

heliotek

N71-24042

a Division of **textron** Inc. 12500 Gladstone Ave., Sylmar, Calif. 91342 / Tel. (213) 365-4611 / TWX: 910-496-1488

CASE FILE COPY

Development and Pilot Line Production
of Lithium Doped Silicon Solar Cells

Second Quarterly Report

by

P. A. Payne

March 1972

JPL Contract No. 953171

This work was performed for the Jet Propulsion Laboratory,
California Institute of Technology, as sponsored by the
National Aeronautics and Space Administration under Contract
NAS7-100.

Heliotek, Division of Textron Inc.
12500 Gladstone Avenue
Sylmar, California 91342



This report contains information prepared by Heliotek, Division of Textron Inc., under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration.

SUMMARY

Scaling up the BCl_3 without O_2 diffusion beyond the 30 to 40 cells achieved during the last quarter was investigated by using a 100 cell capacity diffusion boat which held the cells vertically. Sheet resistances and I-V curves were uniform with 10 to 20 cells spaced along the entire boat, so the quantity was increased to 40 and then 60 cells per diffusion. There was no change in cell output and uniformity going from 20 to 40 cells per diffusion; however only half the lithium cells fabricated from slices diffused in the 60 cell diffusion had efficiencies of 11% or better.

Although uniform sheet resistances and I-V characteristic curves were obtained with up to 60 cells in the BCl_3 with O_2 diffusion during the last quarter, the short circuit currents were ~15% lower than the anticipated 135 to 140 mA. Consequently, work on this diffusion process during the quarter has been aimed solely at increasing the short circuit current. The diffusion temperature was lowered from 1055° to 1000° and 950°C, and at each of these temperatures variations in diffusion time were investigated. At 1000°C short circuit currents were approximately 10 mA higher, 130 rather than 120 mA average.

The short circuit currents obtained with diffusions at 950°C were similar, but the sheet resistances were extremely high, 60 to 90 ohms/square. Even with diffusion times approaching an hour, the sheet resistances were 40 ohms/square; therefore, the diffusion temperature was raised back to 1000°C and additional time variations were investigated. Lithium cells were fabricated using boron diffusions varying from an 8-5-5 (time in minutes for warmup - deposition - diffusion) to an 8-30-10 schedule and efficiencies of 11% or better were obtained. Cells with an 8-5-5 diffusion exhibited higher short circuit currents, but also higher series resistance than cells subjected to an 8-30-10 diffusion; the optimum diffusion schedule is probably between these two.

Since only small quantities of slices were used in these diffusions, scaling up, as well as optimizing the diffusion schedule will both need to be investigated during the next quarter.

During the previous quarter comparison of 3 and 6 minutes sintering times showed that the open circuit voltage degradation observed in ~10% of the cells sintered 6 minutes did not occur with a 3 minute sinter. Further investigation of sintering during this quarter involved varying the sintering time from 1 through 6 minutes to determine whether one particular time produced the best output. Comparison of current at maximum power showed that for sintering times of 2 to 5 minutes the final currents (130 - 132 mA) as well as the change in current (6 - 8 mA) were similar.

Capacitance measurements performed before and after sintering a group of about 20 cells showed a very small change in lithium density gradient with sintering. Capacitance measurements also showed that within each of four groups of cells with various material and diffusion parameters the range in lithium density gradients was less than a factor of two. This is a considerable improvement since lots of cells shipped during previous contracts have exhibited as much as two orders of magnitude variation in lithium density gradient within the same lot.

Spectral response measurements were used to evaluate lithium cells before and after sintering. An increase of 5 to 10% in the response between 4000 and 5000Å was observed; this improvement was duplicated by control cells without any lithium.

Spectral response measurements of cells diffused using a BCl_3 with O_2 diffusion showed a lower response at long wavelengths for cells with an 8-5-5 diffusion than for cells with an 8-30-10 diffusion. Additional measurements after lithium diffusion showed a 10 to 20% improvement at longer wavelengths in the previously low response cells from the 8-5-5 diffusion, whereas no change was observed with an 8-30-10 diffusion.

In fabricating lithium doped P/N cells for the second shipment to JPL, the boron and lithium diffusion parameters were the same as those used for the first lot. The electrical yield of 87% for the first lot was practically duplicated by the 85% electrical yield of the second lot and, as with the first lot, more than 50% of the cells had efficiencies of 12% or better.

TABLE OF CONTENTS

Section	Description	Page
1.0	Introduction	1
2.0	Technical Discussion	3
2.1	Boron Diffusion Studies	3
2.1.1	Background	3
2.1.2	Diffusion Studies Using BCl_3 Without O_2	4
2.1.3	Diffusion Studies Using BCl_3 with O_2	5
2.2	Sintering	11
2.3	Cell Evaluation	18
2.3.1	Capacitance Measurements	18
2.3.2	Spectral Response	26
2.4	Cells for Shipment	29
3.0	Conclusions	29

LIST OF FIGURES

Figure	Description	Page
1	Comparison of 40 and 60 Cell BCl_3 (no O_2) Diffusions Cells measured at 280C in solar simulator	6
2	Capacitance vs. Voltage for Lithium Doped P/N Cells Before and After Sintering	14
3	Donor Density vs. Depletion Width for Lithium Doped P/N Cells Before and After Sintering	15
4	Effect of Additional Sintering Time on Donor Density vs. Depletion Width of Lithium Doped P/N Cells	16
5	Range in Capacitance vs. Voltage. Twenty Lithium Doped P/N Cells diffused 3 Hours at 360°C	20
6	Donor Density vs. Depletion Width. Twenty Lithium Doped P/N Cells diffused 3 Hours at 360°C	22
7	Donor Density vs. Depletion Width for Lopex and Crucible Grown Lithium Doped P/N Cells	23
8	Range in Donor Density vs. Depletion Width for Lopex Lithium Doped P/N Cells	25
9	Spectral Response vs. BCl_3 with O_2 Diffusion Schedule	27
10	Spectral Response before and after lithium diffusion	28
11	Load Current Distribution of Lithium Doped P/N Cells. Crucible grown cells (364) Lithium diffused 3 hours at 360°C, measured at 28°C in solar simulator	30

LIST OF TABLES

Table	Description	Page
I	Electrical Characteristics of P/N Solar Cells fabricated using $\text{BCl}_3 + \text{O}_2$ diffusion	7
II	Electrical Characteristics of Lithium Doped P/N Cells fabricated using BCl_3 diffusion with O_2	10
III	Electrical Characteristics* of Li Doped P/N Cells as a Function of Sintering Time+	12
IV	Influence of Sintering	16

INTRODUCTION

It has been demonstrated that lithium doped P/N solar cells offer an alternative to the conventional N/P cell with respect to their behavior under space radiation environments. It would appear that higher efficiencies than the present N/P cell can be achieved. In addition to this advantage there is evidence that lithium doped P/N cells can be tailored to specific missions, since recovery characteristics can be controlled by appropriate choice of starting material.

In order to be considered as a serious candidate for space missions, it must be demonstrated that these cells can be manufactured in an economical fashion. The purpose of this program is to conduct a pilot line fabrication effort leading to the reproducible and consistent production of space quality lithium doped silicon solar cells in quantities of at least three thousand usable cells per month.

Since the boron and lithium diffusions are the rate limiting steps in processing, the emphasis for this program shall be to scale up these operations. In scaling up the boron diffusion the following areas will be investigated:

1. Use of a gas distribution system which would insert dopant directly over cells instead of from one end of the tube in order to reduce nonuniformities from one end of the boat to the other.
2. BCl_3 with and without O_2 with the emphasis on incorporating O_2 , since in the absence of O_2 , BCl_3 etches silicon and then not only uniform doping but uniform etching is of concern.
3. Diffusion boat design in order to study vertical versus horizontal cell position.

4. Flow rates of BCl_3 , O_2 and N_2 .

The lithium diffusion can be scaled up to 150 to 200 cells by vertically positioning the cells with an evaporated lithium layer in a slotted diffusion boat which accommodates 15 to 20 cells across the boat and as many rows as the length of the boat and the controlled heat zone in the diffusion furnace permit. Since this does not pose any problems, the major effort will be concentrated on investigation of the lithium evaporation in order to obtain cell-to-cell uniformity and repeatability from run to run. The factors to be studied in scaling up the lithium evaporation include cell preparation before evaporation, thickness of the lithium layer, and the influence of substrate heating. Experiments will also be performed to determine whether transference of the lithium evaporated cells from the vacuum system to the diffusion furnace must be accomplished in an inert atmosphere and whether or not the cells can be stored between lithium evaporation and lithium diffusion.

In addition, control points will be established in order to check the consistency and reproducibility of cells fabricated. Four shipments of three hundred cells each will be delivered during the contract period, and in fabricating these cells scale-up of processes will be demonstrated when possible. At the end of the contract three thousand cells which have been fabricated within a thirty-day period will be delivered to Jet Propulsion Laboratory.

2.0 TECHNICAL DISCUSSION

2.1 BORON DIFFUSION STUDIES

2.1.1 Background

The lithium doped P/N cell has been improved to the point that AMO efficiencies of 11 to 12.5% can be attained. These efficiencies have in the past been obtained only with diffusion processes which have not been scaled up for large numbers of cells; for example, the quantity typically processed in each boron diffusion has been ten 2 x 2 cm cells. The objective of the boron diffusion investigation during this contract is to increase the quantity to 100 to 200 cells per diffusion without sacrificing cell output or uniformity.

The boron diffusion process which has been used to fabricate high efficiency lithium doped P/N cells utilizes BCl_3 with nitrogen as the carrier gas. In this process the silicon is etched by the BCl_3 .

The uniformity of this etch reaction is difficult to control and consequently only limited investigation of the scale-up potential of this process has been done.

The major emphasis in the boron diffusion investigation has been to develop a process in which the nonuniformities of the BCl_3 -Si etch reaction could be eliminated by producing a boron glass layer as the diffusion source.

This boron glass layer can be obtained using any number of boron sources such as BCl_3 , BBr_3 , or B_2H_6 with O_2 . The resulting glass layer can then be removed leaving a surface unblemished by the nonuniform etching observed when O_2 is not used.

2.1.2 Diffusions Studies Using BCl_3 Without O_2

At the beginning of this program the BCl_3 diffusion without O_2 was selected, on the basis of previous comparisons, ⁽¹⁾ as the best boron diffusion process for producing high efficiency lithium doped P/N cells. This process has been used on fabricating cells for both the first and second cell shipments to JPL on this contract. While fabricating these cells, experimental work was performed to scale-up this BCl_3 without O_2 diffusion process.

As mentioned earlier, at the beginning of this contract, only 10 cells were typically processed in a boron diffusion. The cells were diffused horizontally on a complex leg-supported diffusion boat which allowed the gases to flow under the wafers as well as above. Maintaining horizontal placement, but with the cells on a simple flat diffusion boat, the diffusion was scaled up to ~30 cells during the first quarter. Since the uniform heat zone of the diffusion furnace was 16" long, 30 to 40 cells placed horizontally was the limit using a single layer diffusion boat. The alternative was to use a multiple-tiered diffusion boat or place cells vertically on a diffusion boat.

The method which has been investigated during this quarter employs vertical placement of cells in a specially designed diffusion boat, having a capacity of ~100 cells. This design was selected to minimize the non-uniformities in the etch reaction encountered when vertical placement in a slotted boat was used.

Starting at 10 cells, plus scrap blanks, distributed along the length of the boat, the quantity of cells per diffusion was gradually increased to 60. For runs containing up to 40 cells, the sheet resistances were uniform, 23 to 26 ohms/square. Lithium cells were fabricated using blanks from these boron diffusions and the distributions of outputs are shown in Figure 1. Outputs from the 40 cell diffusion were comparable to those obtained for cells in the first and second shipments to JPL, where the quantity for the majority of the boron diffusions was 10 to 20 cells.

The 60 cell boron diffusion resulted in cells with lower efficiencies - 80% had efficiencies of 10.5% or better, but only 50% of the cells met the contract minimum efficiency requirement of 11%. The lower output was due to lower I_{sc} and V_{oc} , as well as poorer curve shape.

2.1.3 Diffusions Studies Using BCl_3 with O_2

2.1.3.1 Diffusion Time and Temperature Variations

During the first quarter of this contract all the BCl_3 diffusions with O_2 were performed at 1055°C. Although uniform sheet resistances and I-V characteristic curves were obtained with up to ~60 cells per diffusion, cell output was low. Typically cell short circuit current was 115 to 120 mA rather than the 135 to 140 mA anticipated. These low values of short circuit current indicated that the junction was too deep; therefore, the following diffusion time and temperature variations to reduce the junction depth were investigated: 1) reduction in diffusion time at 1055°C, and 2) investigation of different diffusion schedules at both 950 and 1000°C. The results of all these diffusions are shown in Table 1.

The diffusion schedule of 8-5-10 (time in minutes for warmup-deposition-diffusion) was changed to 8-5-5 and 8-5-2 at 1055°C. In both cases the improvement in short circuit current was less than 5 mA.

Diffusions were then performed at 1000°C using an 8-5-10 diffusion

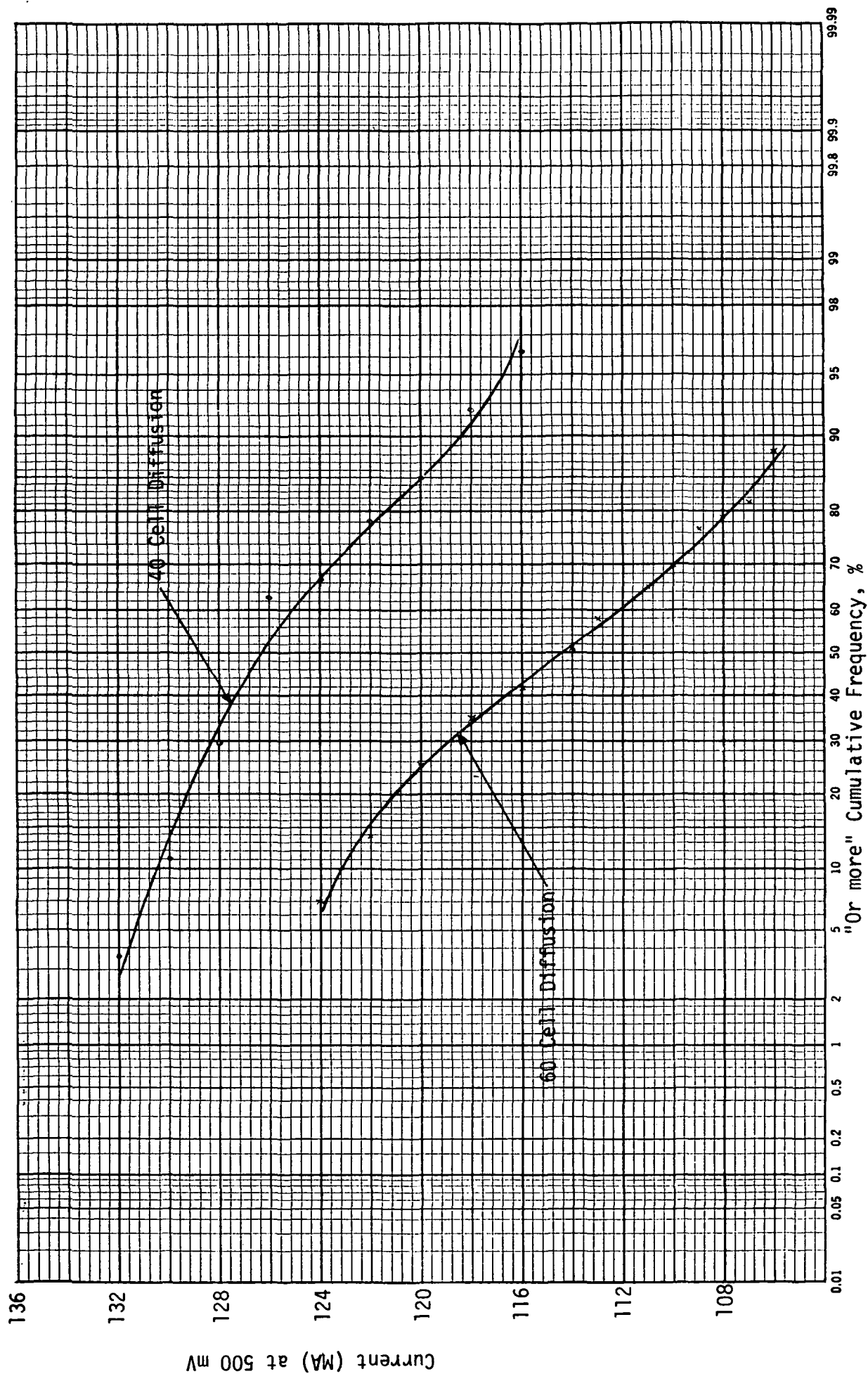


Figure 1. Comparison of 40 and 60 Cell BCl_3 (no O_2) Diffusions
Cells measured at 280C in solar simulator

Table I
Electrical Characteristics of P/N Solar Cells
Fabricated Using $\text{BCl}_3 + \text{O}_2$ Diffusion

Run #	Diffusion Temp.	Schedule	ρ_s ohms/ $\square$	I_{sc} mA
1	1055	8-5-10	15-25	114-122
2	1055	8-5-2	26-40	116-124
3	1000	8-5-10	25-35	119-126
4	1000	8-5-10	30-40	124-134
5	1000	8-5-5	40-45	128-133
6	1000	8-5-5	54-60	122-128
7	1000	8-5-2	50-55	119-125
8	1000	8-5-2	55-65	113-124
9	950	8-5-10	65-75	128-132
10	950	8-5-10	85-95	122-130
11	950	8-50-5	35-45	--
12	1000	8-35-5	29-31	131-134
13	1000	8-30-10	26-28	134-136

schedule. The results of three separate diffusions varied, but the best run produced short circuit currents ~10 mA higher than the 120 mA average typical of 8-5-10 diffusions at 1055°C. Similar short circuit currents were obtained with an 8-5-5 diffusion schedule. Therefore, the diffusion temperature was reduced to 950°C to determine whether any further improvement could be made.

Although the short circuit currents obtained with an 8-5-10 diffusion at 950°C, ranging from 123 to 132 mA, were similar to the results of diffusions at 1000°C, sheet resistances which were already as high as 60 ohms/square for diffusions at 1000°C increased to 60 to 90 ohms/square. Since increasing the sheet resistance increases the series resistance and thereby causes power loss, longer diffusion times were used in order to reduce the sheet resistance. Since boron tends to redistribute itself to give relatively low values of surface concentration, the deposition to diffusion time ratio was made large to limit this behavior. A diffusion schedule of 8-50-5 was arbitrarily chosen. The sheet resistances were reduced to 37 to 45 ohms/square without any loss in short circuit current. These sheet resistances were still somewhat high, but rather than increase the diffusion time even more at 950°C, which would not be particularly desirable in terms of a manufacturing process, the diffusion temperature was raised back to 1000°C. Using a diffusion schedule of 8-35-5, sheet resistances of 26 to 28 ohms/square were obtained; again no loss in I_{sc} occurred. In summary, although these variations in diffusion time at both 1000 and 950°C produced a wide range in sheet resistance, 25 to 90 ohms/square, the short circuit currents were typically between 125 and 135 mA.

2.1.3.2 Fabrication of Lithium Cells Using BCl_3 Diffusions with O_2

Selection of the best boron diffusion parameters must be based upon what provides the best lithium cell output; therefore cells from the various boron diffusions at 1000 and 950°C were fabricated into lithium

cells for analysis. In order to get the closest possible correlation between boron diffusion characteristics and lithium cell output, the actual P/N cells which had been fabricated and had I-V curves measured to evaluate the boron diffusions were reprocessed; that is, the contacts and AR coating were removed and the stripped cells were then lithium diffused, recontacted, and recoated. In this way the interaction between the boron and lithium diffusions could be evaluated more precisely than would be possible if the boron diffusion lots were merely split, with half fabricated as P/N cells and half as lithium doped P/N cells. Actual changes in short circuit current, curve factor, power, and open circuit voltage due to the lithium diffusion could be measured.

The short circuit current and current at 480 mV (122 mA needed for 11% efficiency) for each group of 5 to 8 of lithium cells are shown in Table II. The short circuit current prior to lithium diffusion is also listed to show that the power output gained with the lithium diffusion is due not only to higher open circuit and maximum power voltage, but also higher short circuit current. Lithium cells with efficiencies $\geq 11\%$ were obtained with all but one of the boron diffusions. However, only four of the diffusions resulted in lithium cell efficiencies $\geq 11\%$ for more than half the cells: the 8-5-5 (#57), 8-5-10 (#53), and 8-30-10 (#74) diffusions at 1000°C as well as the 8-50-5 diffusion (#65) at 950°C.

Run #73, the 8-30-10 diffusion at 1000°C had sheet resistances of 26 to 28 ohms/square. The lithium cells fabricated from this boron diffusion had lower short circuit currents, but better curve shapes than the cells from the other diffusions with sheet

Table II

Electrical Characteristics of Lithium Doped P/N Cells
Fabricated Using BCl_3 Diffusion with O_2

Run #	Boron Diffusion Sched., Temp.	ρ_s ohms/ $\square$	I_{sc} (mA) After boron Diffusion	I_{sc} (mA) After Li Diffusion	I at I_{sc} (mA) 480 mv
53 (7 cells)	8-5-10, 1000°C	35-40	128-134	139.5-142	115-125
57 (8 cells)	8-5-5, 1000°C	40-45	128-133	140-143	118-130
58 (6 cells)	8-5-5, 1000°C	50-60	121-128	138-144	118-130
61 (8 cells)	8-5-10, 950°C	65-75	127-132.5	136-142	114-124
62 (7 cells)	8-5-10, 950°C	85-95	--	134-140	101-114
65 (5 cells)	8-5-5, 950°C	35-45	129-132	140-142	118-127
74 (6 cells)	8-30-10, 1000°C	26-28	129-133	133.5-142	122-128

resistances of 35 to 45 ohms/square. As a result of the boron diffusion investigation combined with fabrication of lithium cells from these diffusions, it has been determined that lithium cell efficiencies of 11% or better can be obtained with boron diffusions from 8-5-5 to 8-30-10 at 1000°C and sheet resistances ranging from ~25 to 45 ohms/square. This range in diffusion time and sheet resistance provides a great deal of flexibility for optimizing this process.

2.2

SINTERING

During the previous contract (JPL Contract #952547, Part II) the sintering of lithium doped P/N cells was investigated. For most cells sintering for 6 minutes at 605°C improved cell output; however, about 10% of the cells exhibited open circuit voltages which were 10 to 40mv lower after sintering. Comparison of 3 and 6 minute sintering operations during the first quarter of this contract showed that 3 minutes was superior, since no suppressed open circuit voltages were observed.

Continuing this investigation, an experiment was performed in which the sintering time was varied from 1 to 6 minutes in 1 minute increments. Six groups of 8 to 10 cells each were used. In this way previous data obtained at 3 and 6 minutes could be verified and, with the additional data points, optimum sintering time at 605°C could be determined. The average changes in electrical characteristics as a function of sintering time are shown in Table III. The average current at 500mV after sintering 1 minute was lower than the initial average. Although cells sintered 6 minutes showed improvement, the current at 500mV was definitely lower than for cells sintered 2 to 5 minutes. Based upon these

Table III

Electrical Characteristics* of Li Doped P/N Cells as a Function of Sintering Time+

Sintering Time (min)	I _{sc} (Before)	I _{sc} (After)	ΔI_{sc}	I at 500 Before	I at 500 After	ΔI_{500}	V _{oc} Before	V _{oc} After	ΔV_{oc}
1 (8 cells)	139.2	144.3	5.1	124.6	122.2	- 2.4	610	615	5
2 (10 cells)	139.3	144.4	5.1	123.8	132.3	8.5	610	620	10
3 (9 cells)	139.1	143.6	4.5	125.4	131.7	6.3	610	618	8
4 (10 cells)	138.2	143.4	5.2	123.3	130.6	7.3	609	619	10
5 (10 cells)	138.3	144.4	6.1	122.6	131.0	8.4	608	620	12
6 (10 cells)	135.9	141.9	6.0	122.6	128.4	5.8	610	615	5

*AMO, 28°C

+Sintering temperature 605°C

observations and the similarity in the current at 500mV achieved with 2 to 5 minutes sintering time, it appears that a time anywhere in the range of 2 to 5 minutes could be selected. In order to minimize lithium movement, sintering times of 2 to 3 minutes have typically been used.

In order to evaluate changes in the lithium concentration and distribution due to sintering, capacitance was measured before and after sintering a group of 20 cells. The cells, which were fabricated from crucible grown silicon, were lithium diffused 3 hours at 360°C; the sintering time was 2.5 minutes at 605°C.

Figure 2 shows typical capacitance versus applied voltage* curves before and after sintering the slope of the curve which was .281 before sintering increased to .304 after sintering. From the measured capacitances, the donor density was calculated (see next section), and as shown in Figure 3, the effect of sintering on the lithium distribution near the junction was found to be insignificant. For example, at a depth of 1.2 μ the donor density changed from 1.1×10^{15} before sintering to 1.0×10^{15} after sintering, while the lithium density gradient changed from 1.5 to 1.35 $\times 10^{19}/\text{cm}^4$.

Further investigation included sintering cells previously sintered 1 and 2 minutes, an additional 2 minutes to determine whether any significant changes in I-V characteristic curves occurred. With an initial sintering of one minute cells exhibited an average short circuit improvement of 5mA; but even with this improvement, the power was lower due to curve shape deterioration as was shown in the previous section. When sintered an additional 2 minutes, (3 minutes total) these cells showed little change in short circuit current, but the current measured at 500mV increased as much as

* A more detailed description of the technique used for measuring capacitance and calculating donor density is presented in the next section of the report.

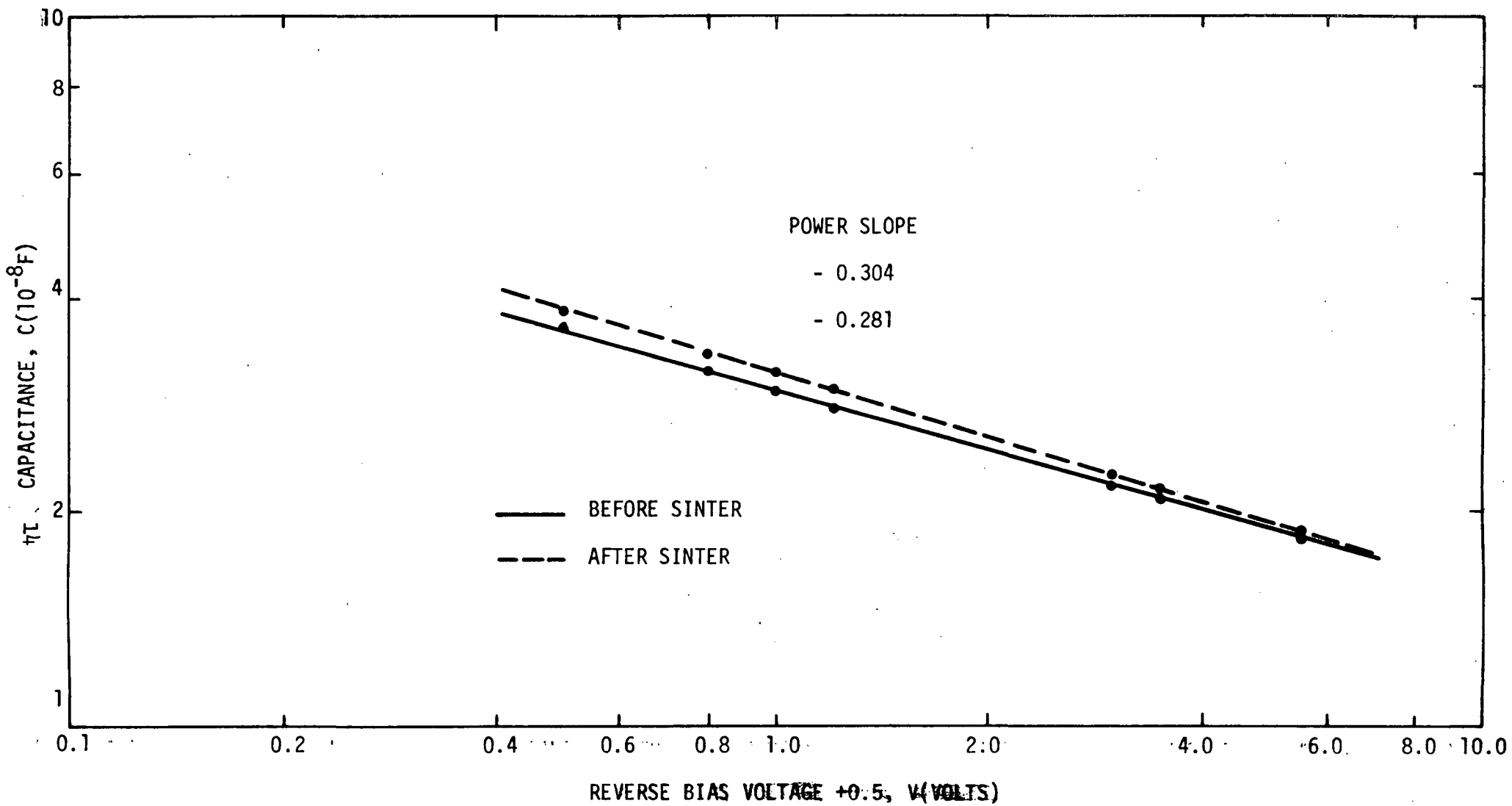


Figure 2. Capacitance vs. Voltage for Lithium Doped P/N Cells Before and After Sintering

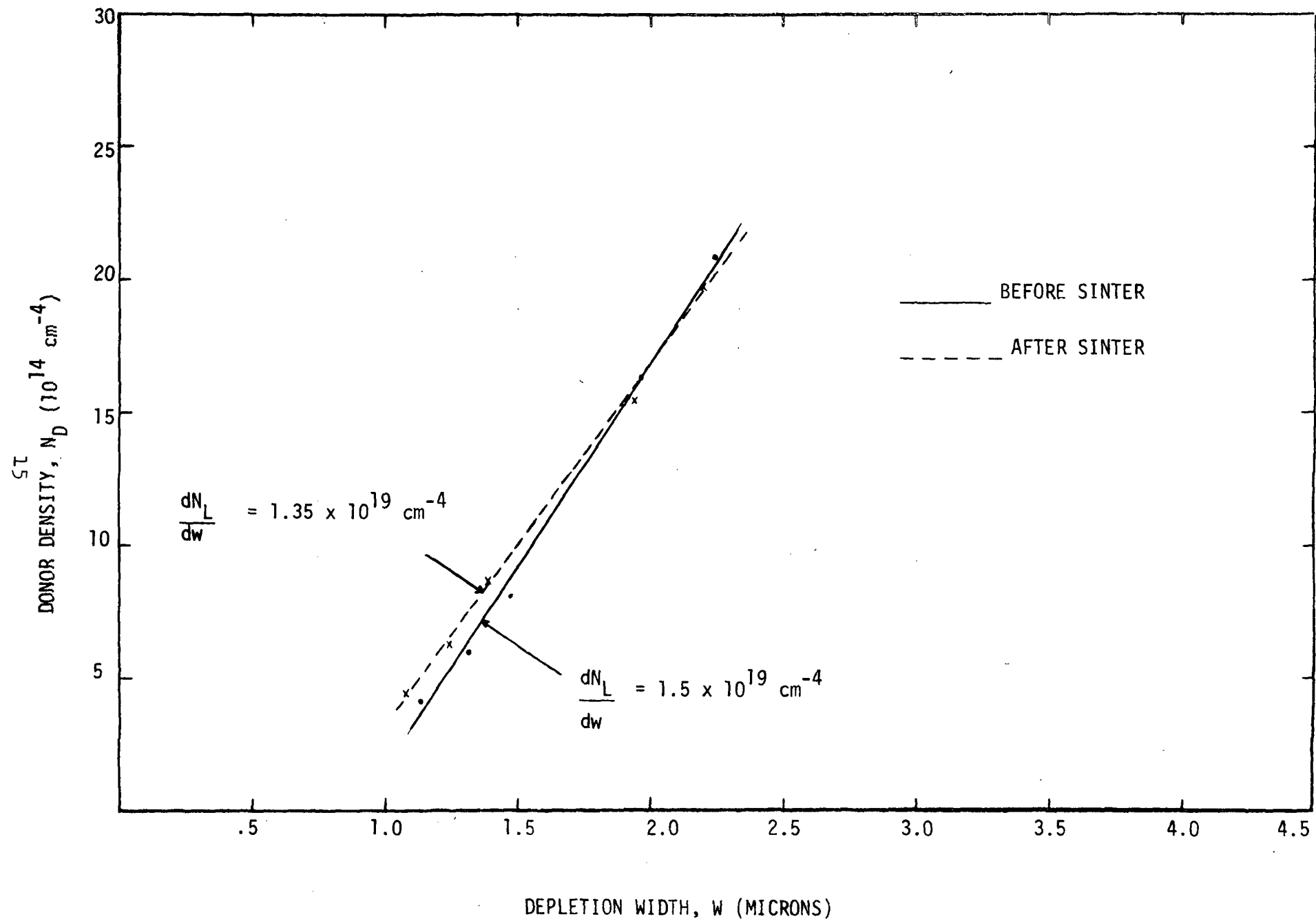


Figure 3. Donor Density vs. Depletion Width for Lithium Doped P/N Cells Before and After Sintering

16 mA (Table IV). The resulting currents of 131 to 136 mA (at 500 mV) represented a significant improvement over the 114 to 130 mA obtained after the one minute sintering time.

The cells which had been sintered 2 minutes initially, showed no change in short circuit current, maximum power, or open circuit voltage after the additional 2 minutes. Capacitance measurements performed before and after the additional 2 minute sinter showed a slight increase in the slope of the capacitance versus voltage curve, from .29 to .30. This accompanied by very small changes in the actual capacitance values, indicated that changes in the lithium distribution and concentration were minor. As shown in Figure 4, the difference in donor density within $2\mu\text{M}$ of the junction is within the range of measurement error.

It would appear that cells which show curve shape degradation with short sintering times can be re-sintered to improve the output, without significantly altering the lithium concentration and distribution. However, this can only be of value if cells are solderless when tested.

TABLE IV
INFLUENCE OF SINTERING
I (mA) at 500 mV, AMO, 28°C

Before Sinter	After 1 min. Sinter	Additional 2 min. Sinter
128	130	136
121	114	131
124.5	128.5	132
126	121	132

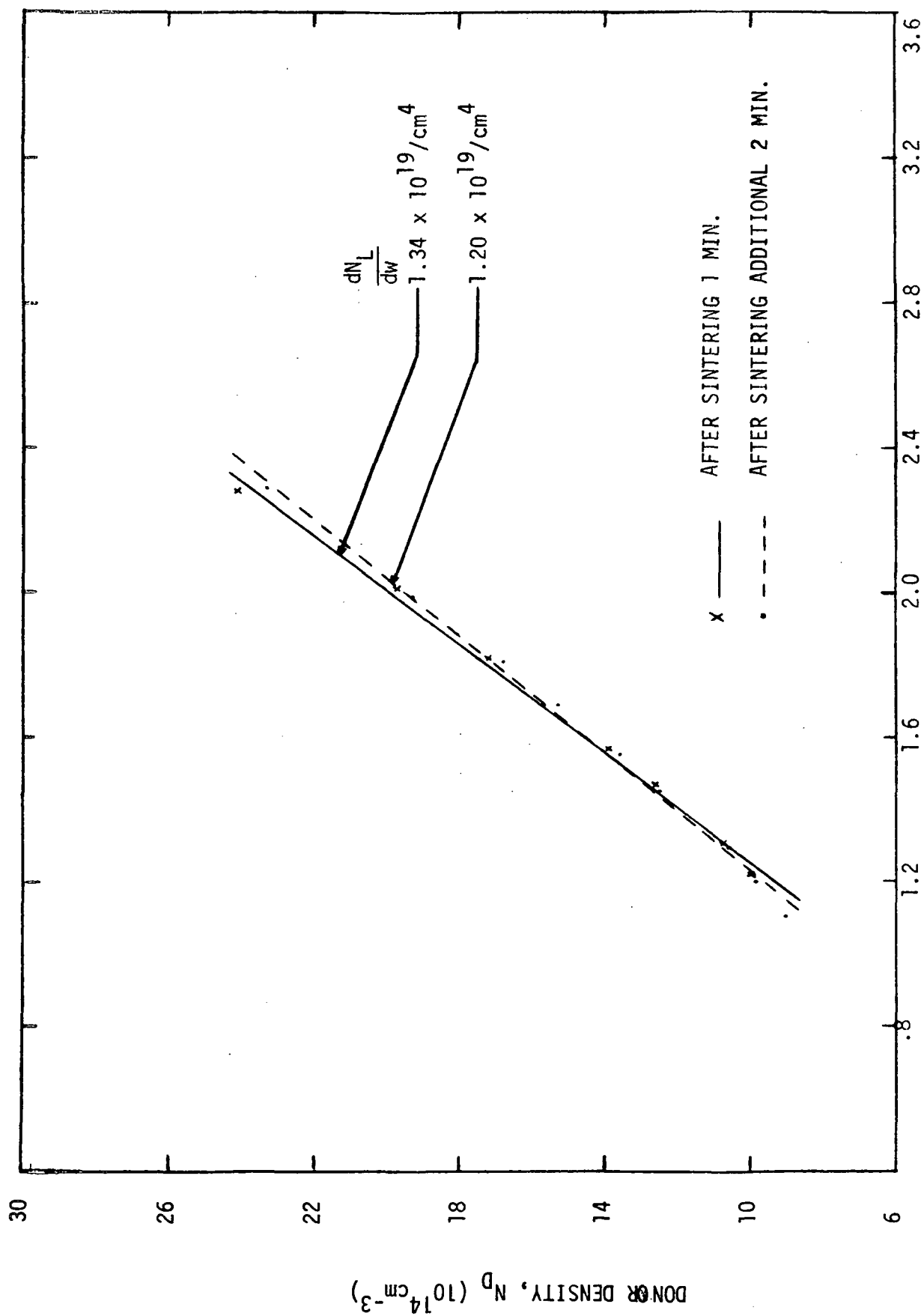


Figure 4. Effect of Additional Sintering Time on Donor Density vs. Depletion Width of Lithium Doped P/N Cells

2.3 CELL EVALUATION

2.3.1 Capacitance Measurements

By using capacitance-voltage measurement techniques the donor concentration as a function of distance from the junction as well as the lithium density gradient can be calculated. In the extensive capacitance studies of lithium doped P/N cells ^{2,3} the primary conclusion has been that the lithium density gradient, dN_L/dw , is one of the most important parameters in determining cell recovery after exposure to radiation.

In our previous work, information about the lithium diffusion has been obtained by incrementally lapping cells and measuring the sheet resistance; from this the lithium concentration profile could be calculated. Determination of the lithium distribution in this manner would be performed using two to five samples and once this information was obtained the only measurement used for monitoring the lithium diffusion for large quantities of cells was a sheet resistance measurement of the lithium diffused region. As indicated by the capacitance and radiation recovery analyses, the sheet resistance measurement does not provide enough information about the lithium concentration and density gradient near the junction, so that it can be used by itself to predict uniformity of cell behavior. Consequently during this contract, in addition to sheet resistance measurements of every cell in order to monitor changes in average lithium concentration, capacitance measurements have been performed on a sample basis. The objectives have been to evaluate ranges in lithium concentration and density gradient for groups of cells with the same diffusion parameters, as well as to examine changes due to sintering (see previous section), starting material, and differences in lithium diffusion parameters.

The capacitance as a function of reverse bias voltage was measured over a range of 0 to ~5 volts. The donor density as a function of depletion width was then calculated using the following equations:

$$N_D = \frac{V + \phi}{q \epsilon \epsilon_0} \frac{C}{A} \quad 2$$

$$w = \epsilon \epsilon_0 \frac{A}{C}$$

where N_D = donor concentration

V = voltage

ϕ = built-in voltage of junction

C = capacitance

A = area of junction

q = electrical charge

E = dielectric constant

E_0 = permittivity of free space

m = slope of $\log C$ vs. $\log (V + \phi)$ plot

w = depletion width

Initial capacitance measurements were performed on a group of twenty crucible grown cells which had been lithium diffused 3 hours at 360°C. Rather than calculate concentration vs. depth for every cell, the capacitance measurements at each reverse bias voltage were averaged and an average concentration vs. depth was plotted. In addition the concentration for cells with the highest and lowest capacitance values was calculated to determine the range. Figure 5 shows $\log C$ versus $\log V$ for cells with the highest and lowest measured capacitances; the slopes of the two curves are -0.316 and -0.280, respectively.

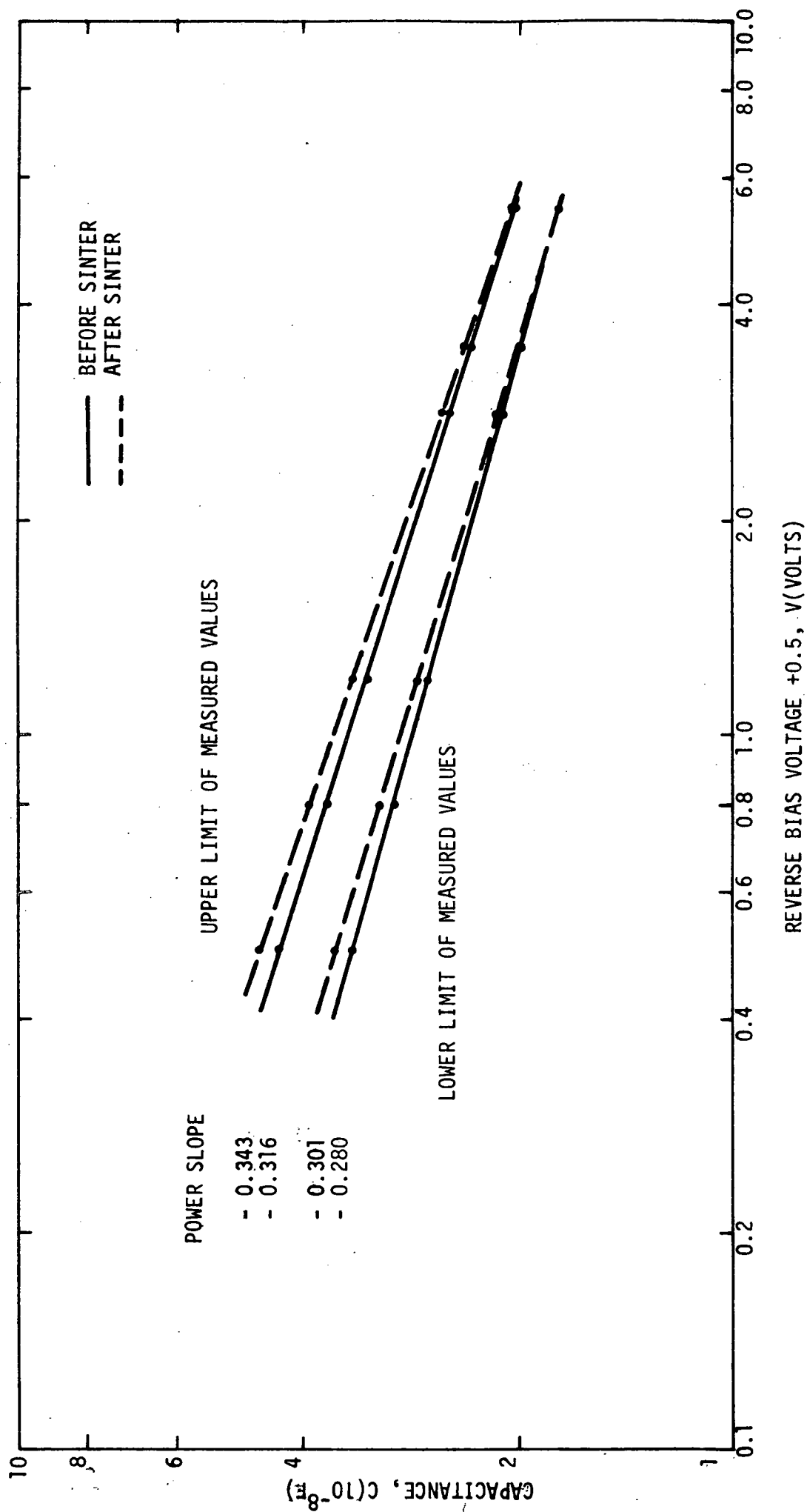


Figure 5. Range in Capacitance vs. Voltage. Twenty Lithium Doped P/N Cells Diffused 3 Hours at 360°C

Donor density versus depletion width was calculated for these capacitance values and is shown in Figure 6 as the upper and lower limit. The curve calculated from the average capacitance values is also shown. The range in lithium density gradient for this group of cells was 1.3 to $1.6 \times 10^{19}/\text{cm}^4$. Capacitance measurements were also performed after sintering; although the calculated gradients changed, the range was still narrow, 1.1 to $1.4 \times 10^{19}/\text{cm}^4$.

Additional capacitances were performed comparing crucible grown cells diffused 1 and 3 hours at 360°C as well as Lopex cells diffused 3 hours at 360°C , to Lopex cells diffused 2 hours at 400°C . The donor density versus depletion width calculated from averaged capacitance values for each of the groups is shown in Figure 7. As anticipated, the lithium density gradient of the crucible grown cells diffused 3 hours was higher than those diffused 1 hours; the difference was a factor of four. The Lopex and crucible grown lithium cells both diffused 3 hours at 360°C exhibited almost a factor of two difference in gradient, with the Lopex cells having the highest gradient. This observation of higher lithium concentration and density gradient for Lopex cells subjected to the same diffusion conditions as crucible grown cells is in agreement with the findings of previous investigators.²

Since, once the diffusion temperature is raised above 200°C , the diffusion constant of lithium in silicon is unaffected by the oxygen level, the difference in density gradients must be due to the formation of neutral lithium-oxygen pairs.⁴

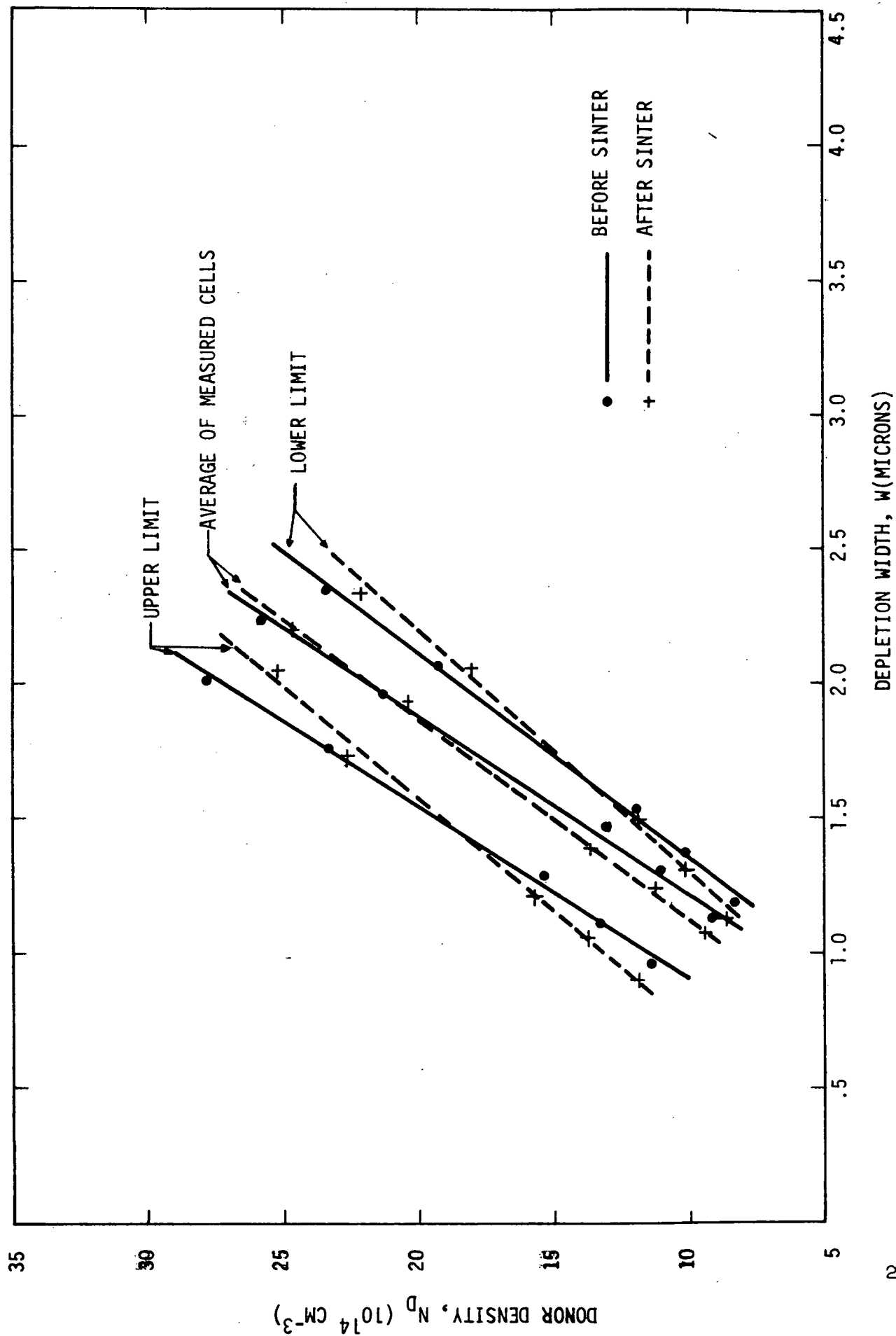


Figure 6. Donor Density vs. Depletion Width. Twenty Lithium Doped P/N Cells Diffused 3 Hours at 360°C

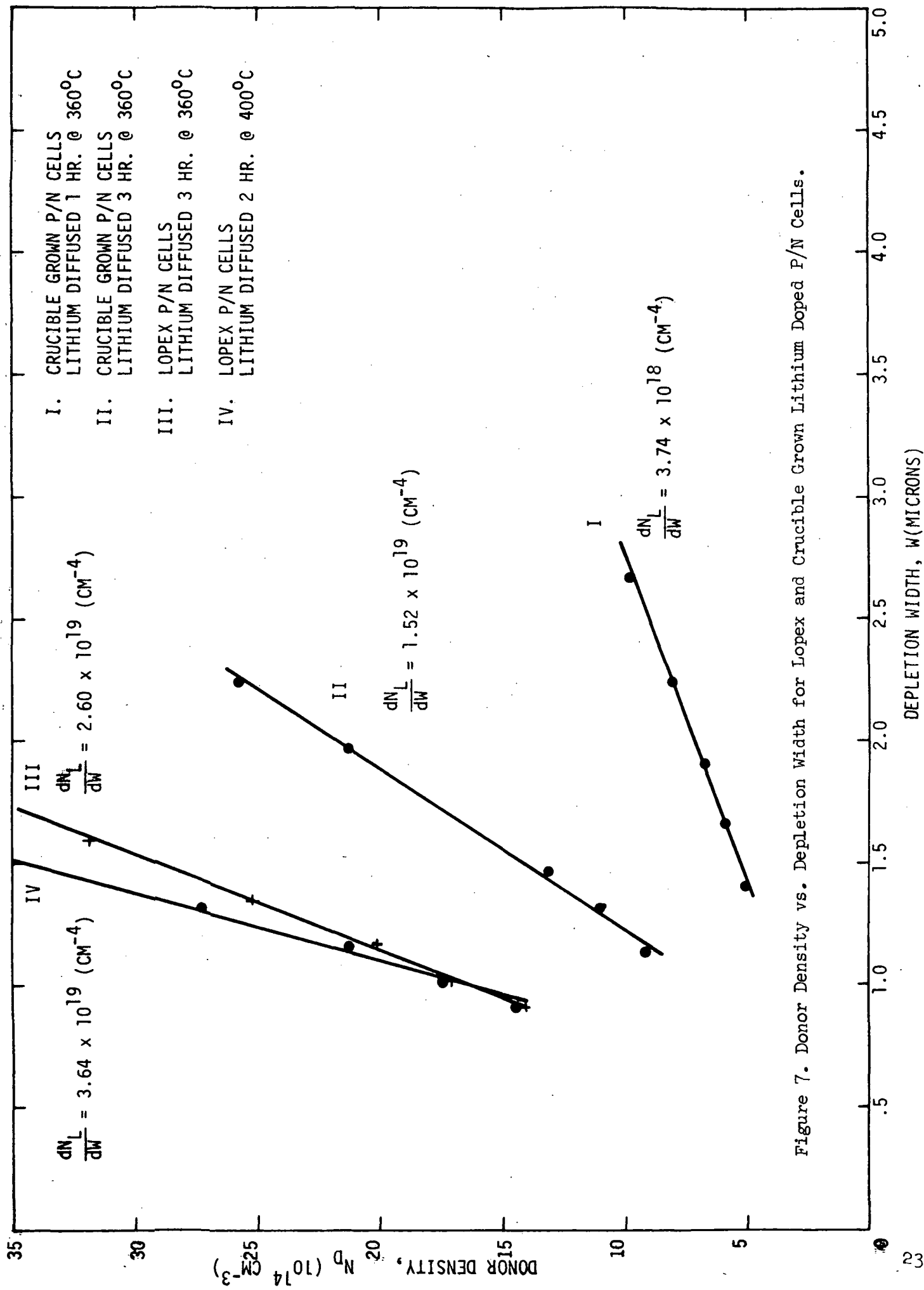


Figure 7. Donor Density vs. Depletion Width for Lopex and Crucible Grown Lithium Doped P/N Cells.

The density gradient of Lopex cells diffused 2 hours at 400°C was approximately 1.5 times that of cells diffused at 360°C. As shown in Figure 8, these two sets of diffusion parameters produced an overlap in the range of concentration versus depletion width, and the difference between the highest density gradient for the one group and the lowest density gradient for the other group is slight, 3.4 versus $3.6 \times 10^{19}/\text{cm}^4$.

The narrow range in density gradients for both the crucible grown and Lopex lithium cells described in this section indicates that improvements in uniformity have been achieved. In each of these groups of cells, the difference between the minimum and maximum density gradient was less than a factor of two. Variations in lithium density gradients of as much as two orders of magnitude within the same lot have previously been reported.²

All the crucible grown and Lopex cells described were diffused 1 to 3 hours using evaporated lithium as the diffusion source. The narrow range in density gradients resulting lends support to earlier conclusions by RCA regarding effects of diffusion time and source on uniformity of density gradients, namely, that the uniformity could be improved by using 3 to 4 hour rather than 7 to 8 hour diffusions and evaporated lithium rather than painted on lithium as the diffusion source.

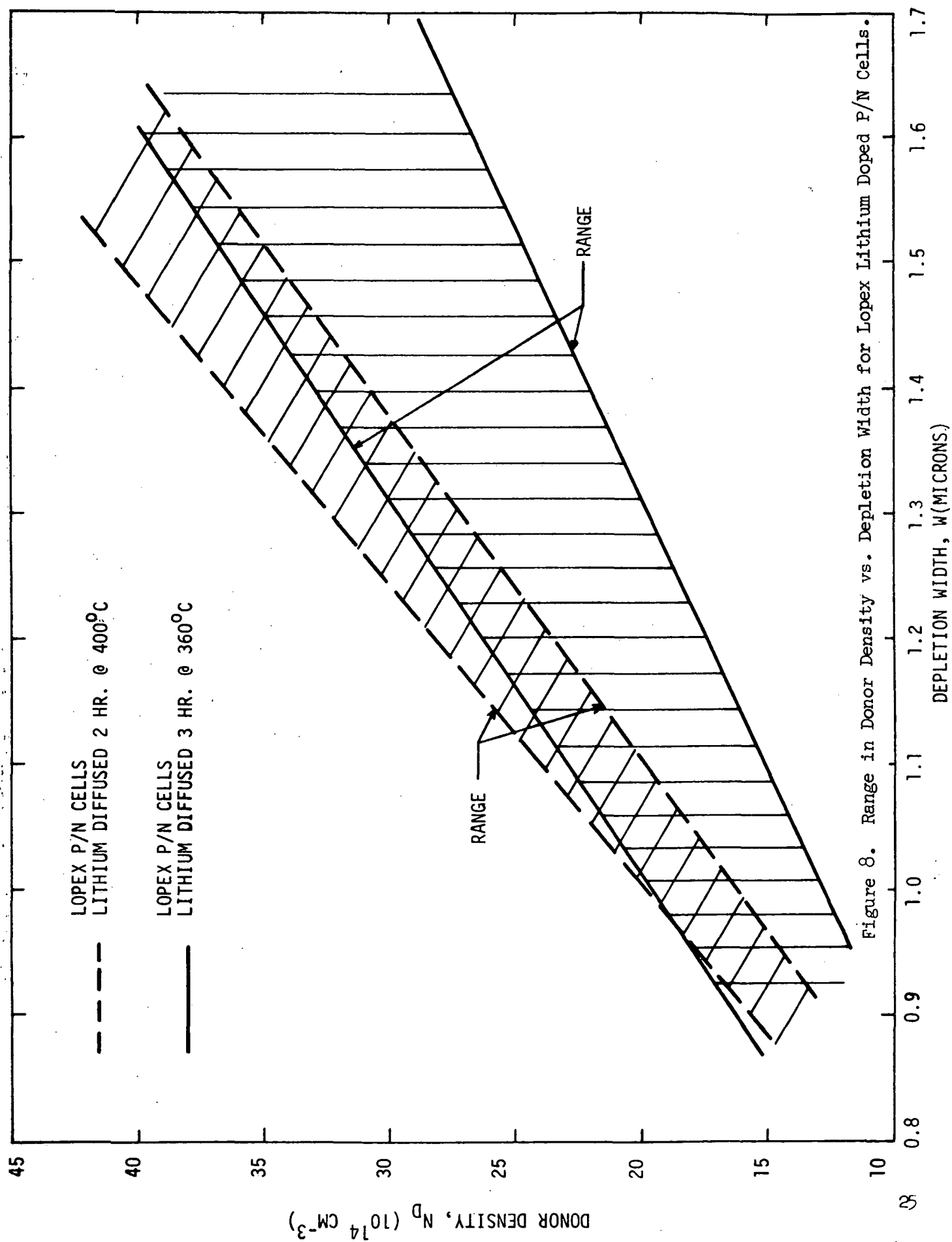


Figure 8. Range in Donor Density vs. Depletion Width for Lopex Lithium Doped P/N Cells.

2.3.2 Spectral Response

Solar cell spectral response determined by measurement of short circuit current at various wavelengths between 4,000 and 10,000 Å can be used to determine differences in such characteristics as junction depth, bulk lifetime, AR coating, etc. Spectral response measurements have been used during this contract to evaluate cells from the BCl_3 diffusion with O_2 , evaluate the effect of the lithium diffusion, and investigate the influence of sintering.

Spectral response measurements of cell diffused using BCl_3 with O_2 showed that the long-wavelength response was low for short diffusion times at 1000 and 950°C; increasing the diffusion time at 1000°C improved the long-wavelength response considerably (Figure 9). This might indicate that in the longer diffusion gettering occurs, producing a lifetime improvement.

Lithium diffusion of low long-wavelength response cells which had been boron diffused at 1000 and 950°C in all cases produced an improvement in the long-wavelength response similar to that shown for Run 58 in Figure 10. On the other hand, lithium diffusion of cells from Run 73 which exhibited a high long-wavelength response after boron diffusion produced no significant change in the response.

Lithium cells fabricated using the BCl_3 diffusion without O_2 have consistently shown short circuit current improvements of 4 to 6 mA after sintering. Spectral response measurements performed before and after sintering indicated that this could only be explained

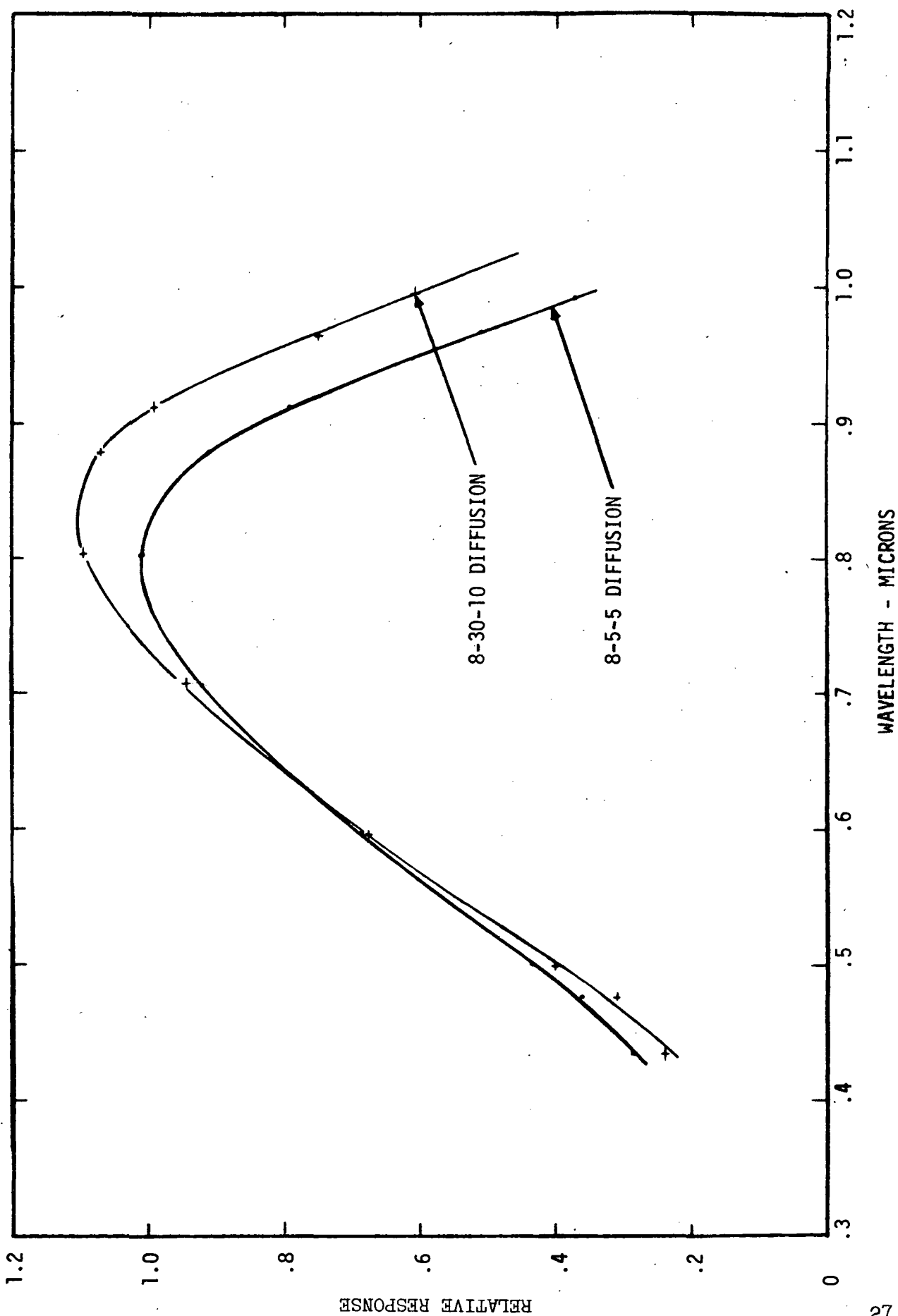


Figure 9. Spectral Response vs. BCl_3 with O_2 Diffusion Schedule

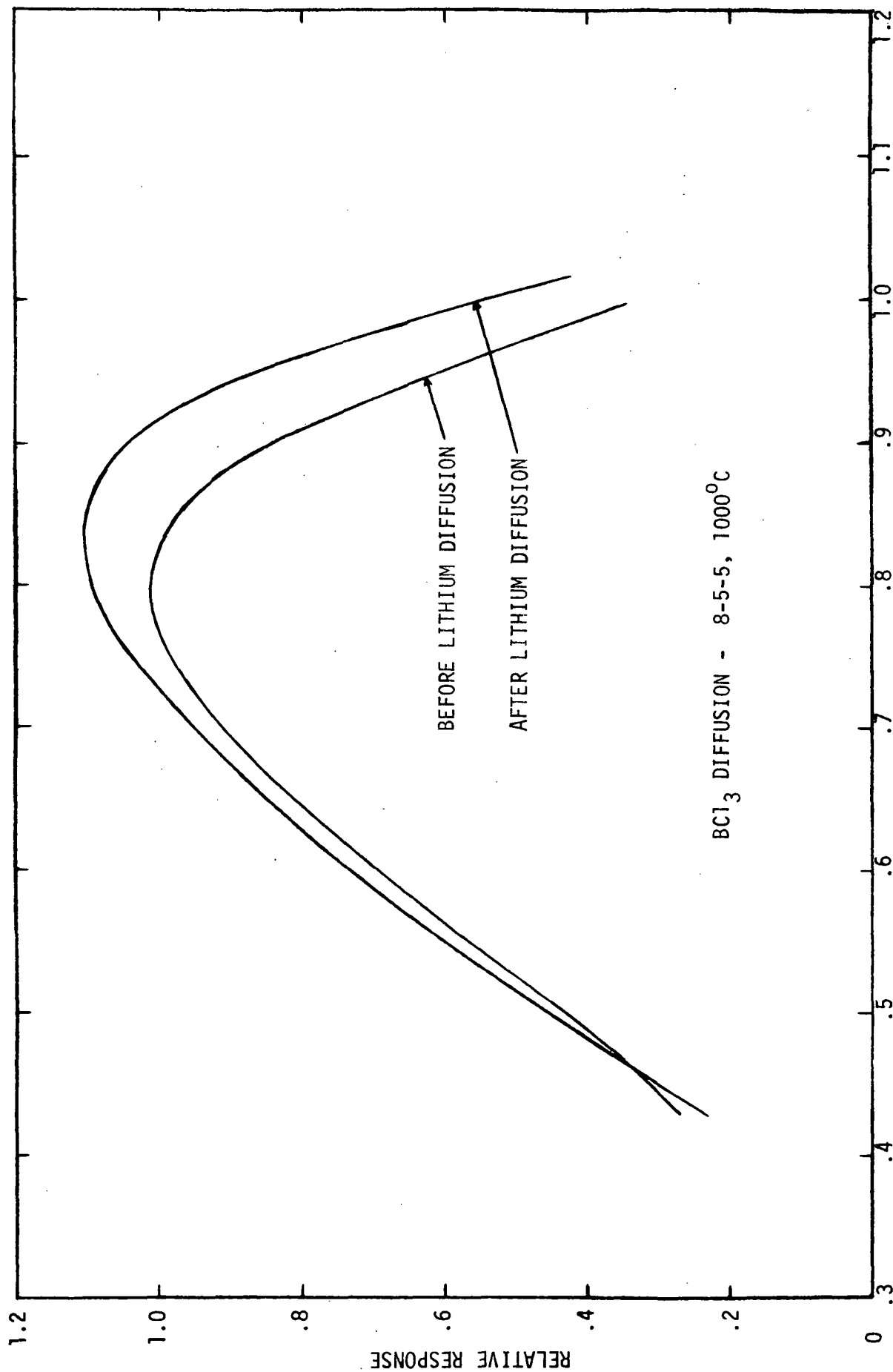


Figure 10. Spectral Response Before and After Lithium Diffusion

by a 5 to 10% improvement over a narrow range between 4000 and 5500 Å, since no change occurred at longer wavelengths. Similar behavior was observed in sintering P/N cells with no lithium indicating that the improvements in short circuit current were not due to changes in the lithium distribution.

2.4 CELLS FOR SHIPMENT

Cells for the second shipment were fabricated from 20 ohm cm crucible grown silicon. They were diffused using an 8-2-7 schedule that employed BCl_3 without O_2 as the boron source. The lithium was applied by evaporation and the cells were diffused three hours at 360°C. All cells were sintered ($2\frac{1}{2}$ minutes) and then soldered.

In order to complete lots 1 and 2, 351 cells were shipped; the distribution of the 364 cells meeting the minimum efficiency of 11% is shown in Figure 11.

The cells were measured at 28°C in the solar simulator ($140\text{mW}/\text{cm}^2$). The output was determined by measuring the cell current at 500 mV, and the cells were categorized in 2 mA groupings. Approximately 60% of the cells have outputs of 63.8 mW (127.8 mA at 500 mV) which is equivalent to 12% efficiency. The median output was approximately 64.5 mW. This output distribution represents only those cells with efficiencies of 11% or better. The actual electrical yield for cells with 11% efficiency or better was approximately 85% (364 good out of 425).

3.0 CONCLUSIONS

At present, the BCl_3 diffusion without O_2 is limited to 40 cells per diffusion. Attempts to process 60 cells per diffusion have produced large variations in cell output as well as lower efficiencies.

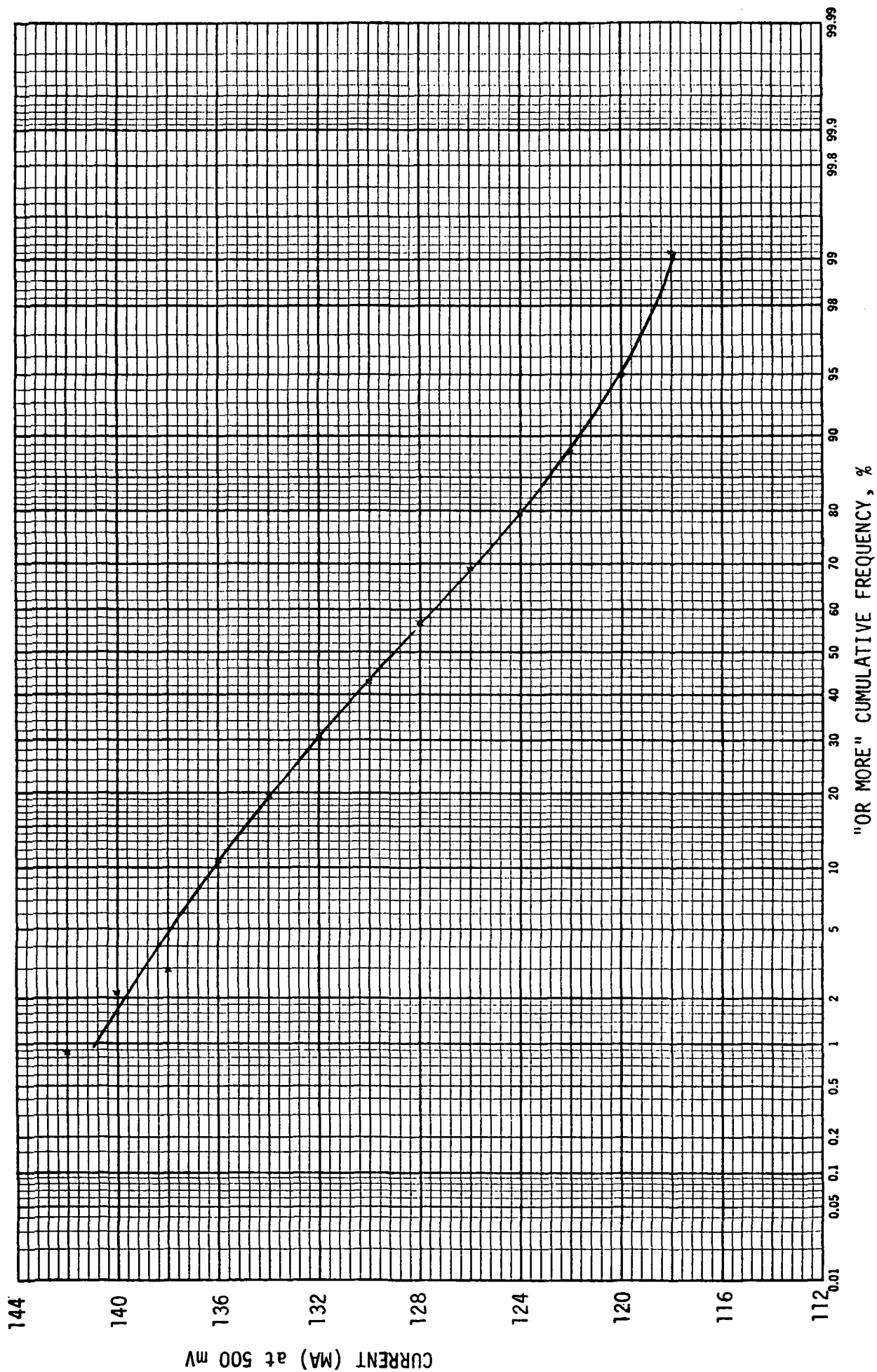


Figure 11. Load Current Distribution of Lithium Doped P/N Cells. Crucible grown cells (³⁶⁴) Lithium Diffused 3 Hours at 360°C, measured at 28°C in Solar Simulator.

During the first quarter investigation of the BCl_3 with O_2 diffusion resulted in uniform sheet resistances and I-V characteristic curves for as many as 60 cells per diffusion; however, the cell output was low. As a result of the work performed during the quarter, lithium cell efficiencies of 11% can be obtained with this diffusion process. Using a temperature of 1000°C , the diffusion schedule can be varied from 8-5-5 to 8-30-10 to yield a maximum number of high output cells per diffusion.

A sintering time between 2 and 5 minutes can be used to improve lithium cell output ~5% without encountering the suppressed voltage observed with ~10% of the cells sintered 6 minutes. Capacitance measurements performed before and after sintering indicate that the change in lithium density gradient is minor.

Better uniformity is being obtained in the lithium diffusions as has been determined through capacitance measurements and calculation of lithium density gradients. Within groups of cells with the same material and diffusion parameters, the variation in lithium density gradient is less than a factor of two. This improvement in uniformity can probably be attributed to short lithium diffusions, 1 to 3 hours, and the use of evaporated lithium as the diffusion source.

Spectral response measurements indicated that higher red response is achieved with 8-30-10 BCl_3 with O_2 diffusions at 1000°C than with 8-5-5 diffusions. The low red response of cells from an 8-5-5 diffusion can be improved 10 to 20% by lithium diffusion, whereas, the cells from the 8-30-10 diffusion which initially exhibit high red response after boron diffusion show no improvement with lithium diffusion.

Spectral response measurements of cells before and after sintering showed a 5 to 10% improvement between 4000 and 5500 Å. Since this improvement was observed for cells with and without lithium, it was concluded that changes in the lithium distribution were not responsible for the improved response.

Cells were fabricated for the second lot using the same boron and lithium diffusion parameters as those used for the first lot. The electrical yield of 85% of the cells with efficiencies of 11% or better closely duplicated the 87% electrical yield for the first lot.

REFERENCES

1. NASA Contract Report, "Development of Lithium Diffused Radiation Resistant Solar Cells," P. Payne and H. Somberg, Heliotek Division of Textron, JPL Contract 952547, Final Report - Part II, November, 1971, Jet Propulsion Laboratory.
2. NASA Contract Report, "Study to Determine and Improve Design for Lithium-Doped Solar Cells, G. Brucker, T. Faith, and A. Holmes-Siedle, RCA, Contract 952555, Final Report, December, 1971, Jet Propulsion Laboratory.
3. NASA Contract Report, "Study and Determination of an Optimum Design for Space Utilized Lithium Doped Solar Cells," R. G. Downing and J. R. Carter, TRW, Contract 952554, Final Report - Part II, July, 1971, Jet Propulsion Laboratory.
4. G. Bertolini and A. Coche (ed.), Semiconductor Detectors, John Wiley and Sons, Inc., New York (1968).