heliotek

Development and Pilot Line Production of Lithium Doped Silicon Solar Cells

FINAL REPORT

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SUMMARY

This report describes work performed over the period of September 1971 to August 1972 to develop production processes for fabrication of lithium doped P/N cells. In some cases, this involved development of new processes while in others it was merely a matter of scaling up and optimizing existing processes.

The boron diffusion investigation was a major part of this contract. At the beginning of this contract the $BC\ell_3$ diffusion without O_2 was selected as the optimum diffusion process for fabrication of lithium doped cells. An 8-2-7 (warm up - deposition - drive-in time in minutes) diffusion schedule at 1055°C was used for the first two lots (300 cells each) delivered to JPL. Cell efficiencies ranged from 11.0 to 13.7% based on an AMO of 135.3 mW/cm^2. These high efficiencies were obtained using from 10 to 40 cells per boron diffusion; increasing the quantity beyond 40 resulted in lower outputs. At this point, the emphasis was placed on investigation of a $BC\ell_3$ with O_2 diffusion which had been going on concurrently. Through evaluation of the effects of diffusion time and temperature, gas flow rates, and deposition plus drive-in vs. continuous deposition and no drive-in cycles, diffusion parameters were finally arrived at which produced short circuit currents of 136 ± 4 mA for ten cells spaced along 12" of the diffusion boat. The next step was to increase the quantity; 60, 100, and 150 cell diffusions were performed with no more variation in cell short circuit current than observed with 10 cells.

The lithium evaporation and diffusion studies included investigations of substrate heating during evaporation, transfer from the vacuum system to the diffusion furnace, simultaneous diffusion of two different lithium evaporation lots, and evaluation of the effective operating lifetime of the lithium evaporation vacuum system. The investigation of substrate heating during lithium evaporation indicated more uniform sheet resistances were obtained when the cells were heated to about 75°C.

To determine whether two evaporation lots could be diffused at the same time, cells from one evaporation lot were stored in a helium atmosphere while a second evaporation was performed and then the two lots were placed in the same diffusion. The sheet resistances, 1.1 to 2.7 ohms/square, were in the same range as those obtained with diffusion of a single evaporation lot.

Short circuit current degradation of 5 to 10 mA as a result of the lithium evaporation - diffusion sequence was a problem encountered late in the program. Although contamination in the lithium evaporation was suspected and a thorough cleaning of the vacuum system eliminated the problem, the six lithium evaporations performed in the cleaned system were insufficient to determine whether the problem was again arising as the lithium contamination of the vacuum system increased.

Scaling up the lithium evaporation to 100 cells and the diffusion to 200 cells was accomplished without encountering any problems. Capacitance measurements indicated that control of lithium density gradients were within a factor of three of one another with the scaled up processes.

In fabricating cells for lots 3 and 4 (600 cells for delivery) the scaled-up boron diffusion and lithium evaporation and diffusion processes were used. The efficiencies of these cells ranged from 10.5 to 12.5% with an approximate electrical yield of 60% for cells with efficiencies ≥ to 11%.

The sintering studies performed on lithium doped P/N cells during this contract showed that a metal - semiconductor barrier was forming at temperatures as low as 360°C and that the barrier increased in the soldering operation, where the temperature is only 220°C. Significant maximum power degradation (as much as 10%) in soldering tabs to cells has also been indicated and this could be related to the same problem. On the grounds that ohmic contact is achieved without sintering lithium cells, the sintering process could be eliminated but then an absorbing SiO layer causes lower short circuit current, and problems will still be encountered in soldering operations. The barrier formation was found to be extremely variable and is an area which sould be investigated to determine whether minor changes in the present contact system or completely different contact materials are needed.

The final item is radiation analyses of high efficiency lithium cells. The purpose of these tests should be to determine whether lithium cells with higher initial efficiencies than N/P cells offer any advantage in a radiation environment. Since initial degradation might be greater, 12 to 13% efficiency may offer no advantage over 10.5 to 11.5% cells.

TABLE OF CONTENTS

List of Figures

List of Figures (Cont'd)

1.0 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 has been shown that in small quantities certain lithium gradients yield cells with higher efficiencies than the present N/P cells. In addition 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 lithium cells can be manufactured in an economical fashion. Economical manufacturing of lithium doped P/N cells would involve scaling up various processes and controlling these processes so that lithium cell behavior both before and after irradiation would be reproducible and consistent. The purpose of this program was to attempt to scale up the fabrication processes in order to demonstrate that lithium cells could be manufactured in production quantities with the same level of quality achieved by the standard N/P solar cell. The original goal of this work was to conduct a pilot line fabrication effort leading to a production run of 3000 space quality cells. Unfortunately the program was delayed by a number of unexpected technical problems which led to financial difficulties that prevented the 3000 cell production run from being made. However we were able to scale up the most important production processes and deliver over 1000 lithium cells which met the electrical requirements of this contract.

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

1. Use of a gas distribution system which delivered the dopant directly over the cells instead of it being carried from one end of the tube. This would reduce nonuniformities from one end of the boat to the other.

2. $BC\ell_3$ with and without O_2, with the emphasis on incorporating O_2, since in the absence of O_2, $BC\ell_3$ etches silicon.

3. Diffusion boat design in order to study vertical versus horizontal cell position.

4. Flow rates of $BC\ell_3$, O_2 and N_2.

The lithium diffusion can be scaled up to 150 to 200 cells by vertically positioning the lithium coated cells 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 posed no problem, the major effort concentrated on investigation of lithium evaporation in order to obtain cell-to-cell uniformity and repeatability from run to run. The factors studied in scaling up the lithium evaporation included cell preparation before evaporation, thickness of the lithium layer, and the influence of substrate heating. Experiments were also performed to determine whether transferring the lithium evaporated cells from the vacuum system to the diffusion furnace needed to be accomplished in an inert atmosphere and whether or not the cells could be stored between lithium evaporation and diffusion.

In addition, control points were established in order to check the consistency and reproducibility of cells fabricated. Four shipments of three hundred cells each were delivered during the contract period, to demonstrate the scaled-up processes.

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 in small quantities. 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 $BC\ell_3$ with nitrogen as the carrier gas. Because an oxide layer is absent the silicon surface is attacked by the $BC\ell_3$ and two competing processes occur, etching and diffusion. During a typical diffusion (8-2-7) at 1055°C approximately 2.5 μm of silicon is removed. It is thought that diffusion does not take place until the $BC\ell_3$ flow ceases, thus the diffusion time is only ~5 min. since it takes a few minutes to clear the gas from the tube after the deposition step. A fairly shallow diffusion results, ~0.3 - 0.5 μm.

There are certain advantages to this diffusion. The etching action of the chlorine assures a fresh silicon surface free of impurities for the subsequent diffusion. The formation of the boron glass may prevent contamination from the tube walls or other parts of the system, thus preserving minority carrier lifetime in silicon(1).

Comparison of boron diffusions with and without oxygen indicate no difference in long wavelength response which is most sensitive to bulk lifetime (Figure 1). This would argue that it is not necessary to have an etching reaction to conserve lifetime and justifies work aimed at developing a large scale diffusion process that does not etch the silicon surface.

The major emphasis in the boron diffusion investigation has been to develop a process in which the nonuniformities of the $BC\ell_3$ -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 sources such as $BC\ell_3$, 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 $BC\ell_3$ Without O_2

At the beginning of this program the $BC\ell_3$ diffusion without O_2 was selected, on the basis of previous comparisons, (2) as the best boron diffusion process for producing high efficiency lithium doped P/N cells. This process was used to fabricate 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 the $BC\ell_3$ without O_2 diffusion process.

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 (See Figure 2). 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.

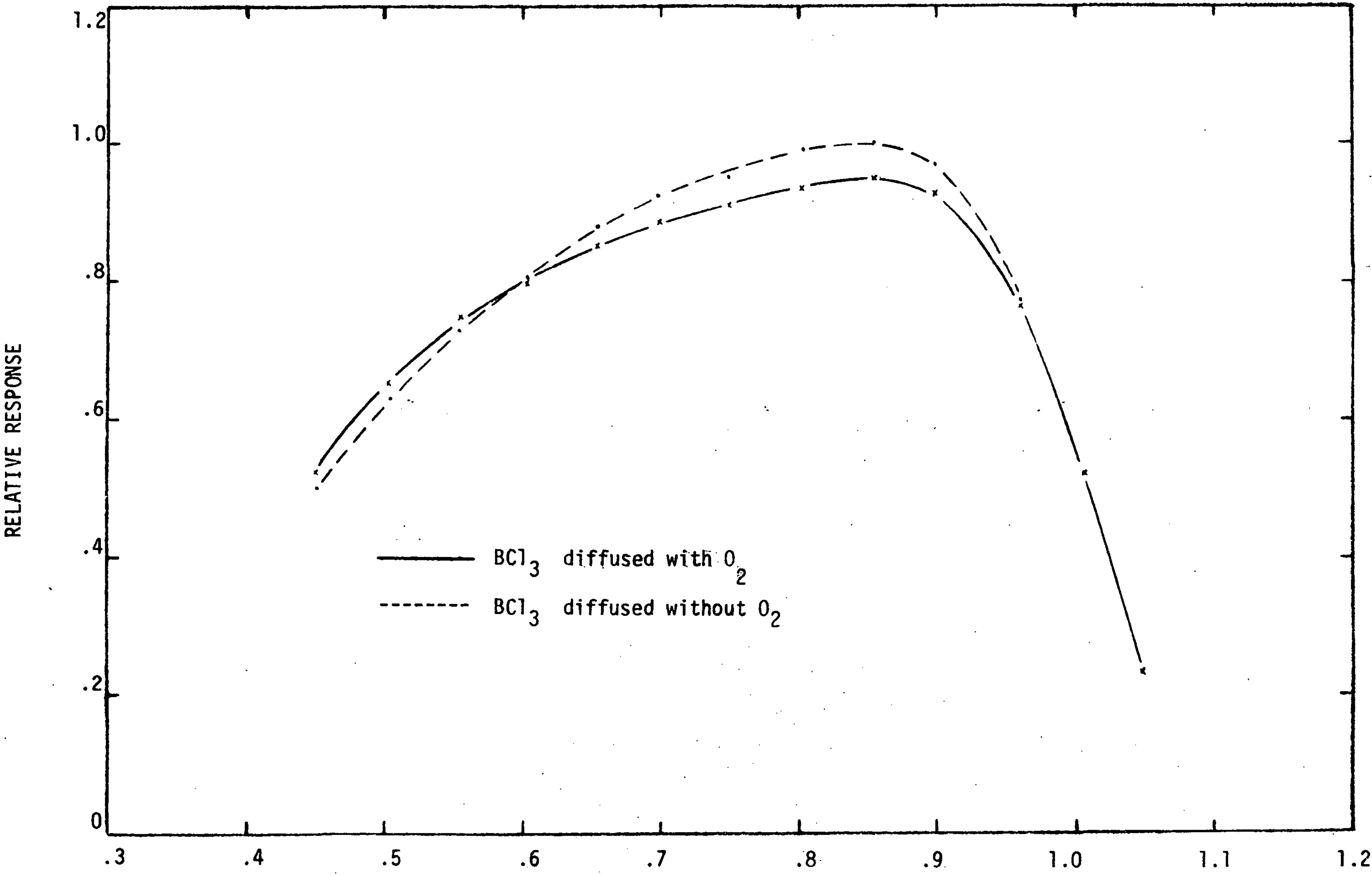

Figure 1. Spectral Response of $BC\ell_3$ Diffused Cells with and without Oxygen

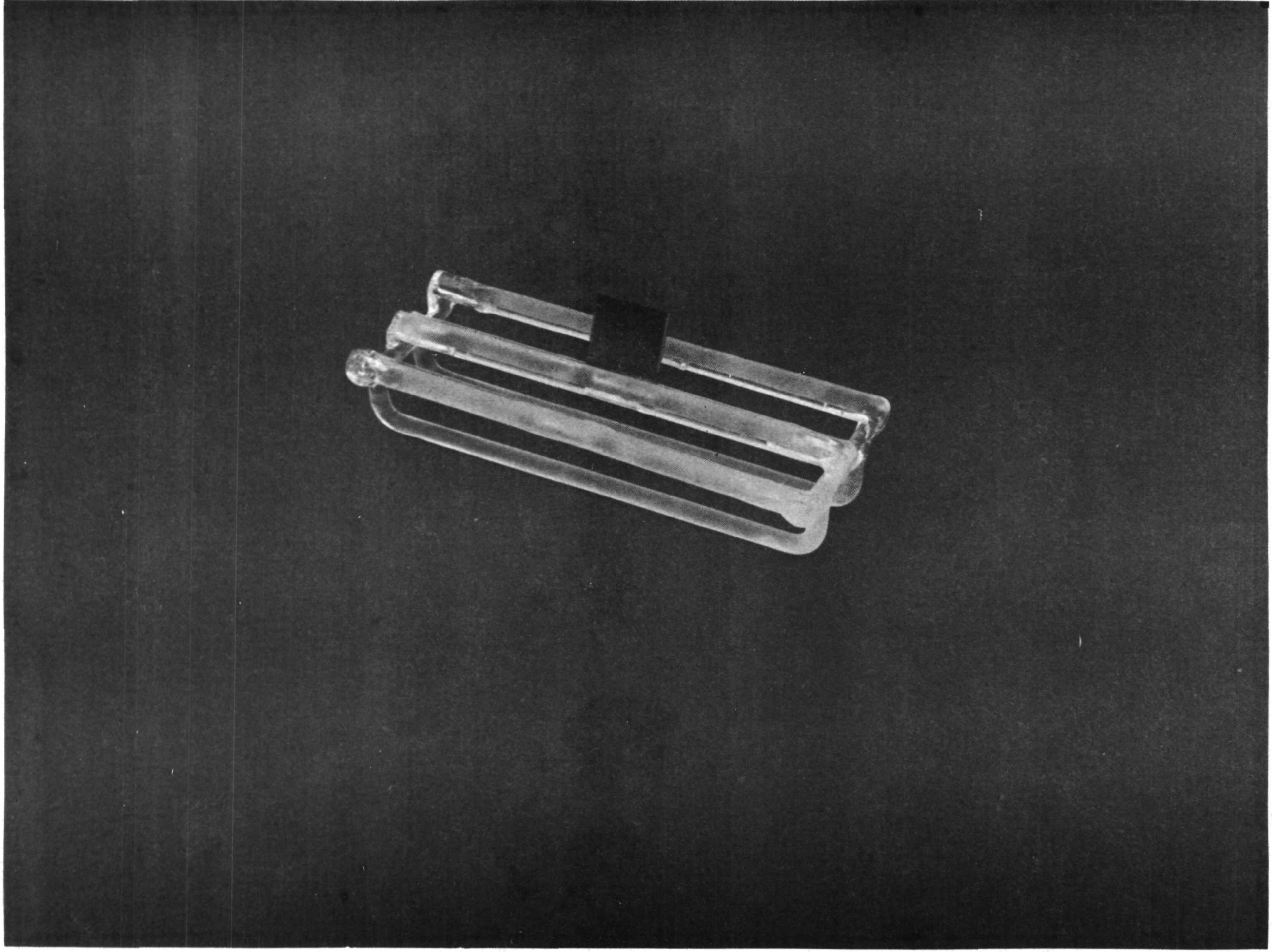

Figure 2. Leg-Supported Diffusion Boat

An alternative method which was investigated during this contract employed vertical placement of cells in a specially designed diffusion boat, having a capacity of ~100 cells (See Figure 3). This design was selected to minimize the nonuniformities 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 4. 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 cells 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 $BC\ell_3$ with O_2

2.1.3.1 Gas Distribution System

Modifications were made in the diffusion system geometry used for the $BC\ell_3$ with O_2 diffusion. A schematic of this is shown in Figure 5. The major change was incorporation of a distribution

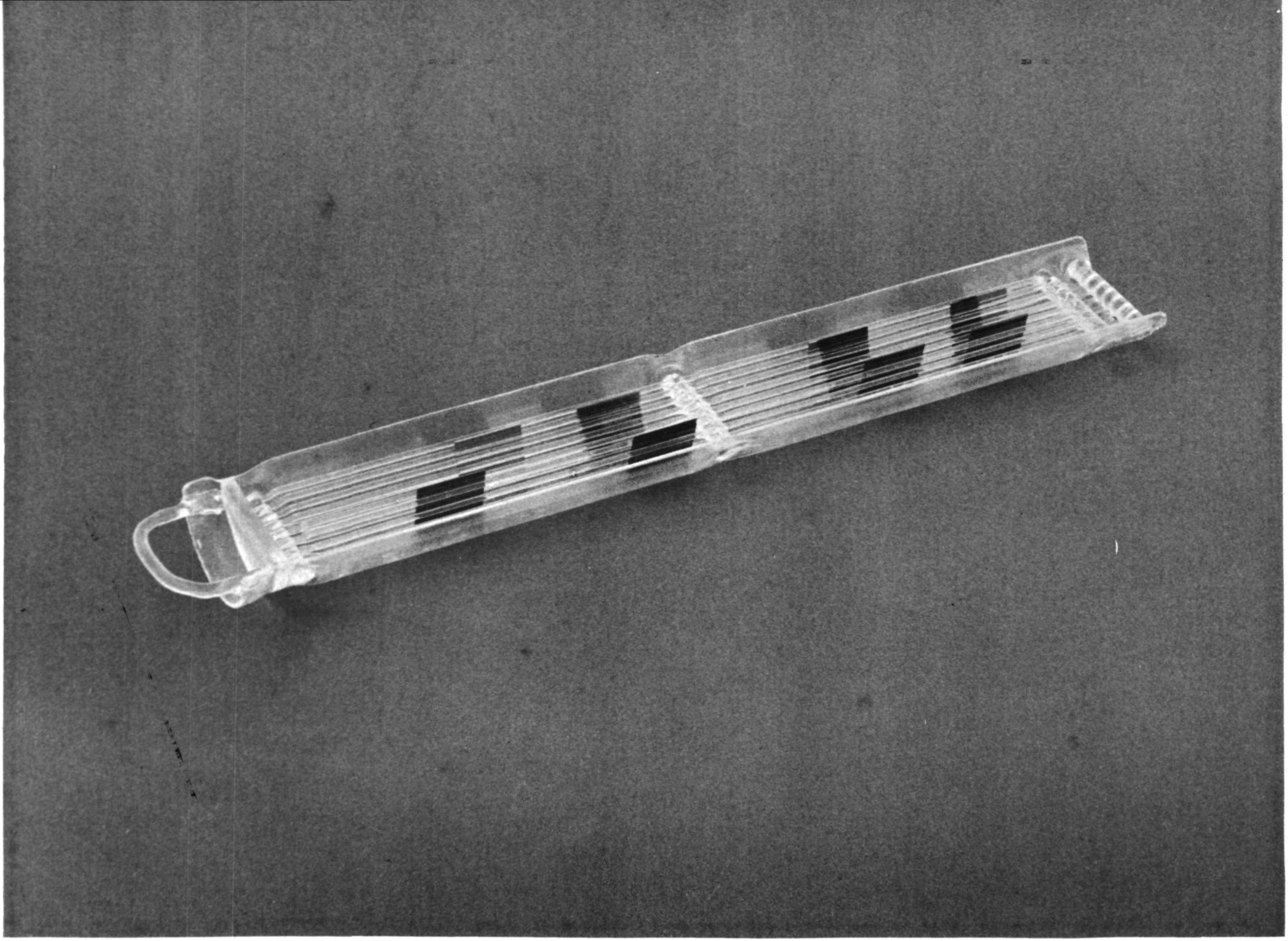

Figure 3. Open Slot Boron Diffusion Boat

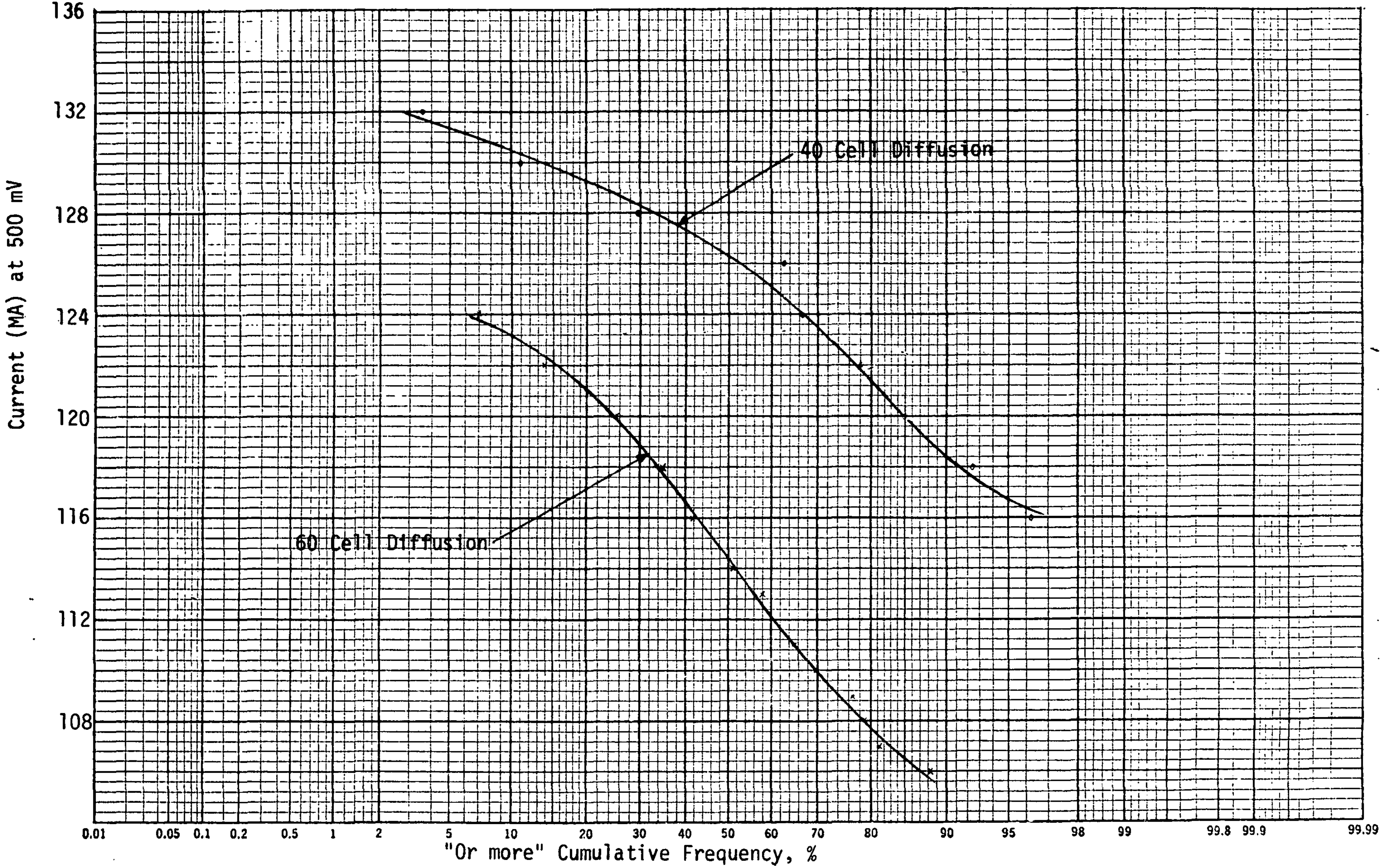

Figure 4. Comparison of 40 and 60 cell BCl_3 (no O_2) Diffusions
Cells measured at 28°C in solar Simulator

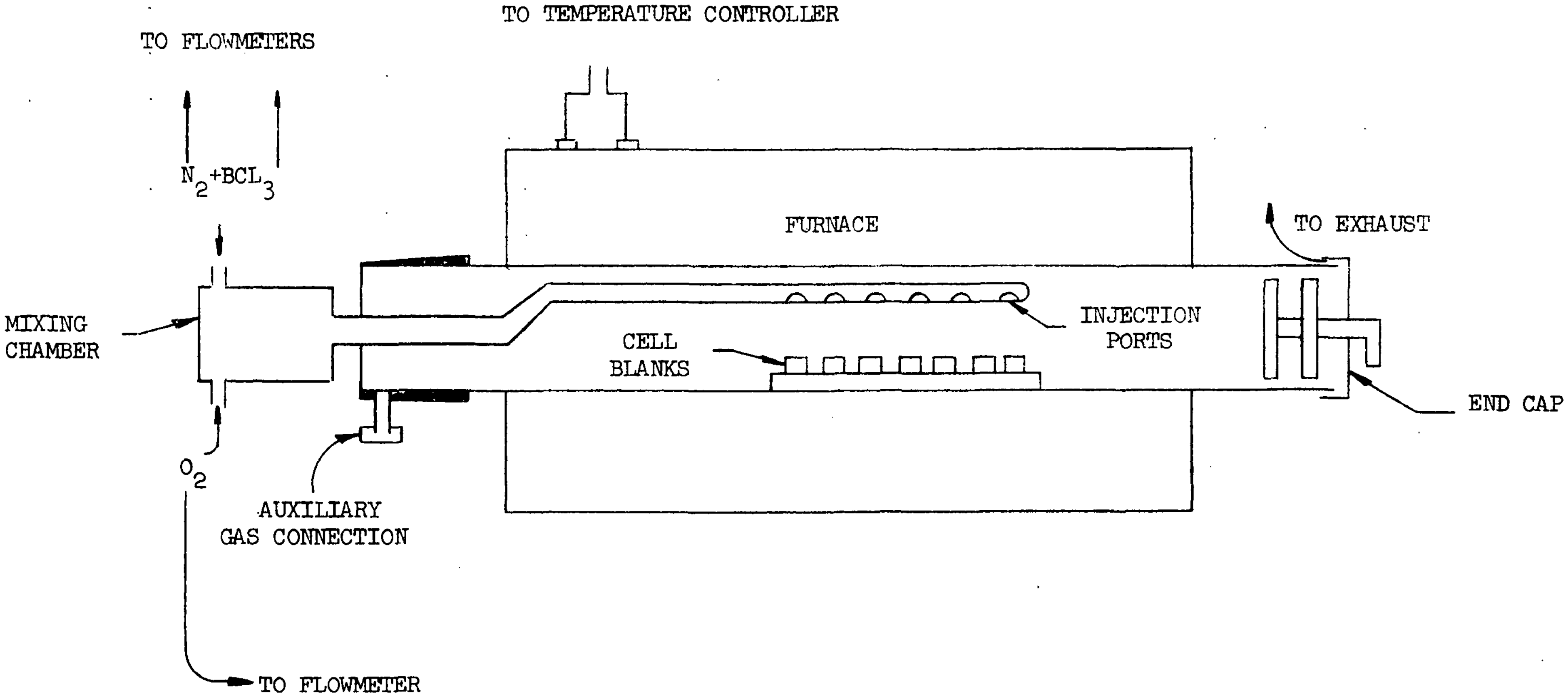

Figure 5.

SCHEMATIC OF BORON DIFFUSION SYSTEM

tube and mixing chamber in order to eliminate cell nonuniformities from the front to the back of the boat which are typically observed when the diffusant is injected directly into the diffusion tube at one end. This 36" long distribution tube extended from one end of the diffusion tube to the far end of the diffusion zone and had injection holes cut out at 4" intervals along the section of tube in the diffusion zone. N_2 was used as the carrier gas and the N_2, O_2, and $BC\ell_3$ were all passed through the mixing chamber and injected into the diffusion tube directly over the slices. Due to the difficulty in handling this distribution tube and the frequency of repair, later in the program a straight open-ended tube ~18" long, which brought the gases into the diffusion tube at a temperature close to the diffusion temperature was investigated. The new distribution tube design was superior in producing uniform sheet resistances on both cell surfaces. The sheet resistances of the two surfaces in some cases varied as much as 50% with the earlier design, whereas, with the latter the variation was less than 10%.

2.1.3.2 Diffusion Time and Temperature Variations

Initial $BC\ell_3$ diffusions with O_2 were performed at 1055°C using various diffusion schedules. 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 150 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.

Table I

Electrical Characteristics of P/N Solar Cells Fabricated Using $BC\ell_3 + O_2$ Diffusion

	Diffusion		ρs	I_{sc}
Run #	Temp.	Schedule	ohms/□	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

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

2.1.3.3 Fabrication of Lithium Cells Using $BC\ell_3$ Diffusions with O_2

Selection of the best boron diffusion parameters must be based upon what provides the best lithium cell output; therefore, before proceeding further in the boron diffusion optimization, 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.

Table II

Electrical Characteristics of Lithium Doped P/N Cells Fabricated Using $BC\ell_3$ Diffusion with O_2

Run #	Boron Diffusion Sched.,Temp.	ρs ohms/	I_{sc} (mA) After boron Diffusion	I_{sc} (mA) After Li Diffusion	I at I(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)	8-50-5, 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

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 cirrents, but better curve shapes than the cells from the other diffusions with sheet 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 was determined that lithium cell efficiencies of 11% or better can be obtained with boron diffusions from 8-5-5 to 8-30-10 at a temperature of 1000°C. At this point, it was necessary 1) to determine more specifically the optimum diffusion schedule and 2) scale-up to at least 100 cells per diffusion.

2.1.3.4 Optimization of Boron Diffusion Schedule

Comparison of 8-20-10, 8-10-10, and 8-5-10 revealed no consistant trend in sheet resistance, ρs. Although one would expect the ρs to decrease with increasing deposition and/or drive-in time, the absence of this trend could be due to the increasing glass layer thickness with longer deposition times, which would tend to inhibit the boron diffusion. In addition the ρs varied sufficiently from run to run using exactly the same diffusion schedule, to produce a situation in which sheet resistances from an 8-10-10 diffusion might be the same or even higher than those obtained with an 8-5-10 diffusion.

In order to determine the extent of this problem of reproducibility, six diffusions were performed in sequence using an 8-5-10 diffusion schedule. In each diffusion eight cells were spaced along a 12" section of the diffusion boats. Each cell was identified so that both sheet resistance and I-V characteristic could be correlated to position on the diffusion boat; the data from these diffusions are shown in Table III. The same degree of variation in sheet resistance as mentioned above was observed; the difference between

TABLE III

Electrical Results with Repetition of 8-5-10 Diffusion

Diff. #	Cell #	$\overset{\downarrow}{\rho s}$ ohms/□	I_{sc}* mA	Diff. #	Cell #	$\overset{\downarrow}{\rho s}$ ohms/□	I_{sc}* mA
A	1	37	90.5	D	1	32	96.5
	2	40	91.0		2	36	99.0
	3	47	92.0		3	39	102.0
	4	49	95.5		4	44	103.0
	5	47	98.0		5	48	103.5
	6	45	99.0		6	49	103.5
	7	45	101.0		7	51	102.5
	8	47	102.0		8	49	100.0
B	1	29	85.0	E	1	43	98.0
	2	30	92.5		2	49	98.5
	3	32	96.5		3	52	100.5
	4	36	100.0		4	56	101.0
	5	36	101.0		5	58	101.0
	6	37	100.0		6	60	101.5
	7	38	100.0		7	56	102.5
	8	40	102.0		8	60	102.0
C	1	37	101.0	F	1	38	103.0
	2	42	98.0		2	42	102.0
	3	47	100.0		3	46	--
	4	49	105.0		4	49	103.5
	5	54	103.0		5	53	103.0
	6	56	102.0		6	56	102.5
	7	58	102.5		7	60	103.5
	8	56	102.5		8	60	103.5

* AMO 28°C Cells had no SiO coating

the lowest value, 29 ohms/square, and the highest value, 60 ohms/square, was approximately a factor of two. In general, cells with sheet resistances <35 ohms/square had short circuit currents lower than 98 mA (AMO measurements of cells with no SiO coating). Once sheet resistances were above 35 ohms/square, there was no correlation to short circuit currents.

Considering that the segregation coefficient, defined as

$$m = \frac{\text{equilibrium concentration of impurity in silicon}}{\text{equilibrium concentration of impurity in } SiO_2}$$

of boron is less than one,(3) during a drive- in or redistribution period the boron at the silicon surface will diffuse back into the glass layer producing the undesirable effect of a lower surface concentration. In addition the degree of diffusion back into the glass layer would vary with the thickness of the glass layer. The diffusion of boron during the deposition period would be completely different due to the constant addition of more source. Diffusions were performed without a drive- in to evaluate the effect of deposition time and determine whether more consistent sheet resistances and higher outputs could be obtained by omitting the drive-in period. Diffusion cycles of 8-10-0, 8-15-0 and 8-20-0 were used. Sheet resistances and short circuit currents of cells from these diffusions are shown in Table IV. As one would expect, the sheet resistances decreased with increasing deposition time. In addition, cells from the 8-20-0 diffusion with sheet resistances which were lower than 35 ohms/square did not exhibit the low short circuit currents observed when a deposition drive-in cycle was used.

Table IV

Electrical Characteristics vs. Deposition Time
20 ohm cm P/N cells, $BC\ell_3$ with O_2 Diffusion

Cell # *1)	ρs, Ω/	I_{sc}, mA *2)
8-10-0		
1	41	92.0
2	56	96.0
3	56	--
4	62	102.5
5	70	102.5
6	79	103.5
7	83	104.0
8	81	104.0
8-15-0		
1	35	--
2	37	98.0
3	44	100.0
4	58	103.0
5	64	105.0
6	69	104.0
7	74	103.5
8	75	103.5
8-20-0		
1	25	101.0
2	28	102.5
3	30	103.5
4	47	102.5
5	52	101.5
6	58	105.0

*1) According to position in diffusion boat

*2) AMO, 28°C measurement; cells had no SiO coating

Using the 8-20-0 diffustion, O_2 to $BC\ell_3$ ratios were also investigated. Similar sheet resistances and short circuit currents were obtained with 3:1, 2:1, and 1:1 ratios; however, in the 1:1 case the oxygen quantity was insufficient and slight etching of the silicon occurred on some of the blanks.

On the basis of this experimental work an 8-20-0 schedule was selected, omitting the drive-in period, and the O_2 concentration was kept higher than the $BC\ell_3$ (3:1) to avoid a $BC\ell_3$-Si etch reaction.

2.1.3.5 Scale-up of $BC\ell_3$ with O_2 Diffusion

In the experimental work described above 8 to 10 cells were spaced along a 12" section of the diffusion boat. The same 12" section of the boat was used in scaling up the boron diffusion and the number of rows of cells was increased. Scaling up in this manner was expected to give a sheet resistance distribution similar to that obtained with 8 to 10 cell diffusion. The quantity was increased from 10 to 70, to 100, and finally to 150 slices per diffusion. In each case the range in sheet resistances was no greater than that observed when only 10 cells were diffused. Table V shows the ranges in sheet resistance and short circuit current for cells from each diffusion. The short circuit current remained at the same level as the quantity of cells was increased, indicating that scaling up to as many as 150 cells per boron diffusion was not a problem.

TABLE V

P/N Cell Electrical Characteristics Using Scaled-up Diffusion

Cells per Diffusion	Sample Size	ρ_s, Ω/□	I_{sc}, mA
10	10	25-58	132-138
70	10	29-41	132-136
70	10	41-47	132-135
100	20	30-37	134-136
150	15	34-37	134-137
150	15	35-42	134-138
150	15	30-46	133-140

2.1.3.6 Influence of $BC\ell_3$ with O_2 Diffusion on other Cell Characteristics

One of the side effects of this new diffusion process was poor adherence of the AR coating. The AR coating came off either in the tape peel test typically used to test the adherence of the Ti-Ag contacts or in the handwiping used to remove the adhesive residue after the tape pull test. Typically a SiO coated solar cell not only goes through this tape pull test, but can withstand erasure abrasion after being subjected to a 30 minute soak in boiling water and steam with no coating delamination.

A cleaning procedure which included boiling the cells in a H_2SO_4-$HC\ell$ -HNO_3 mixture designed to dissolve boron (4) was investigated on the assumption that the poor adherence was due to a reaction between residual boron and the AR coating. This procedure improved the adherence of the AR coating to the extent that no delamination occurred with the water-boil, -steam, and erasure test.

2.2 LITHIUM DEPOSITION AND DIFFUSION

Two methods of lithium application were investigated and used in fabricating lithium doped P/N cells: painting on a lithium mineral oil suspension and evaporation of lithium. Evaporation of lithium was thoroughly investigated during this contract since it is amenable to large-scale production. The following areas were investigated: substrate temperature during evaporation, lithium film thickness, and simultaneous lithium diffusion of two evaporation groups.

2.2.1 LITHIUM EVAPORATION

The objective of the first experiment was to obtain uniform sheet resistance from one run to the next and from cell to cell within the same evaporation and lithium diffusion. The lithium evaporation process has been generally trouble-free and given consistent cell results since helium was introduced as the post-evaporation atmosphere. However, in some cases the sheet resistances measured after lithium diffusion have varied from 2.3 to approximately 400 ohms/square. The 2.3 ohms/square is typical of slices lithium diffused between 340 and 370°C while 400 ohms/square is in the range of sheet resistances measured on bulk 20 ohm cm silicon, indicating that on some slices no lithium diffusion occurred. This variation within the same diffusion could not be attributed to a problem in the diffusion furnace, e.g. an air leak, since one would then expect all slices to exhibit high sheet resistances. Assuming that the lithium was not in intimate contact with the silicon blanks and therefore not alloying and diffusing, the cleanliness of the cell surfaces was examined.

Typical processing prior to lithium diffusion included an etch to remove the boron diffused region from the back of the cell, followed by solvent cleaning to remove the residue from the tape used for masking the front surface. To further clean the surface prior to lithium evaporation, trichlorethylene and methyl alcohol were used. This did nothing to improve the sheet resistances.

Since more adherent films can usually be obtained by evaporating onto a heated substrate, this was the next step in looking for a solution to this problem. The cells were heated to approximately 125°C before starting the evaporation. After deposition they were allowed to cool about 5 minutes. The system was then vented with helium, the cells were loaded onto a diffusion boat, and transferred to the diffusion furnace. The cells were diffused 3 hours and the sheet resistances averaged 2.0 ohms/square with a range of 1.6 to 2.8 ohms/square for the first run and 2.5 ohms/square average with a range of 1.7 to 4.9 ohms/square for the second run (each run had 10 cells), indicating uniform lithium diffusion.

The evaporations just described were set up with the cells above the source and the heater above the cells. Additional cells were included below the source and these would also have heated during the evaporation although the temperature, which was not monitored, was probably not as high. These lower cells came out of the evaporation with the lithium layer broken up into a block-like pattern.

They were diffused along with the other cells in each run and their sheet resistances were in the same range as those mentioned above. However, this broken up layer was felt to be undesirable since lithium particles fell off the cells while transferring them to the diffusion furnace. Since these cells were probably cooler than those next to the heater it was assumed that the lower temperature was responsible and therefore evaporations were also performed at higher temperatures. At 150°C the lithium layer still cracked.

The substrate temperature was then raised to 200°C. The observed reaction of the lithium layer after this evaporation seemed to give us an idea of what was happening in the other evaporations. When removed from the vacuum system the cells had a smooth, continuous lithium film. As the cells cooled, the lithium cracked and popped off the cell, which is indicative of a highly stressed layer. Apparently at lower temperatures the lithium layer was also stressed, but stress-relief (breaking up of the layer) occurred while the vacuum system was being opened. If the cooling is the critical factor then at least four things could have affected the cooling rate: 1) time allowed after evaporation before opening the chamber, 2) temperature of cells just before opening the chamber, 3) placement of cells with respect to the helium inlet, and 4) flow rate of incoming helium.

Several methods might be used to reduce the stresses between the lithium and silicon, so that the lithium layer would not crack up and pop off: 1) determine necessary cooling procedure, 2) maintain elevated cell temperature during transferral to diffusion furnace, or 3) heat cells to lower temperature so that less stresses would be generated in cooling.

Heating cells to a lower temperature during the lithium evaporation was investigated. The substrate temperature was maintained at approximately 75°C and this temperature was used for all the cells fabricated for the first shipment. In eight runs out of nine, the evaporated lithium layer was continuous and did not break up during transfer from the vacuum chamber to the diffusion furnace. In the case of the one run in which the lithium layer broke up, the sheet resistances were the same as those from previous runs.

In all the lithium evaporation work, thick films have been used because the lithium does oxidize in air and if the film were too thin it would completely oxidize prior to diffusion. For evaporation of 40 to 50 cells, lithium wire was evaporated at a source to substrate distance which varied from 7 inches directly under the source to about 8-1/2 inches at the extremes of the cell holder.

The resulting film thickness at the extremes of the cell holder was calculated to be approximately two-thirds the thickness achieved directly under the source (~ 30μM). In order to determine whether this variation in film thickness affected the lithium diffusion, an evaporation lot was split with the cells directly under the source being kept separate from the cells at the extremes of the cell holder. The sheet resistances for the cells at the extremes ranged from 1.76 to 2.45 ohms/square, and for those directly under the source, 1.81 to 2.11 ohms/square, indicating that the thinner lithium layer was not limiting the lithium diffusion. This is not surprising since all cells had excess lithium remaining after the lithium diffusion.

An experiment was performed to determine whether more than one evaporation group could be included in the same diffusion. The following procedure, designed to minimize cell loss if the experiment did not work, was used. After completing one lithium evaporation, 30 out of the 40 cells were put into a diffusion furnace and the standard lithium diffusion procedure was used. The other 10 cells from this run were loaded onto a second diffusion boat and held in a cold zone of another diffusion furnace with helium flowing. A second lithium evaporation was then completed. The boat with 10 cells was removed from the diffusion tube, the cells from the second evaporation were loaded onto the boat and then all cells were diffused for 3 hours at 360°C. The following sheet resistances were obtained: 1.76 to 2.66 ohms/square for the group of 30 cells, 1.07 to 2.32 ohms/square for the 10 cells held for the second diffusion, and 1.12 to 2.58 ohms/square for the cells from the second evaporation which were diffused along with the 10 cells from the first evaporation. Running this experiment a second time produced the same results.

The sheet resistances of the 10 cells held over for the second diffusion being in the same range as the other two groups of cells indicates that more than one lithium evaporation lot could be handled in the same lithium diffusion. This could at least double the lithium diffusion quantity. For example, by scaling up to 100 cells per lithium evaporation and using two evaporation lots, 200 cells could be diffused at once. With this techniquie, the lithium diffusion scale-up is not limited by the evaporation scale-up.

2.2.2 LITHIUM CONTAMINATION EFFECTS

In fabricating the lithium cells for the fourth shipment an unexpected downward trend in short circuit current with each successive lithium diffusion lot was observed. The average short circuit current was 130 mA for the first two lots, 127 mA for the third lot and 125 mA for the last two lots. Considering that the short circuit currents of the boron diffusion control cells ranged from 132 to 140 mA (see Table V) and averaged about 135 mA, the short circuit current loss between the boron diffusion and contact evaporation processes was 5 to 10 mA.

The cells go through three major processes--lithium evaporation, lithium diffusion, and contact evaporation--where this loss might occur. The lithium evaporation step seemed to be the most likely source of the problem since the vacuum system performance deteriorated as the lithium contamination built up; typically the foreline pressure increased with the number of lithium evaporations. In order to investigate the problem the bell jar portion of the vacuum system was thoroughly cleaned and a series of lithium evaporations were performed. Ten cells were included in every other evaporation and these cells were subsequently lithium diffused, contacted, and tested. After six successive evaporations without cleaning the vacuum system, the short circuit current had not yet degraded.

The investigation did not go beyond 6 evaporations because the vacuum system developed a leak. At this point the vacuum system was taken apart to change O-rings and the diffusion pump oil and in doing this, lithium was found throughout the lower part of the vacuum system--in the diffusion pump, cold trap, valves, etc. After thoroughly cleaning the lower part and the bell jar, another lot of 150 cells was processed through lithium evaporation and diffusion. The average short circuit current of this group of cells was 133 mA.

The higher short circuit currents of lithium cells fabricated when the vacuum system was cleaned prior to lithium evaporation indicates that vacuum system maintenance will be an important factor in achieving high output lithium cells. The work described above demonstrates that at least 600 cells (100 per evaporation) can be processed through lithium evaporation before short circuit current degradation occurs. If the number of evaporations could be increased to 10 to 15 before system cleanup was necessary, it would be possible to process 1000 to 1500 cells per week and limit cleaning the system to once a week. Although merely cleaning the bell jar portion produced improved cell output, the extensive lithium contamination of the pumping system indicates that a more rigid maintenance schedule than that required in the case of systems used for evaporating AgTi or SiO may be necessary.

2.3 SINTERING

During the previous contract (JPL Contract #952547, Part II), sintering lithium doped P/N cells was investigated. Initial sintering experiments were done on Lopex lithium cells which had lithium applied by a paint-on technique rather than evaporation, and improvements in I_{sc}, V_{oc} and P_{max} were observed. The majority of the cells fabricated from crucible-grown silicon with the lithium evaporated also showed improved output; however, about 10% had suppressed voltage. Consequently during this contract further investigation of the sintering process was done.

First, ten cells were sintered 6 minutes at 605°C, which was the same time that had been used for cells during the previous contract. The electrical characteristics before and after sintering are shown in Table VI. The majority of the cells exhibited higher short-circuit currents; however, nine out of ten cells exhibited lower voltages and consequently lower current near the maximum power point (500 mV). A group of five cells was then sintered for 3 minutes. These cells exhibited an average increase of 7 mA in short-circuit current and 11 mA in current at 480 mV (Table VII).

Table VI

Electrical Characteristics Before and After Six-minute Sinter

Cell	I_{sc}, mA			I at 500 mV, mA			V_{oc}, Volts		
No.	Before	After	Δ I	Before	After	Δ I	Before	After	Δ V
2	144	149.5	5.5	132	134	2.0	612	607	-5
8	142.5	144	1.5	128.5	126	-1.5	604	600	-4
10	138.5	138.5	0	126	118	-8.0	608	601	-7
14	135.5	138	2.5	123	116	-7.0	603	595	-8
16	130	134	4.0	117	114	-3.0	615	608	-7
18	142.5	148	5.5	130	124	-6.0	608	601	-8
22	144	150	6.0	130	132	2.0	609	608	-1
26	136	143.5	7.5	126	130	4.0	613	615	2
28	144	148	4.0	135	130	-5.0	610	604	-6
32	144.5	150	5.5	132	121	-11.0	608	599	-9

TABLE VII

Electrical Characteristics Before and After Three-minute Sinter

Cell	I_{sc}, mA			I at 500 mV			V_{oc}, Volts		
No.	Before	After	Δ I	Before	After	Δ I	Before	After	Δ V
50	134	140	6	120	126	6	605	621	16
51	143	149	6	124	131	7	601	611	10
52	134.5	141	6.5	106	114	8	584	594	10
53	137	145.5	8.5	128	136.5	8.5	608	620	12
54	136	147	11	123.5	126.5	3	620	614	-6

Since the shorter sintering time produced better results in this small sample, additional cells were sintered for 3 minutes. A group of 45 cells measured before and after sintering exhibited average improvements of 4 mA in the short-circuit current and 6 mA in the current at 500 mV. This corresponds to an improvement of approximately 4% in output.

In order to determine whether 3 minutes is the optimum sintering time, 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 VIII. The average current at 500 mV after sintering 1 minute was lower than the initial average. Although cells sintered 6 minutes showed improvement, the current at 500 mV was definitely lower than for cells sintered 2 to 5 minutes. Based upon these observations and the similarity in the current at 500 mV 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.

Table VIII

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

Figure 6 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 7, the effect of sintering on the lithium distribution near the junction was found to be insignificant. For example, at a depth of 1.2μM the donor density changed from 1.1 x 10^{15} before sintering to 1.0 x 10^{15} after sintering, while the lithium density gradient changed from 1.5 to 1.35 x 10^{19}/ cm^4.

Solar cell spectral response, determined by measurement of short circuit current at various wave lengths between 4000 and 10,000 Å, was used to evaluate the change in short circuit current with sintering. Spectral response measurements performed before and after sintering indicated that the increased short circuit current could only be explained by a 5 to 10% improvement over a narrow range between 4000 and 6000 Å, since no change occurred at longer wave lengths. Similar behavior observed in sintering P/N cells with no lithium indicated that the improvements in short circuit current were not caused by changes in the junction, which in the case of the lithium cells, might occur due to changes in the lithium distribution during the relatively high temperature sintering process. At this point in the cell fabrication, the only other factor which could have a significant influence on the short wave length response would be changes in the AR coating. Rapidly deposited SiO films are in fact strongly absorbing in the ultraviolet but when heated in a reducing atmosphere the short wave length transmission improves.

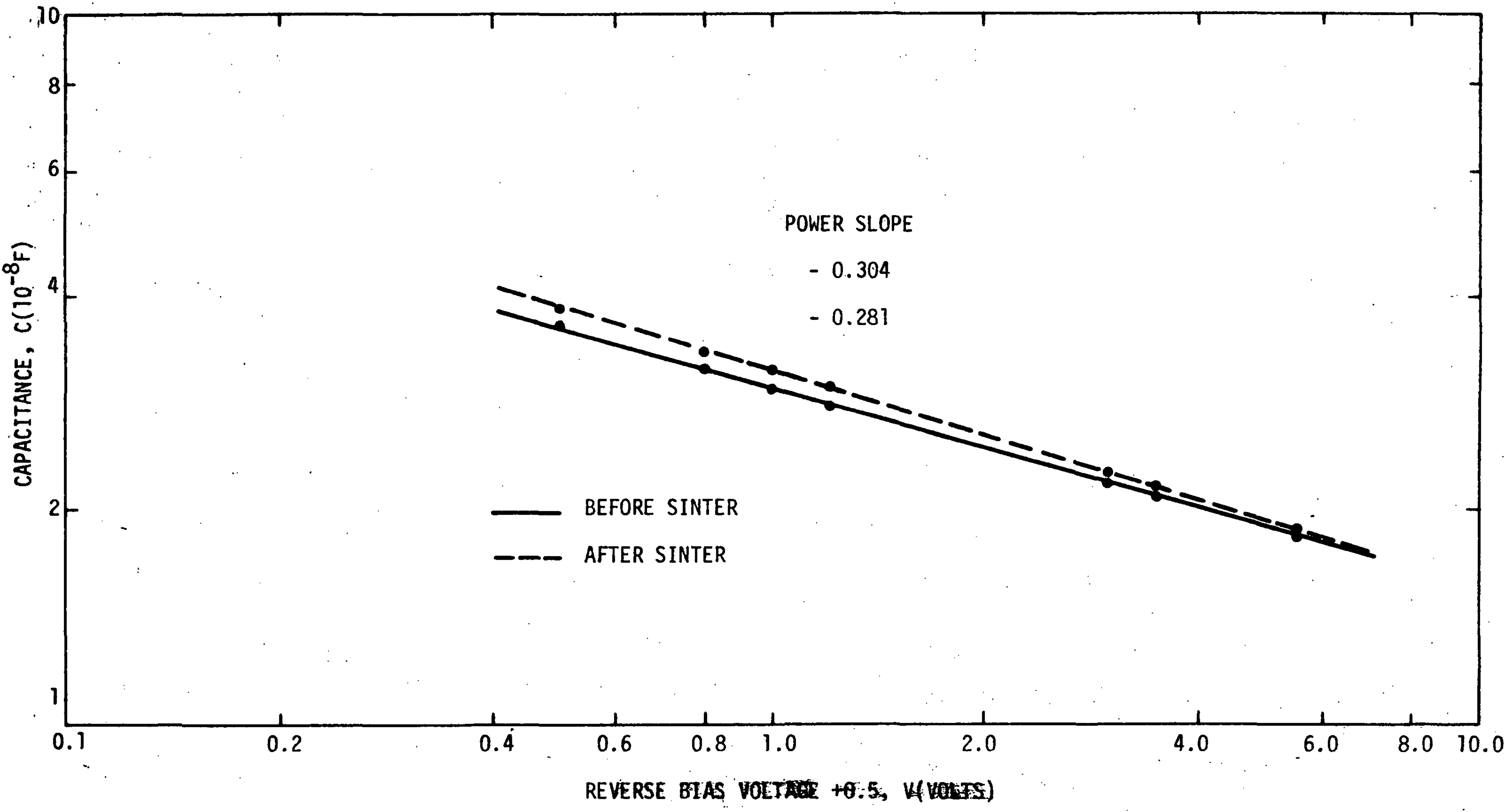

Figure 6 Capacitance vs. Voltage for Lithium Doped P/N Cells Before and After Sintering

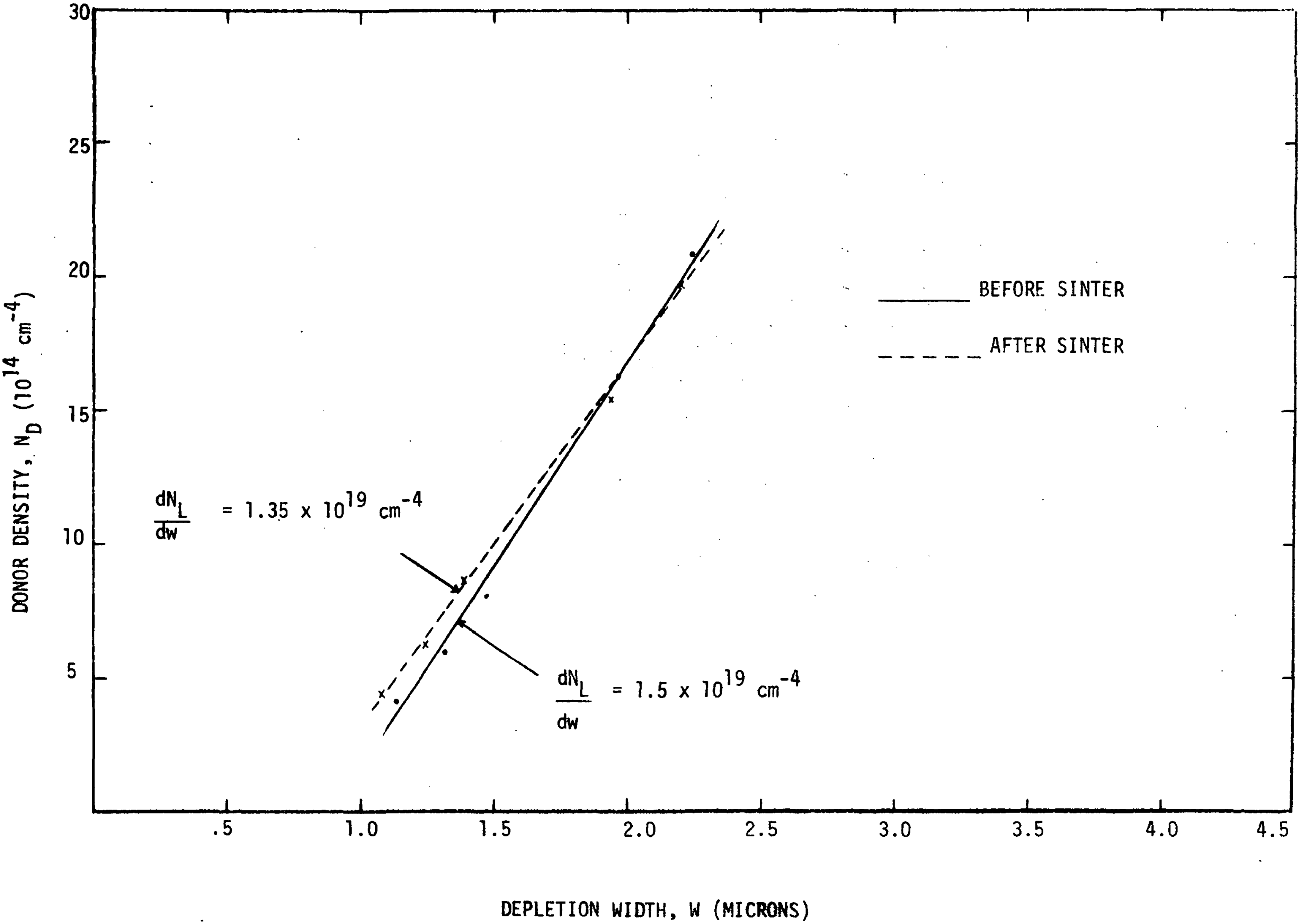

Figure 7 Donor Density vs. Depletion Width for Lithium Doped P/N Cells Before and After Sintering

Measurements of I_{sc}, I at 480 mV, and V_{oc} for cells in the fourth lot delivered to JPL showed a large range in the value of I_{sc} - I at 480 mV, indicating variation in curve shape. Typical values of ΔI range between 6 and 10 mA for normal cells, but many of these cells showed ΔI values of 10 to 23 mA. It was thought that high leakage currents due to poor isolation of the P-contact was responsible for this effect, but dark reverse current measurements as well as visual examination failed to confirm this theory. The cells were then biased in the forward and reverse direction under a 100 mW/cm^2 tungston light source in order to look at the full I-V curve. The curves measured (Figure 8) indicated that the poor curve shapes were a combination of series resistance (Cell B) and barrier formation (Cell C). Cell A exhibits no barrier which was found to be typical of unsintered cells. Cells B and C were cells which had been sintered 2 minutes at 605°C and show the variations in the degree of barrier formation. Cells were heated at 360°C to determine whether the barrier formed at a lower temperature. Although some cells did not exhibit barrier formation until three 5 minute heat cycles were used, others exhibited the effect after 5 minutes. The six groups of cells sintered at 605°C for one to six minutes were remeasured, this time measuring the full I-V curve in all three quadrants. This revealed that these cells also exhibited some degree of barrier formation. However, it was at a higher forward current level and not as pronounced as that found in the lot 4 cells and therefore had no significant effect on cell output.

The barrier formation we observe is not consistent indicating that it may be caused by variations in processing. Possible factors which might have an influence include variations in bulk resistance, i.e., lithium concentration, amount of oxide on the back surface prior to metallization, or contamination in the AgTi evaporation.

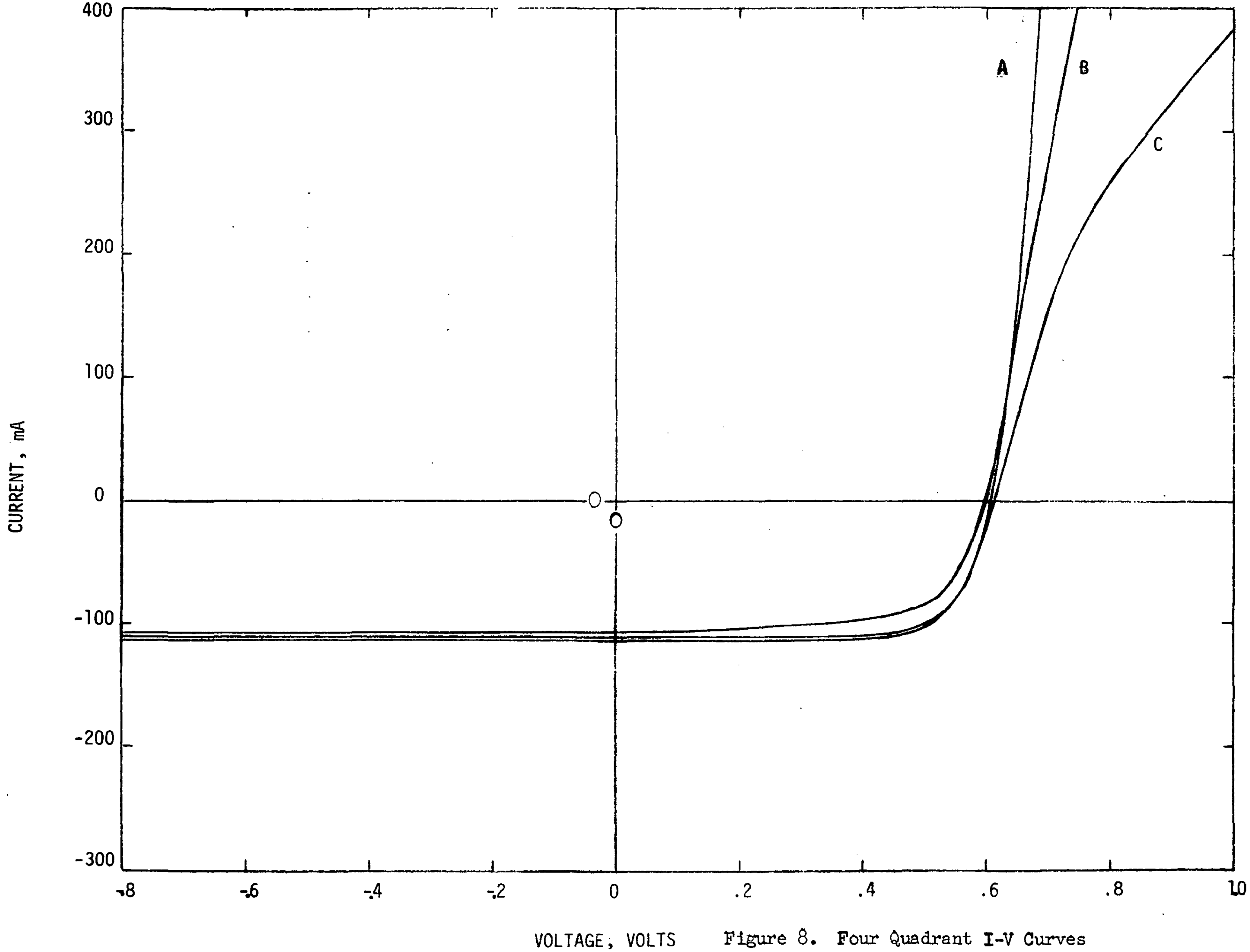

Figure 8. Four Quadrant I-V Curves Illustrating Barrier Formation

This barrier formation can be avoided by not sintering the cells, since ohmic contact is achieved with an unsintered contact, but as was pointed out previously, the SiO coating will not be optimized due to absorption in the short wave length region. This will result in lowered values of both I_{sc} and I_{480}.

2.4 CELL EVALUATION

2.4.1 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 (6, 7) 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 during the following equations:

$$N_D = \frac{V + \phi}{q\epsilon\epsilon_o M} \; \frac{C}{A}^{2}$$

$$w = \epsilon\epsilon_o \; \frac{A}{C}$$

where N_D = donor concentration

V = voltage
ϕ = built-in voltage of junction
C = capacitance
A = area of junction
q = electrical charge
ϵ = dielectric constant
ϵ_o = 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 9 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.

Donor density versus depletion width was calculated for these capacitance values and is shown in Figure 10 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 x $10^{19}/cm^4$. Capacitance measurements were also performed after sintering; although the calculated gradients changed, the range was still narrow, 1.1 to 1.4 x $10^{19}/cm^4$.

Capacitance versus voltage was also measured for a group of 20 cells from the fourth lot of 300 cells delivered to JPL. Like the group described above the cells were fabricated from crucible grown silicon using a 3 hour lithium diffusion at 360°C. For this group a computer program was set up to calculate donor density versus depletion width and the donor density gradient. Donor density versus depletion width for these twenty cells is shown in Figure 11. Although there was more variation within this group the cells had donor density gradients,

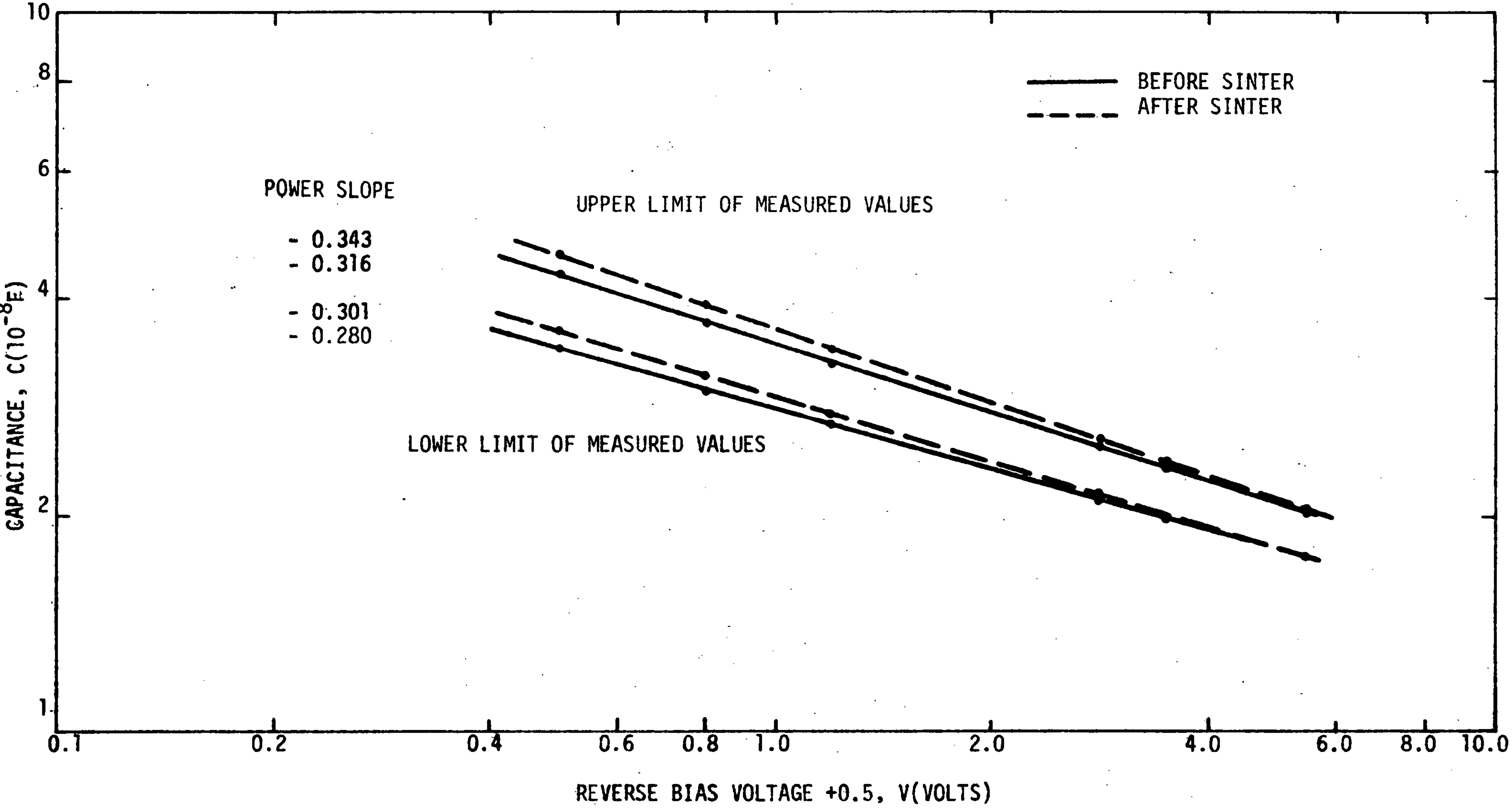

Figure 9 Range in Capacitance vs. Voltage. Twenty Lithium Doped P/N Cells Diffused 3 Hours at 360°C

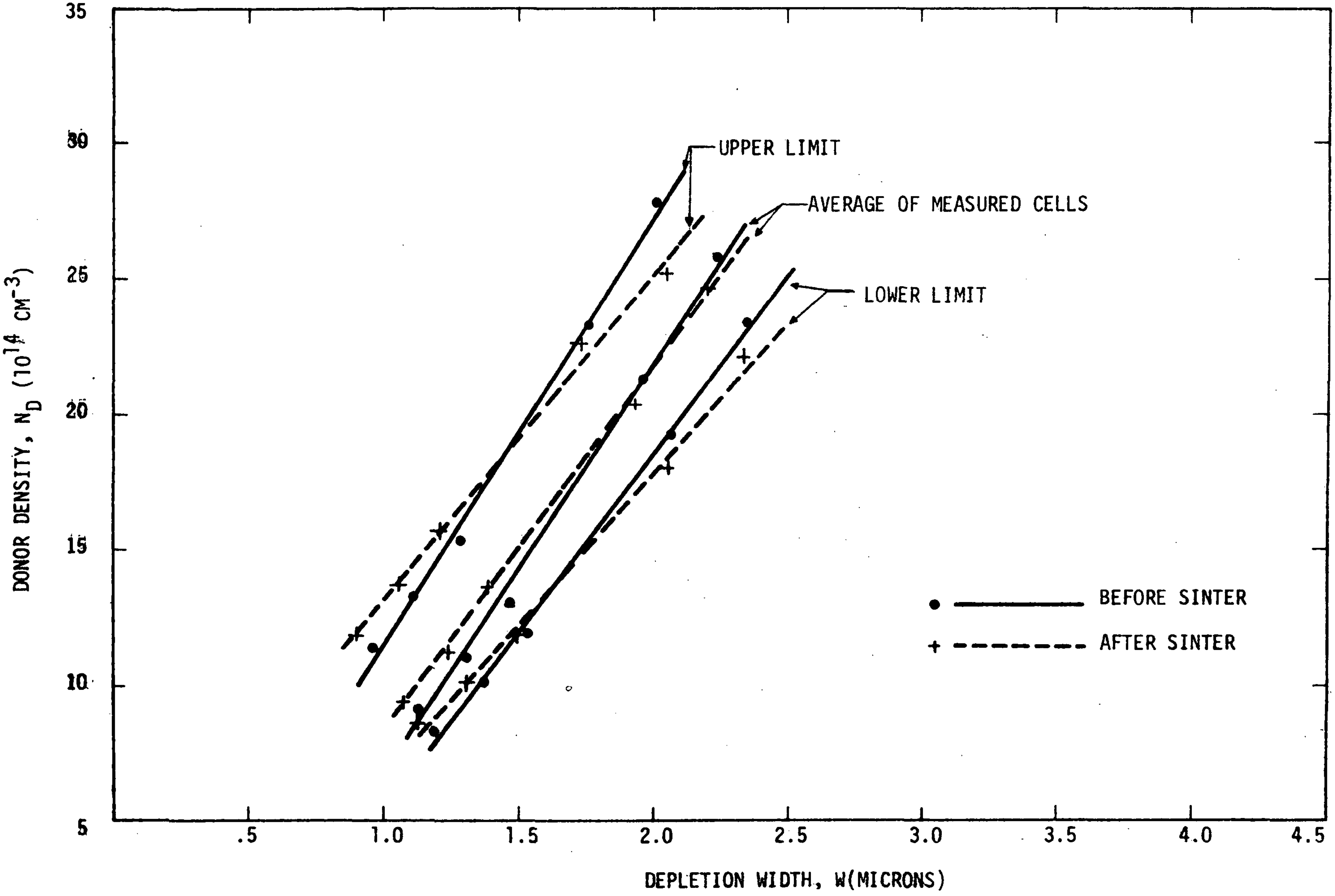

Figure 10 Donor Density vs. Depletion Width. Twenty Lithium Doped P/N Cells Diffused 3 Hours at 360°C

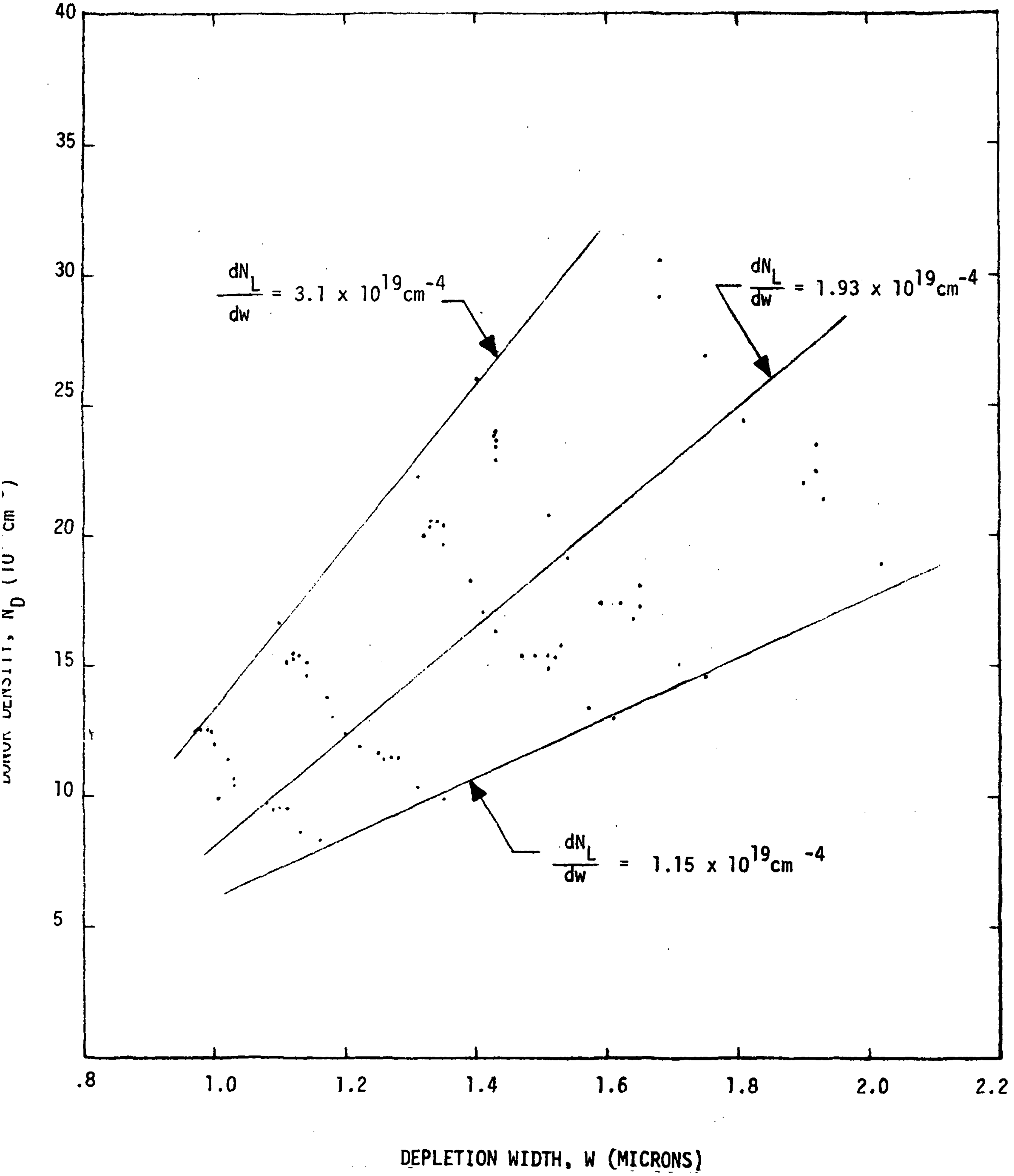

Figure 11. Donor Density vs. Depletion Width (Twenty Cells Lot 4)

ranging from 1.15 to 3.1 x $10^{19}/cm^4$, which were within a factor of three of one another as well as the twenty cells in the first group.

Additional capacitance measurements were made 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 is shown in Figure 12. As anticipated the donor density gradient of the crucible grown cells diffused 3 hours was higher than that of cells diffused 1 hour; the difference was a factor of four. Although there was an overlap in the range of donor density gradient for the crucible grown and Lopex cells diffused 3 hours at 360°C, the average density gradient of the Lopex cells was higher. This observation of higher lithium concentration and density gradient for Lopex cells subjected to the same diffusion conditions as crucible grown cells is an agreement with the findings of previous investigators. (6) Since once the diffusion temperature is raised above 200°C, the diffusion constant is unaffected by the oxygen level, the difference in donor density gradients must be due to the formation of neutral lithium-oxygen pairs. (8) An overlap in density gradients also existed for Lopex cells diffused 2 hours at 400°C and 3 hours at 360°C; however the average density gradient of cells diffused at 400°C was approximately 1.5 times higher.

The 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, the difference between the minimum and maximum density gradient was no more than a factor of three. Variations in donor density gradients of as much as two orders of magnitude within the same lot have previously been reported. (6)

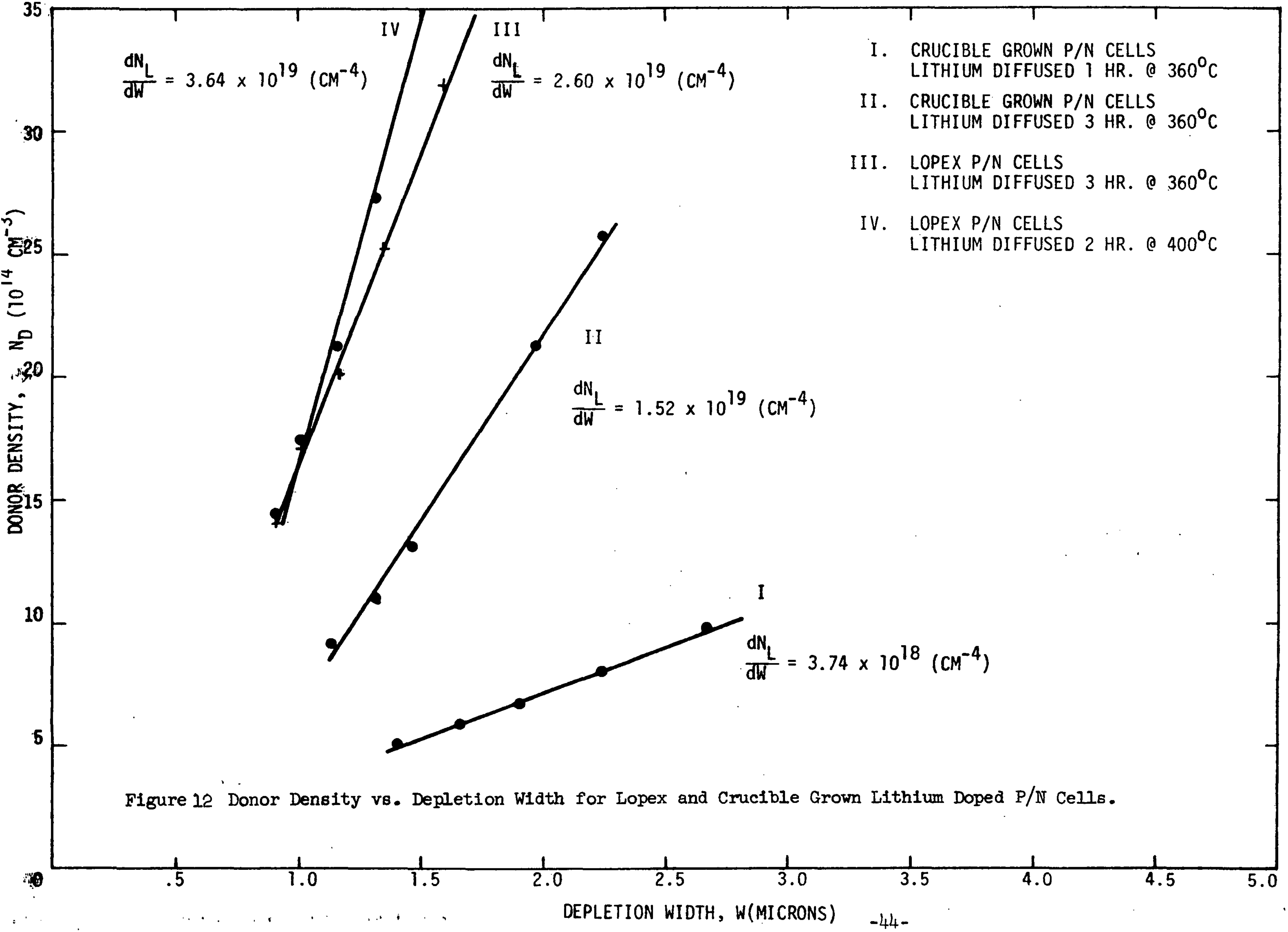

Figure 12 Donor Density vs. Depletion Width for Lopex and Crucible Grown Lithium Doped P/N Cells.

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.

2.4.2 CONTACT EVALUATION

In order to evaluate TiAg contact integrity, lithium doped P/N cells were subjected to pull tests. This test consisted of soldering wires to both front and back contacts and pulling at a 90° angle to the cell surface until contact failure. Eight to ten samples were selected from each of the four groups of cells fabricated for shipment to JPL. The results of these pull tests are shown in Table IX. The front contact of one cell in the first lot failed at the initiation of the pull test. In all other cases where failure occurred at less than 500 grams, it was due to silicon fracture.

A tape pull test was also used to test contact integrity on unsoldered cells using Scotch brand adhesive #810 applied to both front and back contacts. This test was used on all the lithium cells fabricated during this program. Contact failures only occurred in one evaporation lot processed for the fourth shipment. In this group of 140 cells, 27 peeled. Pull tests performed on samples from the remainder of this group indicated that those cells which passed the tape peel test had good contact strength.

TABLE IX

PULL STRENGTH OF LITHIUM DOPED P/N CELLS

		Pull Strength, grams		Failure Mode*	
		Front	Back	Front	Back
Lot 1					
	1	1000	1000	1	1
	2	900	1000	2	1
	3	1000	700	1	2
	4	1000	1000	1	1
	5	0	1000	3	1
	6	400	900	2	2
	7	800	1000	2	1
	8	1000	1000	1	1
	9	1000	1000	1	1
	10	650	1000	2	1
Lot 2					
	1	1000	1000	1	1
	2	700	950	2	2
	3	550	1000	3	1
	4	850	1000	2	1
	5	825	1000	2	1
	6	500	1000	2	1
	7	525	1000	3	1
	8	700	625	2	2
	9	900	775	2	2
Lots 3 and 4					
	1	450	900	2	2
	2	800	750	2	2
	3	200	550	2	2
	4	750	900	2	2
	5	400	325	2	2
	6	975	750	2	2
	7	700	1000	2	1
	8	625	1000	2	1
	9	925	1000	2	1
	10	1000	700	1	2
	11	625	800	2	2
	12	850	925	2	2
	13	525	1000	2	1
Following samples were from evaporation lot with ~ 20% peeling					
	14	975	700	2	2
	15	800	975	2	2
	16	750	1000	2	1
	17	525	1000	2	1

* 1 Contact withstood 1000 grams pull. The test was not continued beyond 1000 grams which was the maximum value on the gauge.

2 Si fracture

3 Contact pulled off

These tests along with similar evaluations on previous contracts indicate TiAg contacts on lithium doped P/N cells, whether sintered or unsintered, meet the 500 gram pull strength requirement of typical specifications.

2.5 Delivered Cells

The 2 x 2 cm lithium doped P/N cells in the four lots of 300 delivered to JPL on this contract were fabricated from 15 to 25 ohm cm crucible grown silicon. The lithium was applied by evaporation and the cells were diffused 3 hours at 360°C. All cells had TiAg contacts. Except for 98 cells in the first lot, Lots 1, 2 and 3 cells were sintered 2-3 minutes at 605°C. A 5 minute sintering period at 360°C was used for the cells in Lot 4. Both sintered and unsintered cells were soldered.

Cells in the first two lots were fabricated using an 8-2-7 diffusion schedule and $BC\ell_3$ (without O_2) as the diffusion source. The quantity of cells per boron diffusion ranged from 10 to a maximum of 40. Figures 13 and 14 show the distribution of current at 480 mV for these two lots. The cells were measured at 28°C in the solar simulator (135.3 mW/cm^2) and were categorized into 2 mA groupings. The cells in these two groups had efficiencies ranging from 11.0 to 13.7%, with more than half the cells having efficiencies above 12%.

Although the $BC\ell_3$ diffusion was used both with and without O_2 in fabricating cells for the third lot, the majority of the cells were fabricated using the $BC\ell_3$ with O_2 diffusion. The diffusion schedule was 8-20-10 and the diffusion temperature, 1000°C. The quantity of cells per boron diffusion was increased from 10 to 60. The efficiency of these cells ranged from 11.0 to 12.5%. (Figure 15)

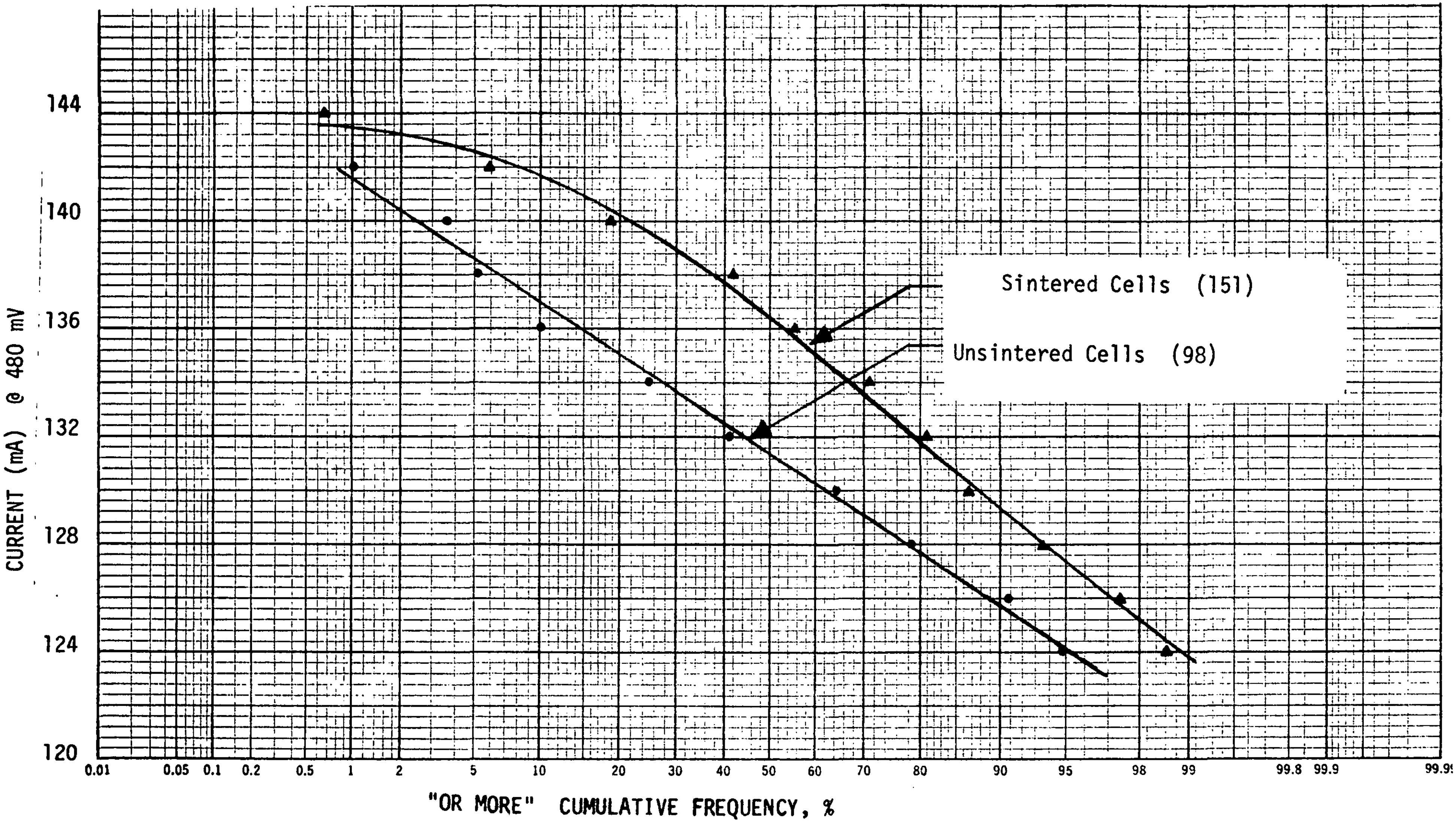

Figure 13. Current at 480 mV Distribution for Lot 1 Cells (28°C)

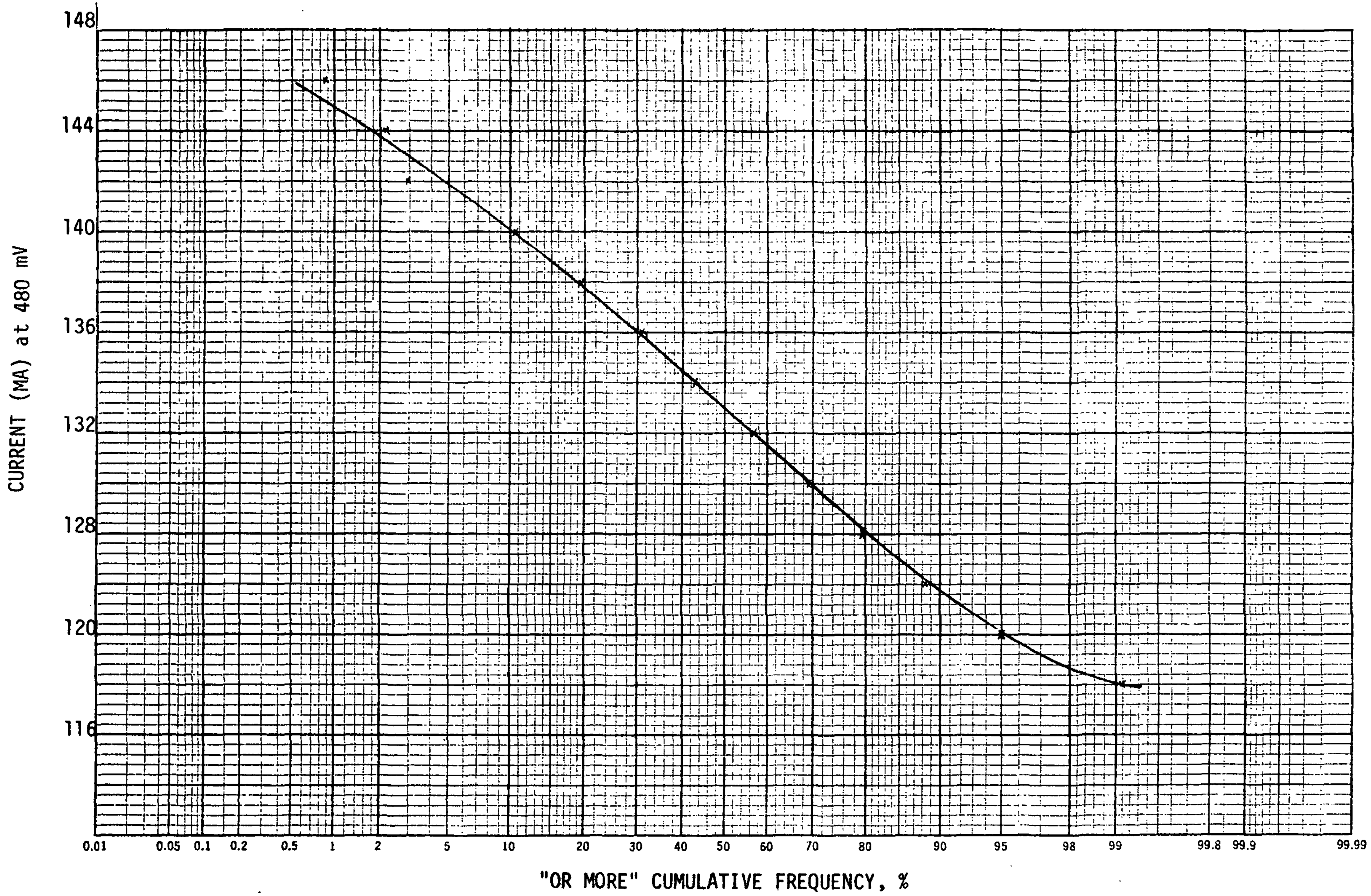

Figure 14. Current at 480 mV Distribution for Lot 2 Cells (28°C)

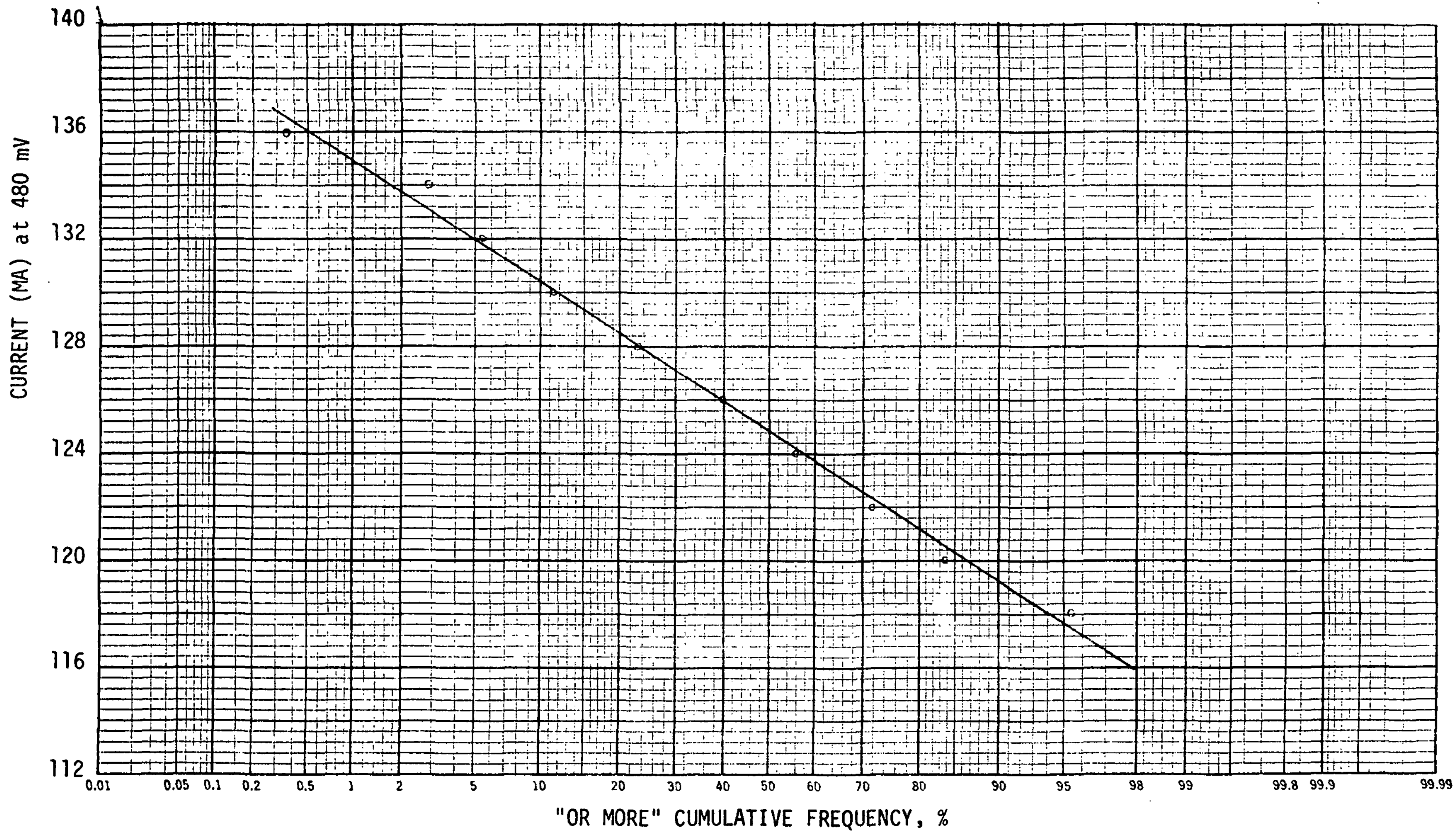

Figure 15. Current at 480 mV Distribution for Lot 3 Cells (28°C)

The $BC\ell_3$ with O_2 diffusion was also used in fabricating cells for the fourth lot; however, the drive-in period was omitted and a boron diffusion schedule of 8-20-0 was used. The boron diffusion lots ranged from 70 to 150 cells with no loss in power observed in going from experimental runs of 10 cells per diffusion to 150 cells. The efficiency ranged from 11.0 to 12.1% for this group of cells. (Figure 16)

It is apparent that the Lot 3 and 4 cell efficiencies are about 10% lower than the lot 1 and 2 cell efficiencies. Since Lots 3 and 4 were fabricated using $BC\ell_3$ with oxygen, we are forced to conclude at this point that the scaled up diffusion process sacrifices some cell efficiency. As discussed in Section 2.1.1 the $BC\ell_3$ without O_2 may have conserved minority carrier lifetime which could not be achieved with the addition of oxygen.

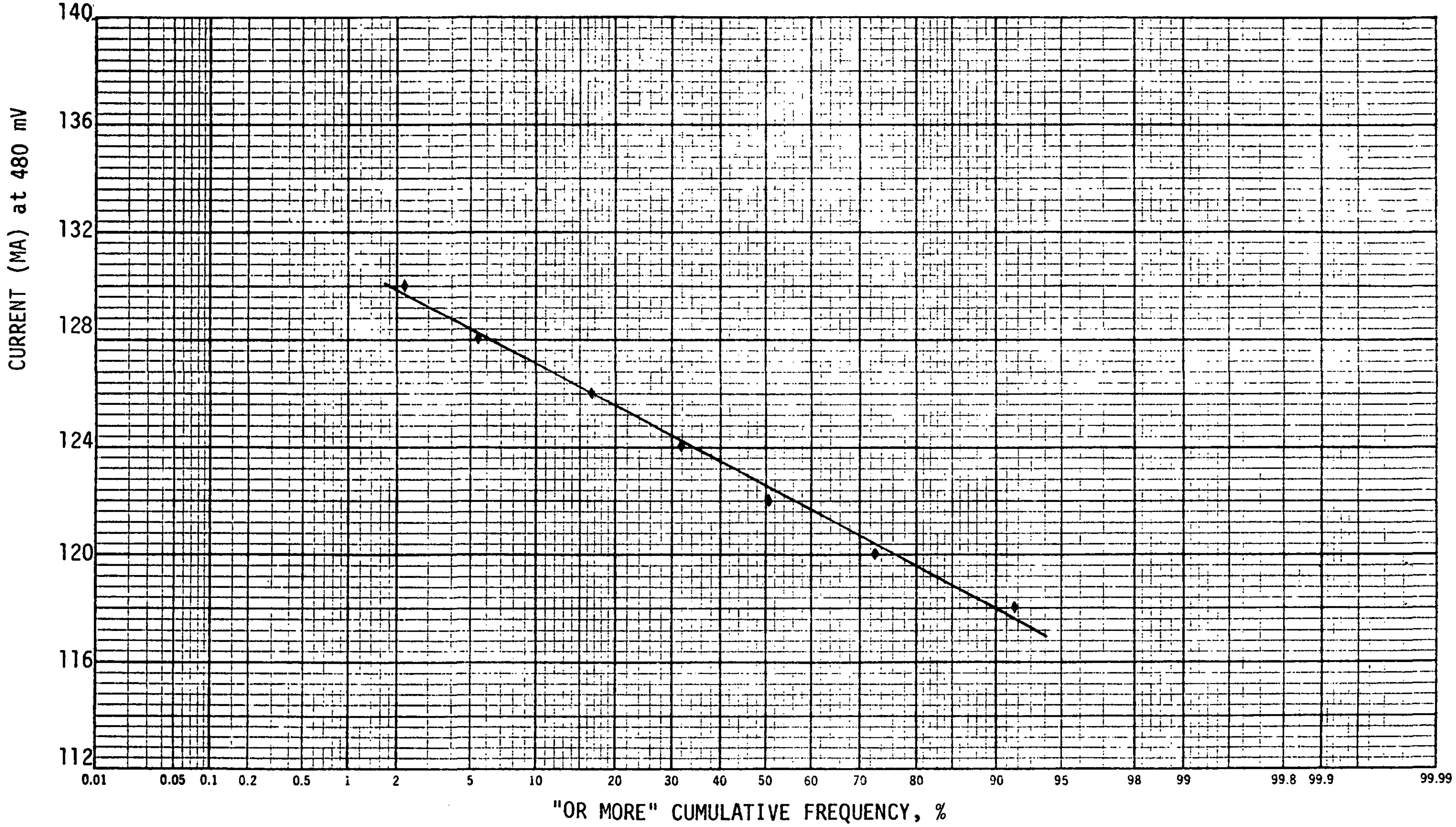

Figure 16. Current at 480 mV Distribution for Lot 4 Cells (28°C)

2.6 HISTORICAL SUMMARY OF LITHIUM CELLS

2.6.1 Initial Performance Characteristics

The lithium doped P/N solar cell has gone through distinct stages of development. Table X shows the characteristics of the more important types of lithium cells which have been analyzed by both solar cell manufacturers and radiation laboratories.

During the initial work (1966-1967) float zone silicon was used. Lithium diffusion times ranged from 5 to 90 minutes, and diffusion temperatures ranged from 350 to 500°C. The concentration gradients in the silicon slices were very steep causing lithium cell instability as exhibited by shelf life degradation and redegradation after post irradiation recovery. In order to reduce this gradient, redistribution cycles (removal of the excess lithium from the cell surface and further heating of the cell to move the lithium deeper into the slice) generally ranging from 60 to 120 minutes were used. Redistribution cycles produced higher output cells with little change in the recovery characteristics. Typical diffusion schedules used as a result of this initial work were 90 minute diffusions with redistributions of 60 or 120 minutes. At this time 90 minutes diffusion with 60 minutes redistribution at 350°C gave the best cell efficiencies, 9.7-12.3%, however, radiation testing indicated that the lithium content was insufficient for good cell recovery level. The best cell in terms of both efficiency and radiation recovery was one with a 90 minute diffusion and 120 minute redistribution at 425°C (Item 3).

The discovery in 1967 of the recovery capabilities of lithium doped solar cells fabricated from crucible grown (C.G.) silicon led to extensive investigation in this area. The higher oxygen concentration C.G. lithium cells exhibited retarded room temperature

TABLE X

SUMMARY OF LITHIUM DOPED P/N CELL CHARACTERISTICS

	Date	Starting Material	Boron Diff.	Lithium Diff.	Li.Conc. Atom/cm^3	ELECTRICAL			CELL CONFIGURATION		Comments
						Voc. mV	I_{sc},mA/cm^2	Efficiency (135.3mW/cm^2)	Description	Thickness	
(1)	1966 - 1967	20 Ω cm F.Z. Lopex	A	425°C 90 - 0	$1\text{-}6 \times 10^{17}$	25°C 565 - 575	28 - 31	8.5 - 10.2	1.1.1	.41 mm	Mode 1
(2)	1966 - 1969	20 Ω cm F.Z. Lopex	A	90 - 60	$10^{16} - 10^{17}$	25°C 580 - 593	30 - 34	8.9 - 10.7	1.1.1	.41 mm	Mode 1
(3)	1966 - 1969	20 Ω cm F.Z. Lopex	A	90 - 120	$3 - 9 \times 10^{15}$	25°C 586 - 596	31 - 36	9.0 - 11.3		.41 mm	Mode 1
(4)	1966 - 1969	20 Ω cm F.Z. Lopex	A	350°C 90 - 60	$2 - 5 \times 10^{15}$ $\frac{dN_L}{dw} = 4x10^{16}/cm^4$	25°C	32 - 39	9.7 - 12.3	1.1.1	.41 mm	Mode 2
(5)	1967 - 1969	20 Ω cm C. G.	A	425°C 90 - 60	$\frac{dN_L}{dw} = 10^{19}/cm^4$	25°C	29.3-36.4	9.7 - 11.8	1.1.1	.41 mm	Modes 1 and 3
(6)	1969 - 1970	20 Ω cm C. G.	A	90 - 120		25°C	32 - 38	9.5 - 11.8 9.0 - 11.7	1.2.2 1.2.1	.41 mm .41 mm	Modes 1 and 3
(7)	1969 - 1970	20 Ω cm C. G. Lopex	A	325°C 480 - 0	$.3\text{-}1x10^{17}$ $\frac{dN_L}{dw} = \frac{10^{17}-10^{19}}{cm^4}$	25°C	32 - 39.5	10.1 - 12.4	1.2.1	.41 mm	Modes 3 and 4
(8)	1969 - 1970	20 Ω cm F.Z. Lopex	A	325°C 480 - 0	$.3\text{-}1x10^{17}$	25°C	30.5 - 38.5	8.5 - 11.3	1.2.1	.41 mm	Mode 1
(9)	1970	20 Ω cm F. Z.	A	425°C 90 - 60				8.9 - 10.5* 8.3 - 9.8 @	1.3.2	.34 mm	Slow Radiation
(10)	1970	20 Ω cm F.Z.	A	425°C 90 - 120				9.1 - 11.3* 8.5 - 10.6@	1.3.2	.34 mm	Slow Radiation
(11)	1970	20 Ω cm C. G.	A	425°C 90 - 60				9.2 - 11.7* 8.6 - 10.9@	1.3.2	.34 mm	Slow Radiation

KEY:
A BCl_3 without O_2 (8-8-10)
B BCl_3 without O_2 (8-2-10)
C BCl_3 with O_2

Sintered Cells
* Bare Cell
@ Cell with Cover & Tab

1.0.0 1 x 2 cm
2.0.0 2 x 2 cm

0.1.0 Corner Dart
0.2.0 Bar Contact
0.3.0 Bar Contact on 2 cm side

0.0.1 AgTi
0.0.2 Aℓ

SUMMARY OF LITHIUM DOPED P/N CELL CHARACTERISTICS

					ELECTRICAL			CELL CONFIGURATION		
Date	Starting Material	Boron Diff.	Lithium Diff.	Li.Conc. Atom/cm^3	Voc. mW	I_{sc},mA/cm^2	Efficiency (135.3mW/cm^2)	Description	Thickness	Comments
(12) 1970	20 Ω cm C.G.	A	325°C 480 - 0				9.8 - 12.6* 9.4 - 11.4●	1.3.2	.34 mm	Slow Radiation
(13) 1970	20 Ω cm Lopex	A	360°C 180 - 0	1x10^{15}-junct. $\frac{dN_L}{dw} = \frac{2.3x10^{19}}{cm^4}$	25°C	31 - 35	9.3 - 11.3	1.2.1	.41 mm	Mode 1
(14) 1971	20 Ω cm Lopex	B	360°C 180 - 0	1 x 10^{15}-junct. $\frac{dN_L}{dw} = \frac{2-3x10^{19}}{cm^4}$	25°C 600 - 630	35 - 38 36 - 40#	10.5 - 12.5 11.2 - 13.6#	1.2.1	.35 mm	Mode 4
(15) 1971	20 Ω cm C. G.	B	370°C 180 - 0		25°C 600 - 630	36 - 41#	10.9 - 13.2#	1.2.1	.35 mm	Mode 4
(16) 1971	20 Ω cm C. G.	B	370°C 180 - 0		25°C		10.2 - 12.2#	2.2.2	.20 mm	
(17) 1971	20 Ω cm C. G.	B	360°C 180 - 0	.8-1.6x10^{15}-junct. $\frac{dN_L}{dw} = 1\text{-}3x10^{19}/cm^4$	28°C 600 - 630	36 - 40.5#	11.0 - 13.7#	2.2.1	.30 mm	Mode 4
(18) 1972	20 Ω cm Lopex	B	400°C 120 - 0	1.4-1.8x10^{15}-junct. $\frac{dN_L}{dw} = \frac{3.5\text{-}4.5x10^{19}}{cm^4}$	25°C			2.2.2	.30 mm	
(19) 1972	20 Ω cm C. G.	C	360°C 180 - 0	.8-1.6x10^{15}-junct. $\frac{dN_L}{dw} = 1\text{-}3x10^{19}/cm^4$	28°C 590 - 620	32.5 - 38.0#	10.5 - 12.5#	2.2.1	.30 mm	Modes 3 and 4

KEY:
A $BCℓ_3$ without O_2 (8-8-10)
B $BCℓ_3$ without O_2 (8-2-10)
C $BCℓ_3$ with O_2

\# Sintered Cells
* Bare Cell
● Cell with Cover & Tabs

1.0.0 1 x 2 cm
2.0.0 2 x 2 cm

0.1.0 Corner Dart
0.2.0 Bar Contact
0.3.0 Bar Contact on 2 cm side

0.0.1 AgTi
0.0.2 Aℓ

post irradiation recovery; however, recovery rates equivalent to those obtained with low oxygen concentration lithium cells were observed when the cell temperature was raised to between 60 and 100°C. Cell stability, both shelf-life and after radiation recovery, which was poor for some float zone lithium cells, was not a problem, with C.G. lithium doped solar cells. In June 1969 the output of C.G. lithium cells (Item 5) was typically about 2 mW higher (28.3 vs. 26.5 mW) than similarly doped F.Z. lithium cells (Item 2).

The next stage of development was the investigation of lower lithium diffusion temperatures. Eight hour diffusions at 325°C were performed and typical C.G. lithium cell outputs (See Item 7) were approximately 2 mW higher (30.0 vs. 28.3 mW) than C.G. cells diffused 90 minutes and redistributed 60 minutes at 425°C. Three to seven hour diffusion at temperatures between 340 and 380°C were also investigated. It was at this time that a breakthrough in output was made for Lopex and float zone cells, which were typically 1-2 mW lower than similar C.G. cells. Initially Lopex lithium cells diffused 3 hours at 360°C had outputs of 23.9 to 29 mW (Item 13). By changing the deposition time of the $BC\ell_3$ without O_2 diffusion which was being used at that time from 8 to 2 minutes, the stresses produced in the silicon were reduced considerably and the Lopex lithium cell outputs were improved ~10%, even with a 20% reduction in cell thickness (Item 14). The change in slice thickness had to be made at this time due to the reduction in the amount of Si etched away during the 2 minutes deposition as opposed to the 8 minutes step. Previously, slices which were .53 mm thick after cutting were lapped to remove .02 - .05 mm of damage silicon from both surfaces. The .43 mm blank was etched sufficiently during the

8 minutes boron deposition that the damage remaining after lapping was removed. This was not the case with the 2 minute deposition and consequently an additional .02 to .05 mm was removed by etching prior to boron diffusion.

Reduced stresses were obtained when the $BC\ell_3$ deposition time was decreased from 8 to 2 minutes. This made it possible to fabricate 2 x 2 cm cells without experiencing any cell bowing or lower output. The cell thickness could also be reduced and cells as thin as .20 mm have been fabricated in quantities.

An additional improvement in output of 5% was gained by sintering lithium cells (Item 14).

The work performed on the present contract has been aimed at scaling up processes to production quantities. Although the highest cell efficiencies, 11.0 to 13.7%, have been obtained using the $BC\ell_3$ (no O_2) diffusion with a 2 minute deposition period, the process could not be scaled beyond 40 cells without suffering lower output and uniformity problems. A diffusion using $BC\ell_3$ with O_2 was investigated. Although the extremely high efficiencies obtained with 20 to 40-cell $BC\ell_3$ (no O_2) diffusions could not be duplicated, the $BC\ell_3$ with O_2 diffusion was successfully scaled to 150 cells per diffusion and efficiencies of 10.5 to 12.5% were obtained (Item 19).

The transition in lithium diffusion schedules from diffusions with redistributions at 425°C, to 8 hour diffusions at 325°C was made to obtain higher cell outputs. Diffusions of 3 to 7 hours in the temperature range of 340 to 380°C resulted in outputs similar to those obtained with 8 hour diffusion at 325°C; however, evaluation of lithium density gradients led to an emphasis on the shorter diffusions in the 340 to 380°C range. The lithium density gradients obtained with 3 to 4 hour diffusions were generally found to vary by a factor of 3 (Item 17-19) whereas, with longer diffusions density gradients within the same lot varied as much as two orders of magnitude (Item 7).

2.6.2 Post-Irradiation Performance

The recovery characteristics after electron and neutron radiation have been the primary reason for investigating lithium cells and ideally not only the pre-irradiation but the post-irradiation efficiency would be presented in Table X. However, the majority of the radiation analyses were performed using either 100 or 140 mW/cm^2 tungsten light sources and including this data in Table X would merely be confusing since all the pre-irradiation performance data is based upon AMO measurements. Consequently the performance in radiation environments has been described according to different modes of bahavior and then, when possible, AMO output was indicated. The behavior modes are described below.

MODE 1

In this case the cell output after recovery was limited by the initial output. Typically the initial efficiency was 10% or less, compared to typical N/P cell efficiencies of 11%. These cells recovered from 90 to 98% of their initial output after 10^{14} e/cm^2, but even with maximum recovery the post irradiation output was lower due to the large difference in initial output between N/P and lithium P/N cells. After $\sim$ 3 x 10^{15} e/cm^2 the lithium cell and N/P cell outputs were approximately the same. This behavior mode describes the majority of the pre-1971 float zone or Lopex cells and to some extent the pre-1970 crucible grown cells (Items 7-10).

MODE 2

Cells in this category exhibited the highest initial outputs prior to 1970. This lithium diffusion schedule resulted in very low lithium concentration and poor recovery characteristics.

MODE 3

Lithium cells with this behavior mode had initial outputs in the same range as standard N/P cells. After 10^{14} e/cm^2 the output was about the same as, or slightly higher than, N/P cells and after 10^{15} e/cm^2, if the lithium density gradient was $\sim 10^{19}/\text{cm}^4$, the lithium cell outputs were 10-20% higher than the N/P cell outputs. Item 7 cells exhibited this type of behavior. AMO measurements were obtained on a small quantity of these cells both before and after irradiation. The outputs of these cells after 3×10^{15} e/cm^2 ranged from 21.9 to 23.5 mW. Outputs of N/P cells subjected to the same electron fluence were 19.5 mW.

MODE 4

In this category many of the lithium cells exhibit higher outputs than standard N/P cells. Radiation analysis of this type of cell has not been performed, so no specific information can be supplied.

One possibility is that the lithium doped cells would maintain the same output differential compared to the N/P cell at all radiation levels, (a) in the schematic diagram below. The other possibility (b) is that with the higher initial outputs being due to lifetime improvements the output would begin to degrade at lower radiation fluences. With the higher degradation rates the output after 10^{14} or 10^{15} e/cm^2 might end up in the same range as lithium cells with lower initial outputs.

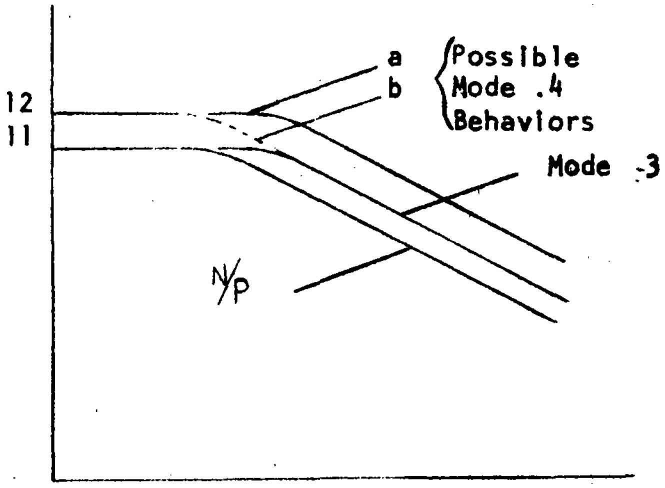

Figure 17 A

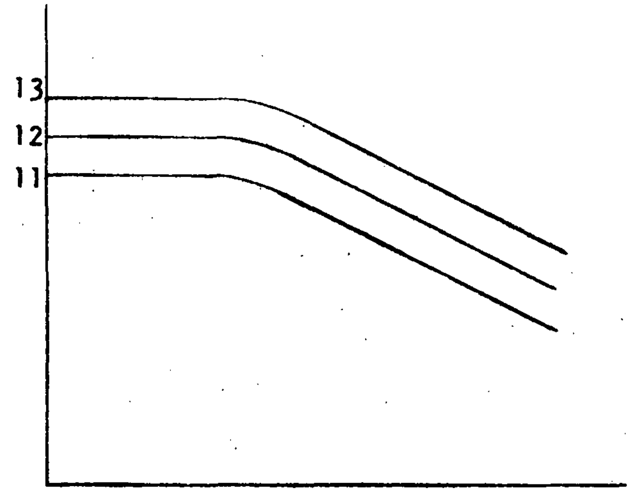

Figure 17 B

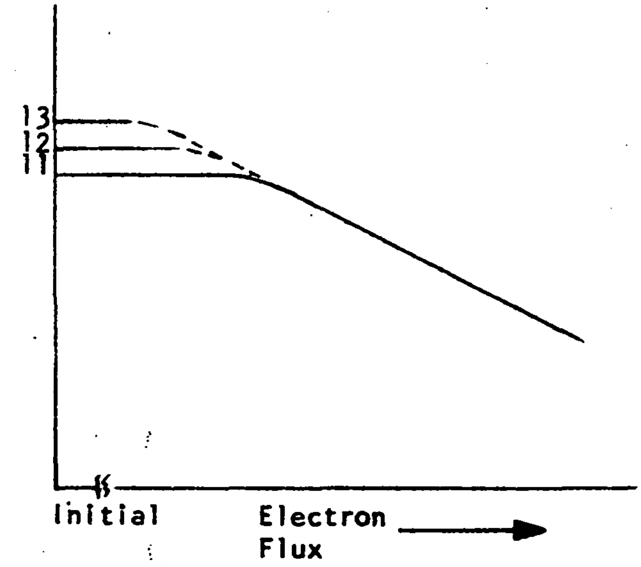

Figure 17 C

SCHEMATICS OF POSSIBLE LITHIUM CELL DEGRADATION

The basic question is whether post-irradiation performance of a group of cells with an efficiency range of 11 to 13% can be described by a family of curves as shown in Figure 17-B or by curves shown in Figure 17-C. If radiation analyses show that the higher efficiency cells do degrade more initially, then the 10% lower output cell obtained with the scaled up processes would begin at some level to perform, on an absolute basis, as well as the cells with higher initial outputs.

2.7 COST ANALYSIS

Independent of yield, the cost of a solar cell is determined by four things: (1) administrative services, (2) labor, (3) overhead, and (4) material. To obtain an accurate estimate of the unit cost of a 2 x 2 cm lithium doped P/N cell, it is necessary to use the cost analysis of a conventional N/P cell as a starting point. By analyzing the new requirements of the lithium cell, it is possible to assign values for each of the four cost elements and from this determine the percentage difference between the standard cell and the lithium cell.

It has been our experience that administrative services represent approximately ten percent of the final cell price. This is a fairly constant cost item and is not influenced by the technological problems that may occur in any particular cell manufacturing run.

Labor is defined as the cost of those personnel directly involved in the production of the solar cell. This element is the key to cell cost since it determines the level of indirect support which in turn makes up a significant portion of overhead. Labor makes up approximately twenty-five percent of the final cell cost.

Overhead is primarily all those costs that are incurred in direct support of the actual labor force responsible for cell production. It includes quality assurance, purchasing, maintenance, shipping and receiving as well as engineering. This element of overhead is directly proportional to the production labor force. Equipment and facility depreciation are also included in overhead as well as operating costs such as utilities, rent, chemicals and other sundries. Generally overhead represents twice the value of direct labor, thus making up approximately fifty percent of the cell cost.

The final cost element that must be considered is material. Normally material makes up approximately 15 percent of the final cell price. The price of raw material is considered to be fixed and therefore the material cost is strictly determined by silicon utilization which will not be changed by lithium cells.

In all cases this analysis uses dimensionless units since the absolute base price of a cell varies from user to user due to the particular requirements imposed by cell specifications. It is possible to use this analysis to arrive at an absolute cell cost for lithium cells by using the known base cost of any particular cell and applying the ratio given in Table XIII.

The two elements of cost that will show a significant increase are labor and overhead. Normally overhead is a constant multiple of labor, but for the lithium cell the multiple will increase. There are four components comprising overhead: (1) equipment and facility depreciation, (2) staff functions, (3) production supplies, and (4) engineering support.

Table XI shows the breakdown of overhead for a standard N/P cell and the new breakdown for a lithium cell.

TABLE XI

OVERHEAD MULTIPLE

	N/P	Lithium P/N
Equipment and Facility Depreciation	.50	.55
Staff Functions	.50	.50
Production Supplies	.70	.80
Engineering Support	.30	.35
	2.00	2.20

In order to process a lithium cell it is necessary to perform additional operations which demand more equipment. For example, lithium is deposited by evaporation techniques and then diffused at a much lower temperature than a boron diffusion. This implies that extra vacuum systems and furnace will be necessary for efficient production. This buildup of equipment will be reflected in additional overhead costs.

The additional operations in lithium cell production will result in a proportionate increase in production supplies such as chemicals, masking materials, evaporation crucibles and the like. It is estimated that the cost of supplies will rise almost fifteen percent due to the added processing steps.

The final component of overhead, engineering support, will show a pronounced increase because the processing is more complicated, thereby increasing the probability of technical difficulties that require engineering support.

Table XII shows the estimated breakdown of labor costs for a lithium doped P/N cell and a comparison for standard N/P cell labor costs.

TABLE XII

LABOR COST

Operation	N/P	P/N Li CG	P/N Li Lopex
Crystal Growth	09	09	27
Blank Preparation	20	20	20
Junction Diffusion	08	10	10
Glass Layer Removal	-	01	01
Back Etch	-	12	12
Lithium Evaporation	-	12	12
Lithium Diffusion	-	09	09
Back Etch	12	12	12
Final Glass Removal	-	01	01
Contacts	15	15	15
Antireflection Coating	12	12	12
Sintering	05	05	05
Soldering	10	10	10
Testing	09	09	09
Sub Total	100	137	155
Attrition	0	10	10
Total	100	147	165

Labor costs represent approximately 25 percent of the price of a conventional cell. To obtain a reasonably accurate assessment of this item every processing step from crystal growing to final inspection was examined.

For conventional cells there are seven distinct operations necessary to produce a usable silicon blank. Although the 15 to 25 ohm cm N type crucible grown silicon used for lithium cells is not one which is normally produced, it is no more difficult than growing 7-14 ohm cm P type and therefore the cost should remain the same. In the case of growing low oxygen, low dislocation silicon, such as Lopex or Mon-x, the labor was estimated at a factor of 3 greater than crucible grown silicon. The labor increase at this step and its impact upon overhead is the only cost differential between crucible grown and Lopex lithium cells.

The major labor expense is incurred in preparing the silicon blanks. These operations are not changed by going to crucible grown or Lopex silicon and therefore, the labor for this step should be the same as for conventional silicon blanks.

The cell processing sequence can be broken down into three main sections, with an additional section required for lithium cells. The first section takes the silicon slices from classifying and processes them through junction diffusion. There are four labor steps involved, but only one process, the junction diffusion, will be strongly influenced by the lithium cell. The quantity of cells processed per diffusion is about half the N/P quantity and the diffusion time is approximately twice that used for N/P cells. This will result in an estimated increase in labor of 25 percent.

The next phase of processing involves the additional steps required for fabrication of lithium cells and is the major cost difference between lithium doped P/N cells and standard N/P cells.

Two acid boils are necessary to remove the boron compounds from the silicon slices after boron diffusion. A back etch to remove the junction from one surface of a diffused slice used in processing N/P cells represents approximately 12 percent of the total labor. This procedure is the same for P/N lithium cells but since it is done twice in lithium cell processing, an additional 12 percent labor cost results.

In order to estimate the labor costs of the lithium evaporation and lithium diffusion, costs of similar operations used in N/P cell fabrication were simply used. The lithium evaporation is sililar to the antireflection coating operation in terms of masking and loading, so 12 percent was added and the lithium diffusion is similar to the junction diffusion, so 9 percent was added.

The last section of cell processing involves contacting, antireflection coating and sintering. None of these operations is influenced in the fabrication of lithium doped P/N cells and so the same labor factor as a standard cell was assigned.

After processing the cell undergoes testing. For this estimate it will be assumed that the labor index for testing will also be the same as for a standard N/P cell.

There is one more item that must be considered in order to obtain a realistic value for labor rates, and that is cell breakage. Due to additional processing steps and the greater fragility of P/N cells after lithium diffusion, the breakage rate is about 10 percent above standard N/P cells. This attrition rate must be shown as an element of labor cost since a broken cell represents wasted labor and materials.

Table XIII summarizes the cost elements for the lithium cell as compared to the standard N/P device. As has been shown in this analysis, the significant variable in cell cost is labor. From this, we conclude that in production quantities P/N lithium cells will be from 40 to 60 percent more expense, mostly due to the more involved processing costs. This represents cost for present technology, but we would expect substantial reductions in cost as the production technology evolves more efficient processes.

TABLE XIII

CELL COST

Cost Element	2 x 2 cm N/P	2 x 2 cm Li P/N - C.G.	2 x 2 cm Li P/N - Lopex
Material	60	60	60
Labor	100	147	165
Overhead	200	323	363
Administration	40	40	40
Total	400	570	628

The costs indicated are basic lithium cell costs. They will change with yield and the final yield will depend upon electrical, mechanical, and environmental specifications. Since lithium cells have not been subjected to the gamut of tests demanded by typical specifications not much can be said about the absolute final yield. The electrical yield, if estimated on the basis of cells fabricated with scaled-up processes on this contract which had to meet a minimum efficiency of 11%, could be as low as 60% (overall electrical yield for Lot 4). This would almost double the cell cost. It should be pointed out that if N/P cells were required to meet a similar electrical specification minimum, (11.0% AMO) the yield would fall substantially thus increasing the cost of an N/P cell. On the basis that we now understand some of the problems which caused lower outputs, the electrical yield could be projected, using the better sublots in Lot 4, as high as 75% which would increase the cell cost by a factor of 1.5. A final consideration on the electrical yield is whether the customer wants to pay the premium for an 11% minimum efficiency lithium doped P/N cell. Typical minimum values for N/P cells are between 10 and 10.5% efficiency and lowering the number to 10.5% for a lithium doped P/N cell would increase the electrical yield to about 85%.

2.8 FINALIZED PRODUCTION PROCESSES AND CONTROLS

The process sheet for lithium doped P/N solar cell fabrication is shown in Figure 18. Asterisked items are those which have been modified or added as a result of the development phase of this program.

The boron diffusion process has been changed from $BC\ell_3$ without O_2 to $BC\ell_3$ with O_2 in order to both avoid the nonuniform etch reaction which occurs when O_2 is absent and increase the quantity of cells which can be processed in each diffusion. Boiling in an acid mixture which dissolves boron is necessary after the $BC\ell_3$ with O_2 diffusion, since the surface layer is not simply a B_2O_3 layer which can be removed with HF. Incomplete removal of this layer results in poor adherence of the AR coating, so a second acid boil step is included prior to evaporation of TiAg contacts. The lithium evaporation procedure has also been modified, instead of being kept at room temperature the cells are heated to ~ 100°C during the evaporation. This change has resulted in more uniform sheet resistances after lithium diffusion.

The process flow sheet also shows the in-process quality assurance checkpoints. These include sheet resistance measurements on a sample basis after boron and lithium diffusion to check for uniformity and reproducibility. Tape pull testing is performed on all cells to cull out cells with poor contacts.

In addition capacitance measurements are performed also on a sample basis on the completed cells to verify that lithium concentration and density gradients are under control.

Figure 18. Process Sheet for Lithium Doped P/N Cells

	W/E Readings	Heliotek Lithium Doped P/N Cells	Diffusion Lot #

Operation	Operator	Date	Good	Rework	Scrap	Remarks
Clean & Etch Material						
Check Dimensions						
* Boron Diffuse						
HF 15 sec						
* Acid Boil 1 hr.						
) V/I						
Back Etch						
Clean						
Li Evaporation						
Li Diffusion						
Rinse Cell in H_2O						
Remove Residue						
) V/I (see back)						
Back Etch						
Clean						
HF 1 1/2 min.						
* Acid Boil 1 hr.						
HF 15 sec.						
AgTi Contacts						
SiO. clean						
SiO Coat						
Remove SiO from Gridlines						
Sinter						
) Tape Pull Test						
Clean						
Check Weight or Thick						
Solder						
Electrical Test						
Range						
Test Results						

S.O void	Cell D	OhmicD	Frame D	OhmicS	Back S	Chips	Stain	U.A.	Gridlines	Scratch

3.0 CONCLUSIONS

Use of O_2 in a $BC\ell_3$ diffusion made it possible to avoid the non-uniform etch reaction encountered when $BC\ell_3$ is used by itself, and to scale-up the boron diffusion process to 150 cells per diffusion. Good uniformity is obtained with this process as indicated by the short circuit current range of 136 ± 4 mA for P/N control cells.

The lithium evaporation was scaled up to 100 cells and by using two evaporation batches, the lithium diffusion was scaled up to 200 cells. With the scaled up boron and lithium diffusion processes cell efficiencies of 10.5 to 12.5% can be obtained (AMO - 135.3 mW/cm^2). Scaling up the lithium evaporation and diffusion produced no adverse effects in terms of uniformity of the lithium density gradient. The original improvement from variations as large as two orders of magnitude within the same lot to values which were within a factor of three of one another could be maintained with the scaled up processes.

The lithium diffusion time used for all cells during this contract was 3 hours, which is approximately six times the boron diffusion time. For 3000 cells per month this lengthy diffusion is not rate-limiting, however, for larger production quantities it becomes rate-limiting unless there are at least three lithium diffusion furnaces available for every boron diffusion furnace or unless a continuous diffusion furnace is used.

Metal-semiconductor barrier formation which causes lower cell output occurs in lithium doped P/N cells as a result of sintering at temperatures as low as 360°C. The problem cannot be avoided by omitting the sintering process since output degradation which is probably related to this barrier formation even occurs at soldering temperature (220°C).

The extreme variations in this barrier formation as well as the greater sensitivity of Lot 4 cells (fabricated using $BC\ell_3 + O_2$ diffusion) compared to Lot 2 cells (fabricated using $BC\ell_3$ without O_2 diffusion) indicates a possible dependency upon process changes. The solution to this problem may merely involve minor changes in the AgTi contact system or it may require development of a new contact system. It should be noted, however, that elimination of the problem in the 200 to 300°C sintering range is sufficient since a non-absorbing antireflection coating, such as TiO_x, which doesn't need high temperature heat treatment could be applied.

Based upon labor inputs alone, the cost of a lithium doped P/N cell is approximately 40% higher than a standard N/P cell. On the basis of electrical yields ranging from 60 to 85%, this lithium cell price will further increase by a factor between 1.2 and 1.7. The overall yield on the basis of conformance to a typical specification is unknown because this testing has not been done.

4.0 RECOMMENDATIONS

Based upon the results of this program, recommendations related to production processes as well as areas needing further research in order to better understand lithium cell behaviour can be made.

The cost analysis shows that even after scaling up the boron and lithium diffusion processes, the cost of a crucible grown lithium doped P/N cell is ~ 40% higher than the cost of a standard N/P cell. This cost differential is primarily due to the labor costs of the additional processing steps required in fabrication of lithium cells. The lithium evaporation and diffusion, and the additional back etch make up the major portion of the added labor costs. Earlier investigation indicated that back etching to remove the boron diffused layer from the back of the cell prior to lithium diffusion resulted in more uniform lithium diffusion characteristics. However, with the change to the $BC\ell_3$ with O_2 diffusion the silicon surface characteristics also changed and the possibility of eliminating this back etching step should be reconsidered.

The lithium diffusion is shown in the labor cost analysis as an item comparable to the junction diffusion, however, as will be shown in the following discussion, in high volume production it would have to make a greater cost impact due to capital equipment requirements. It becomes apparent in planning a production run of several thousand cells that the lithium diffusion is still a rate limiting step, due to typical diffusion times of 3 hours. For example, at a rate of 150 cells per diffusion, 1200 cells could easily be boron diffused during an 8 hour shift using only one diffusion furnace. In the case of the lithium diffusion, however, even at 150 cells per evaporation and 2 evaporation loads per diffusion three lithium diffusion furnaces would be needed to process 1200 cells during an 8 hour shift. Use of a continuous diffusion furnace should be investigated since it seems to be the only realistic way to handle this lengthy diffusion on a production basis. With a continuous diffusion process, the quantity per diffusion furnace per 8 hour shift would only be limited by the number of lithium evaporations which could be performed during the first five hours.

Another area of production concern is the ability of lithium cells to meet mechanical and environmental requirements of typical specifications. Contact strength and humidity resistance are the only tests in this category which have been performed. Considering the mobility of lithium at relatively low temperatures, it is quite conceivable that in bake tests, thermal cycling, etc. lithium cells will show more change in output than N/P cells. Specifications are not sacred and the fact that lithium cells might not pass the same tests required of N/P cells is not necessarily as important as determining actual lithium cell performance, evaluating it, and establishing new criteria for cell performance.

As a result of work during the past year, we have also realized that there are still aspects of lithium cell behaviour which are not well understood and should be part of additional work on lithium cells. One such area is the effect of lithium on cell lifetime. Both lifetime enhancement and degradation, as a result of lithium diffusion have been observed. The effect on lifetime of varying the lithium concentration is also not clear. Hopefully, by understanding these various behaviour modes, they could be related to process variations.

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