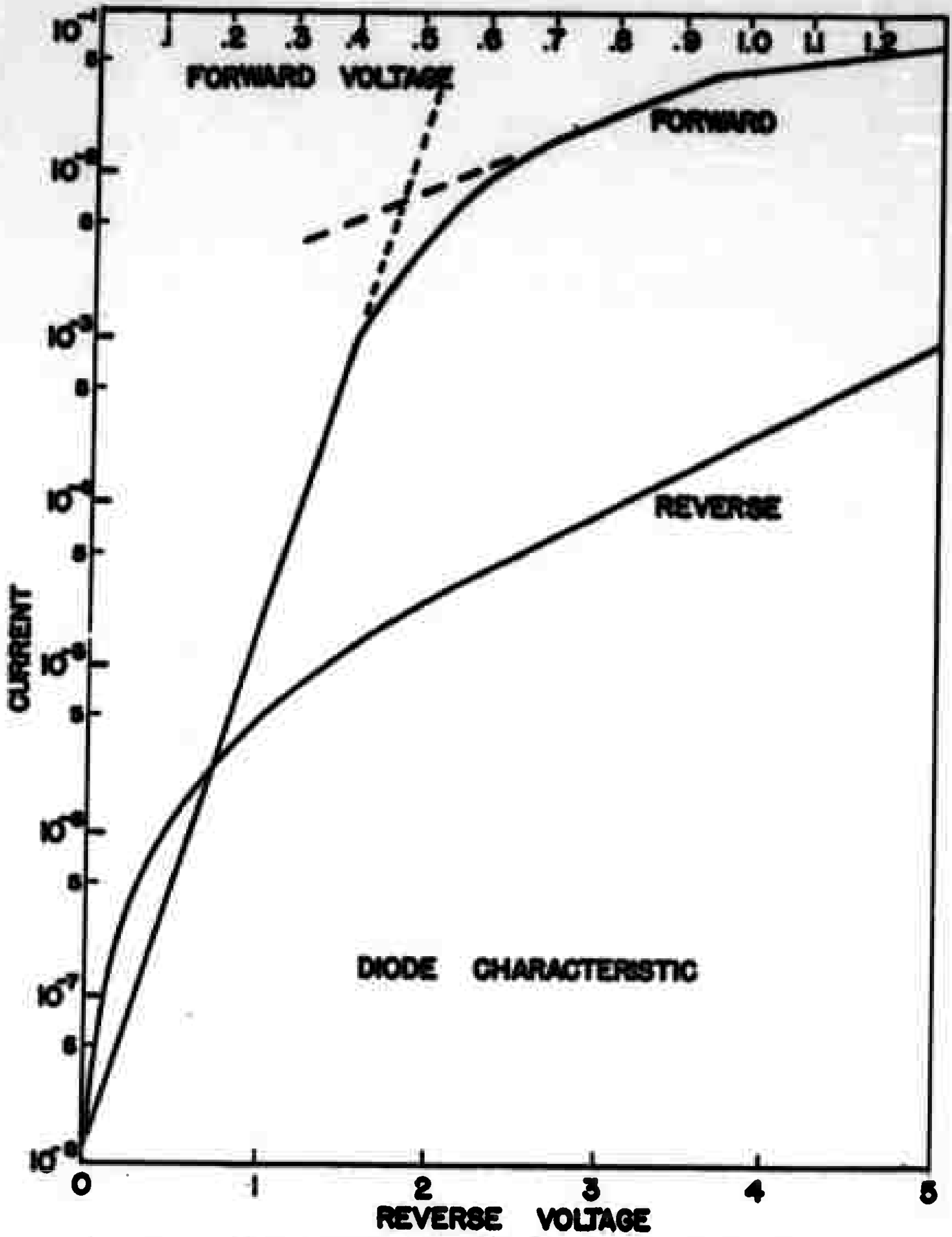

Fig. 7 - DIODE CHARACTERISTIC OF LOW INTERNAL RESISTANCE
700° C FABRICATION - CdTe SOLAR CELL

high conductivity of the n-type base material suggests a low avalanche breakdown potential; based upon the empirical equation used for silicon, the calculated breakdown is 5 volts. We turn now to the low temperature fabricated cells. While the internal resistance of the cells fabricated at 500° C varied between 100 to 1000 ohms, the efficiencies were much higher than the junctions prepared at 700° C. The open voltages varied between 0.3 and 0.5 volt and it was decided to compare the spectral response of the cells made with these junctions to get an indication of junction depth and collection efficiency. For these experiments the silver dopand was either at 500° C - the same temperature as the CdTe sample - or at 300° C - the temperature of the cadmium. Since the internal resistance of these cells was a factor of 50 to 500 times too large, it is believed that when base material is used which is 50 to 100 times lower in conductivity, the internal resistance will be near the optimum range for power conversion. Base material with such a conductivity would be comparable to the material used in silicon solar cells.

XI. SPECTRAL RESPONSE CURVES

While spectral response curves comparing short circuit current versus wavelength allows one a direct way of studying collection efficiency versus absorption depth, this method was not suitable for comparing one cell with another during these initial experiments. The reason is that the surface area varied from cell to cell, as did the internal resistance. However, the reverse diode characteristics of the low temperature fabrication cells were similar so that the following approximation was used. A dominant exponential relationship of the following form was assumed, based upon forward voltage characteristics,

$$I_s = I_o' (e^{\frac{eV}{\alpha KT}} - 1)$$

where I_s is the short circuit current of the solar, I_o' a saturation current assumed constant for the CdTe cells which is the approximation made from reverse diode characteristics, V is the open circuit output voltage and α is taken as 1.4. Expanding this expression for small values of V to second order, one obtains

$$I_s \cong I_o' (\frac{eV}{\alpha KT} + \frac{1}{2} (\frac{eV}{\alpha KT})^2)$$

If one limits the voltage, V, by using only a small intensity of light to a maximum value of 5 millivolts, the ratio of the second term to the first on the right hand side of the equation is 0.07. Therefore, to within 10 percent the equation reduces to

$$I_s \cong (\frac{I_o' \cdot e}{1.4\ KT})\ V \qquad V \leq 5 \text{ millivolts}$$

The spectral response curves were measured using this constraint on the open circuit output voltage. A Bausch and Lomb monochromator was used with a tungsten ribbon source. Color temperature of source was 2390° C at 0.656 microns; calculated temperature of the source was 2910° K using an emissivity value of 0.424[2] for this wavelength at that approximate temperature. The curves were corrected for variation in emissivity with wavelength,[2] and are expressed

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[2] J. DeVos, "A New Determination of the Emissivity of Tungsten Ribbon," Physica, 20, 690 (1954).

in terms of equi-photon segments from the radiation law. The normalized voltages due to the method of normalizing are larger than 5 millivolts in some regions, but the observed voltages were at or below that value. In all of the curves the equi-photon intensity has been held constant so that it is possible to a first approximation to compare different cells by observing the normalized open circuit output voltage which is nearly linear with the short circuit current.

Figures 8 and 9 are representative of the spectral response curves obtained for low temperature diffusion junction fabrication, while Figure 10 shows the spectral response of a chemical junction cell, and Figure 11 is the curve for a sensitive silicon cell under the same conditions. The shallow junction cell, Figure 8, had a fabrication temperature of 500° C, silver dopant temperature 300°, and cadmium at 300° C. The time for fabrication was one hour. The conversion efficiency rises slightly with increasing wavelength, reaches a peak around 0.78 microns, and drops to fifty percent of this value at 0.85 microns. Considering the optical transmission and approximate absorption coefficients (Figure 6) of CdTe, the efficient wavelengths have absorption coefficients in the 10^3 cm^{-1} region and the efficiency drops off with increasing wavelength and smaller absorption coefficients.

However, consider the deep junction curve shown in Figure 9. (Fabrication temperature was 500° C; silver dopant, <u>500°</u> C; cadmium, 300° C - time one hour). In this case the efficiency has a peak in the region between 0.82 and 0.86 microns. It appears that the recombination time or minority carrier lifetime - is longer in the bulk than at the surface which of course is not surprising. One has here an interesting correlation between a photovoltage

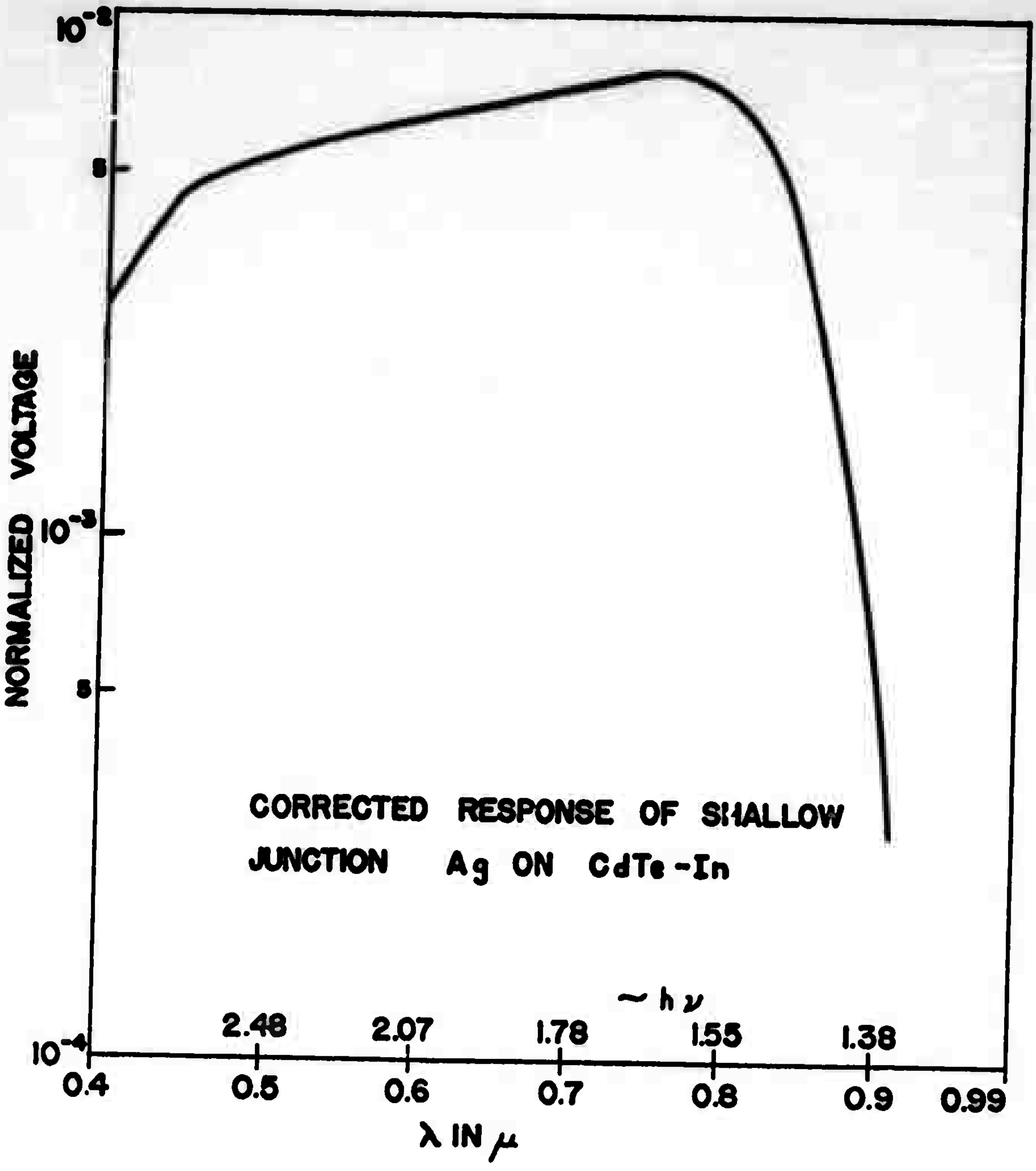

Fig. 8 - SPECTRAL RESPONSE OF SHALLOW JUNCTION - 500° C FABRICATION CdTe SOLAR CELL

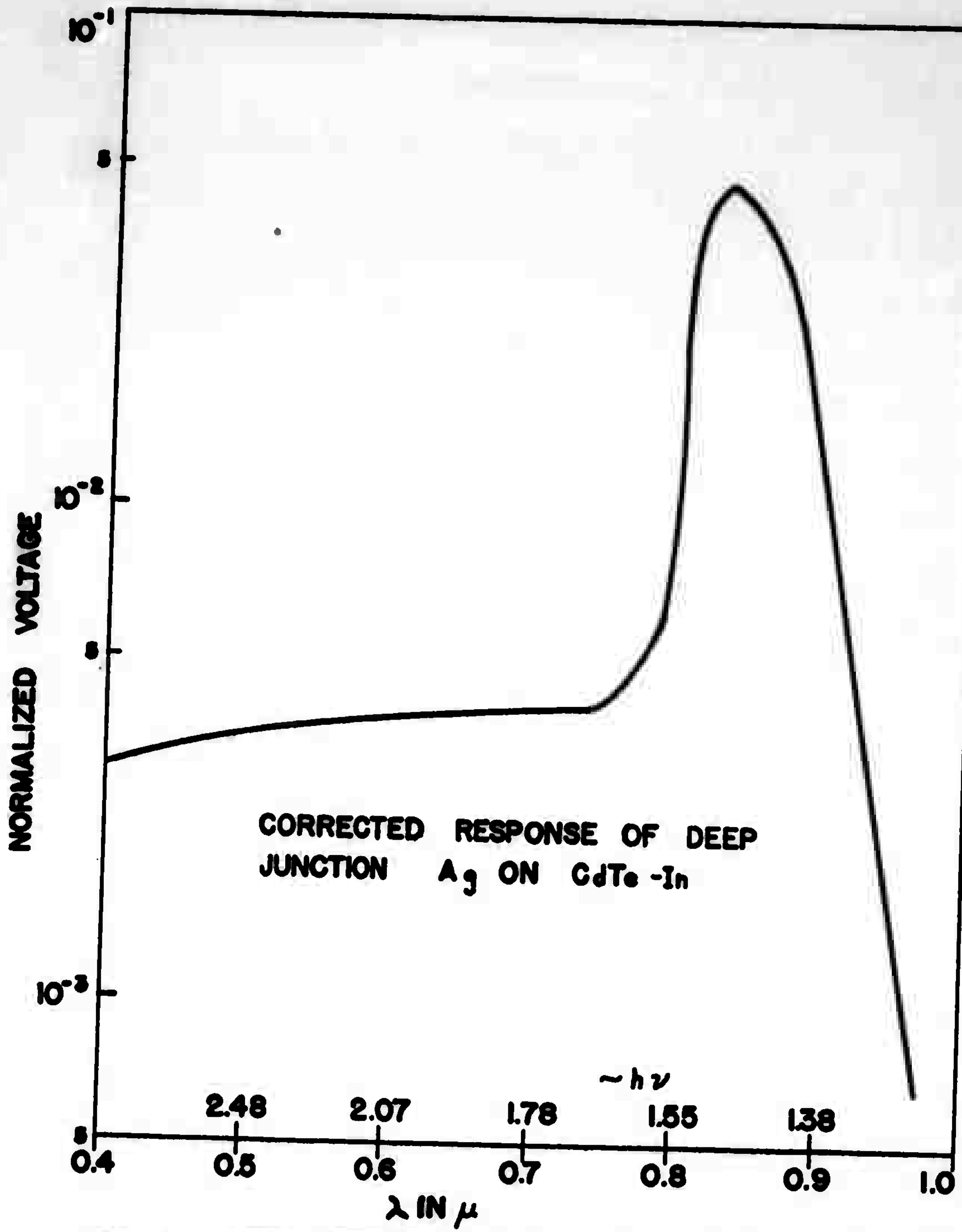

Fig. 9 - SPECTRAL RESPONSE OF DEEP JUNCTION - 500° C FABRICATION CdTe SOLAR CELL

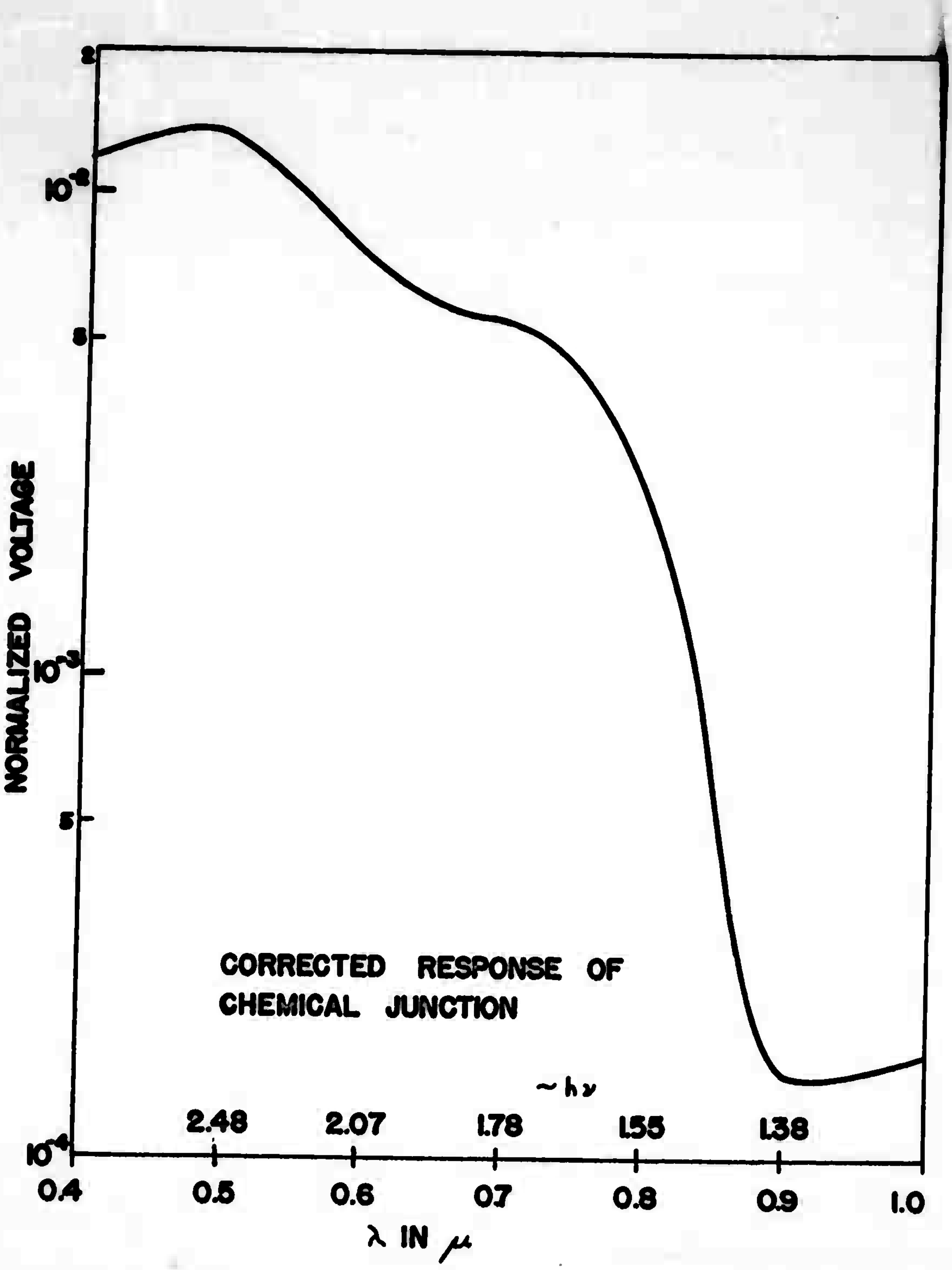

Fig. 10 - SPECTRAL RESPONSE OF CHEMICAL JUNCTION CdTe SOLAR CELL

measured with a monochromator and an optical transmission curve measured with a Cary spectrophotometer, and this is shown in Figure 12. To get a measure of the conversion efficiency in the peak region of the photovoltaic spectral response, short circuit current was measured at the peak. While the effective area of sensitivity on the CdTe had to be estimated, a comparison with short circuit current of the silicon solar cell at that same wavelength showed that the conversion efficiency was a little higher with the CdTe cell. However, as is evident from Figure 11, this is not the peak sensitivity region of the silicon cell. This data, however, does point out the basic arguments made in the Introduction. One is that the absorption coefficient has a slope similar to silicon rather than the Group III-Group V compounds, and secondly, from the spectral response curves, and the peak short circuit conversion efficiency, one can argue that low temperature fabrication can be used for both shallow or deep junctions.

XII. PRELIMINARY HIGH TEMPERATURE PHOTOVOLTAIC MEASUREMENTS

High temperature here means 200° C. A few experiments have been made very recently on the variation of open circuit voltage with temperature using a constant radiation intensity. The intensity of the tungsten source was such that an open circuit voltage of 0.6 volts at room temperature was measured with a sensitive silicon solar cell. A shallow junction CdTe cell showed 0.3 volts and a deep junction CdTe cell showed 0.5 volts under the same radiation intensity. While the silicon cell was not heated beyond 60° C, the change in open circuit voltage appeared to follow the data given in a Hoffman Electronics Corporation publication. If one extrapolates to 200° C for this cell the open

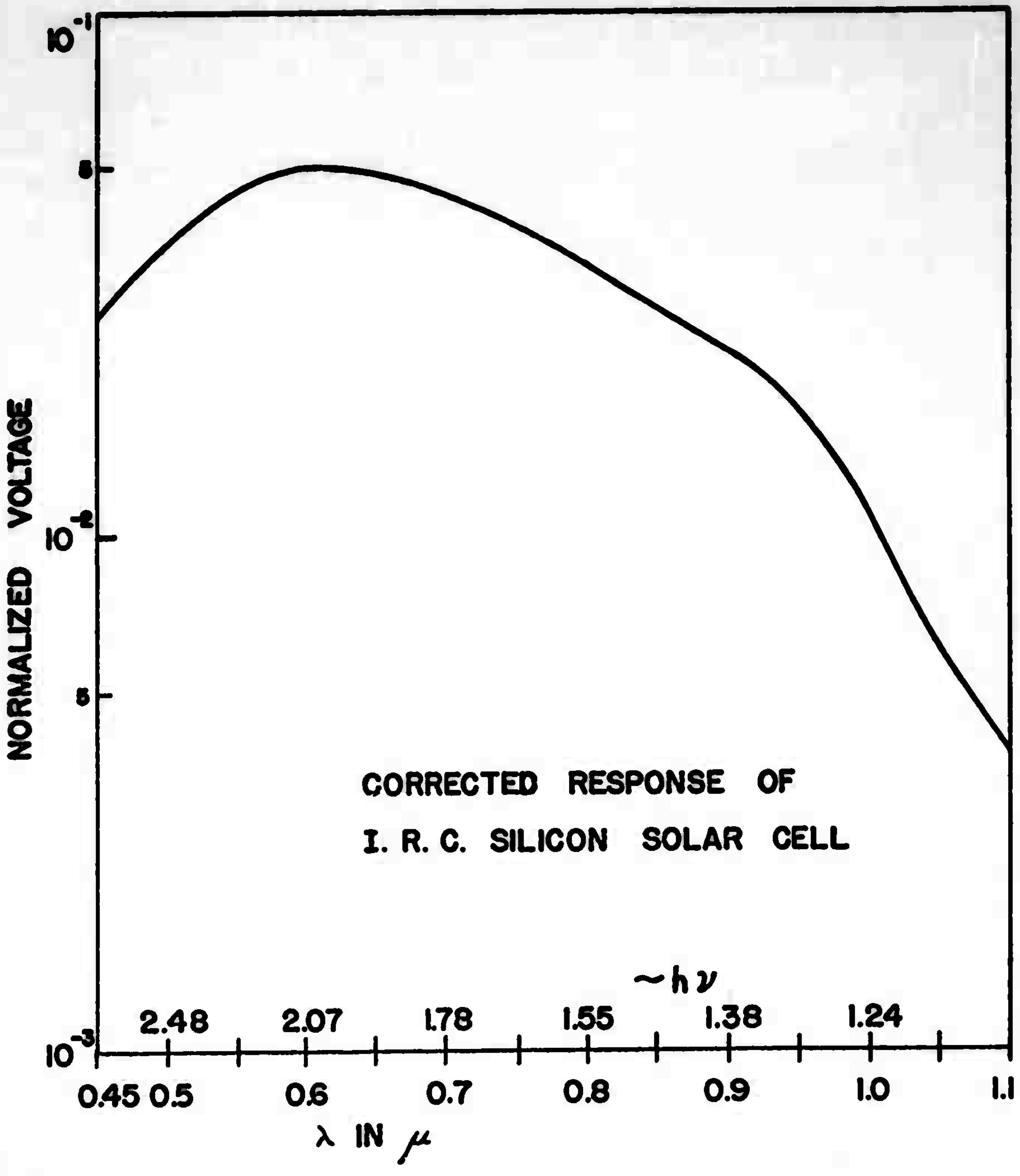

Fig. 11 - SPECTRAL RESPONSE OF SILICON SOLAR CELL

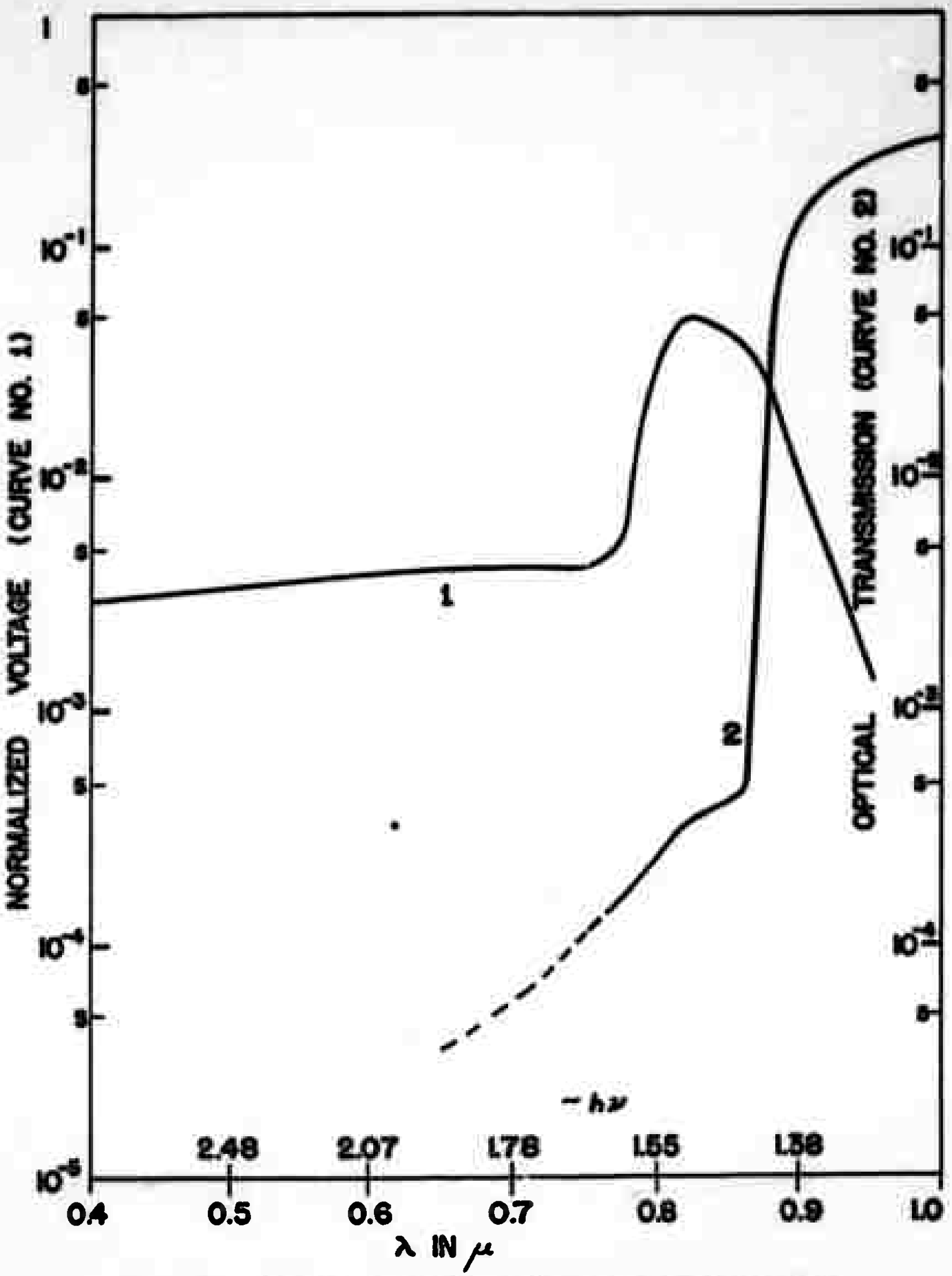

Fig. 12 - COMPARISON OF DEEP JUNCTION SPECTRAL RESPONSE AND OPTICAL TRANSMISSION OF N-TYPE CdTe

circuit would be about 0.23 volts.

The shallow junction CdTe cell which was 0.3 volts at room temperature had an open circuit voltage of 0.2 volts at 200° C. The deep junction CdTe cell which was 0.5 volts at room temperature had a value of 0.31 volts at 200° C. These values are preliminary as was emphasized earlier, yet they do tend to confirm the advantages of CdTe as a high temperature solar converter. However, so little is yet known about these cells, and considering that the room temperature open circuit voltages were low based on what might be expected based upon diffusion current limited photovoltages, we hesitate to compare it with the RCA calculations - photovoltage versus temperature.

This does not, however, preclude our previous arguments in favor of CdTe as a high temperature solar cell, since those arguments were based upon the nature of the material rather than a given cell. It is interesting though that the values obtained to date for high temperature performance are also favorable.

XIII. FUTURE WORK

The experimental results reported herein give a fairly clear indication of the direction the research should take. Future work on this program will emphasize:

a) better cleaning and etching to minimize apparent leakage current,
b) more detailed experimental and analytical study of diffusion junctions,
c) use of lower conductivity base material and
d) a survey of the energy conversion loss mechanisms in CdTe.

XIV. SUMMARY

The principal purpose of the program to make a high temperature solar cell with better characteristics than can be expected from silicon is discussed and the main reasons for choosing CdTe are listed. The early state of the art of this material determined the nature of the program and during the first year emphasis was on crystal growth studies. The many steps from elemental cadmium and elemental tellurium to a completed CdTe solar cell are listed; this report starts with step III, zone leveling CdTe, and proceeds section by section to discuss the development of techniques for slicing, lapping, polishing, chemical etching, chemical junction formation, vapor diffusion junction formation, electroding and mounting on crystal holders. The multizone furnace for fabrication vapor diffusion junction is pictured with its accessory equipment for fabricating diffusion junctions in compound semiconductors. The advantage of versatility in fabrication procedures for early state of the art compound semiconductors is pointed out. Electrical, thermal and optical experiments on the n-type base material are described, and the optical transmission of the n-type CdTe material shows a slope for absorption versus wavelength more similar to silicon than to GaAs or InP. Optical transmission studies now are more meaningful than last year since the early material was too inhomogeneous; this is indicated by the low transmission for the early material in the transparent region where current material has greater than 40 percent transmission. Current emphasis is on forming p-type layers on n-type CdTe by vapor diffusion of silver under a survey of conditions. It is shown that 500° C fabrication is possible and that both shallow and deep junctions can be formed. Spectral response curves of silicon, chemical junction CdTe, diffusion junction CdTe are given and discussed. An interesting correlation is found between the photovoltaic spectral response of a deep junction diffusion solar cell and the optical transmission of n-type CdTe. Preliminary high temperature photovoltaic measurements tend to confirm CdTe for high temperature solar use. Future work will stress more detailed experimental and analytical studies of vapor diffusion to form junctions, better cleaning and chemical etching to lower the apparent leakage currents, and the use of n-type CdTe with conductivity in the one to two ohm-cm range rather than the 0.04 ohm-cm material currently used.

XV. CONTRIBUTING PERSONNEL

J. K. Raney, R. Keller, C. Christensen, S. L. Webb and R. J. Robinson contributed to this fourth period of the program. The author would particularly like to acknowledge the help of S. L. Webb.

XVI. LOGBOOKS

The date for this report are contained in Logbooks 10629, 10630, 10848 and 11417.

Respectfully submitted,

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