



Manufacturer of Space Age Solid State Devices

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F I N A L

FIRST PERIODIC REPORT  
for  
Development and Fabrication  
of  
Radiation Resistant High Efficiency Solar Cells  
24 August, 1966 - 24 February, 1967

Prepared for

Goddard Space Flight Center  
Greenbelt, Maryland

Contract No.: NAS5-10272

by

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

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by

P. Payne  
G. Goodelle  
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## SUMMARY

Lithium doped P on N type solar cells of various designs have been fabricated and submitted to NASA/GSFC for radiation testing and analysis. Methods were developed for fabricating lithium doped solar cells. The lithium diffusion process was studied and controlled so that the lithium concentration and profile could be varied. It was discovered that the open circuit voltage could be increased with increasing lithium concentration up to a voltage of about 585 mV. Further increases in lithium concentration caused a significant decrease in minority carrier lifetime and, consequently, limited further increases in open circuit voltage. Radiation studies also indicated that there would be an optimum lithium atom concentration for a specific radiation flux level. Too little lithium does not give sufficient annealing properties, while a high lithium concentration provides good annealing properties but it also decreases the minority carrier diffusion length so that good electrical output cannot be maintained. A special designed phosphorous diffused lithium doped P on N solar cell has been developed and is described. This type cell has shown unusually good performance at very high flux levels, such as  $10^{15}$  e/cm<sup>2</sup>, while the standard lithium-doped cell is nearly unusable at these high levels due to carrier removal phenomenon.

An analysis of the power output from lithium cells was made. A correlation of radiation damage recovery to the initial power output showed that the higher output cells showed poorer recovery because there were less lithium atoms present. A comparison to standard 10 ohm cm N on P solar cells indicated that slightly improved performance has been obtained with lithium doped cells after a 1 Mev electron flux of  $10^{14}$  e/cm<sup>2</sup>.

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## INTRODUCTION

Studies have been going on for many years in the field of high energy particle radiation effects on semiconductor materials. A great deal of this work has been applied to investigating radiation effects on solar cell performance. The objectives have been to better understand the damage mechanism and the resulting electrical changes in the crystal. With a better understanding of these mechanisms it should be possible to improve the radiation resistance of solar cells,

A great deal of the studies have been directed toward the damage centers formed when high energy particles bombard a semiconductor crystal such as silicon. More recently the studies have been directed toward evaluations of the influence of various impurities in the crystal and the resulting damage center. Electron paramagnetic resonance (EPR) studies have been made on silicon crystals with various impurities, present and comparison made after bombardment with high energy particles<sup>1</sup>. These studies in 1963 and 1964 led to some very interesting characteristics that resulted when lithium atoms were present in the silicon crystal. This work gave new and promising results that warranted further investigations into the effects of lithium on the material characteristics.

Studies were continued by investigating the influence of lithium on solar cell performance<sup>2</sup>. This work concluded that lithium can modify the radiation damage behavior of silicon devices and that the oxygen concentration is important in whether or not these changes can be observed. The above work concluded, however, that the resistance of float zone P on N solar cells was not improved by room temperature annealing despite some

promising experimental results, LOW temperature (near  $100^{\circ}\text{C}$ ) annealing removed about 90% of the radiation damage in cells that contained lithium, while no such annealing occurred in the cell which did not contain lithium.

Continued work on lithium-doped solar cells brought further understanding of the mechanisms involved and improvements in radiation resistance were seen<sup>3</sup>.

In this study it was discovered that room temperature annealing of radiation damage was obtained in lithium-doped float zone P on N solar cells if the phosphorous and oxygen concentrations were kept low. The conclusion of this work was that "solar cells made from N-type silicon, in which the predominant dopant was lithium, have a much greater radiation resistance to electrons and protons than ordinary commercial cells."

The work being done in the present concentrated effort is an attempt to provide various lithium cell designs which will give more information about the possibilities for carrying the previous work forward. The objective is to investigate a large number of solar cell designs with lithium present. Various starting materials are being used to make up experimental solar cells which are to be evaluated and analyzed by NASA for their radiation resistance properties,

Since the previous studies showed a significant dependence on oxygen content, this program is concentrating on float zone grown silicon crystals; however, some Czochralski-grown material was evaluated for comparative purposes. Various resistivities and dopant impurities were investigated. The lithium concentration and profile was varied by changing the lithium diffusion parameters. Experimental solar cells were fabricated throughout the period that showed the effect of changing the various parameters mentioned above. These cells were supplied to NASA/GSFC for radiation bombardment and analysis.

It has become apparent that the optimum lithium doped **solar** cell design requires a trade-off study as is so often the case in solar cell designs. If the lithium concentration is very low, poor radiation **damage** annealing is obtained; however, initial short-circuit current values are very good. As the lithium concentration is increased, there is corresponding improvement in the room temperature annealing characteristics, but the initial short-circuit current suffers due to the decreased minority carrier diffusion length associated with the higher lithium concentration. Therefore, extremely high or low lithium concentrations are undesirable. The optimum design is being determined by empirical studies and appears to be dependent upon the particular radiation flux level anticipated. That is, the optimum cell design for a 1 Mev electron flux of  $10^{14}$  e/cm<sup>2</sup> would not be the optimum design for a **flux** of  $10^{16}$  e/cm<sup>2</sup>. The reason for this is the short-circuit current dependence on lithium concentration discussed above. For the lower flux the lithium concentration does not need to be high in order to adequately anneal out the limited defect centers produced and a high short-circuit current (and consequently a high power output) will be obtained. For the high flux level a high lithium concentration is required to compensate for the high number of defect centers formed and, consequently, a lower short-circuit current (and power) will be obtained. In either case, however, the objective is to optimize the lithium cell design so that it will provide improved radiation resistance over the conventional N on P type solar cell.



## DISCUSSION

### Cell Description

The type of cell used for the study of the effect of lithium doping on the radiation resistance of solar cells was a P /N (1 x 2) cm cell, with silver-titanium contacts. The P region was a shallow boron-diffused region about 0.3 micron deep, The N-type base region, approximately 16 mils thick, was doped to the appropriate resistivity with phosphorous or arsenic, depending on the nature of the experiment being performed. The N-type base region was also doped to various degrees with lithium by means of a controlled diffusion process.

Silver-titanium contacts, which were applied by an evaporation technique, consisted of three grid lines connected to an "isolated" corner dart-type collector on the front: P-side of the cell, and a "picture frame" (also isolated) large area contact on the back N-side of the cell (see figure 1).

The isolation of the contacts from the junction on both sides of the cell minimizes the formation of metallic shunts across the junction, and results in a more reliable and improved device. Both soldered and solderless contact cells of this type have been made. These cells have exhibited contacts with comparable quality and strength to N /P cells with silver-titanium contacts.

A flow chart which describes the process for the lithium-diffused P /N solar cells is shown in figure 2.

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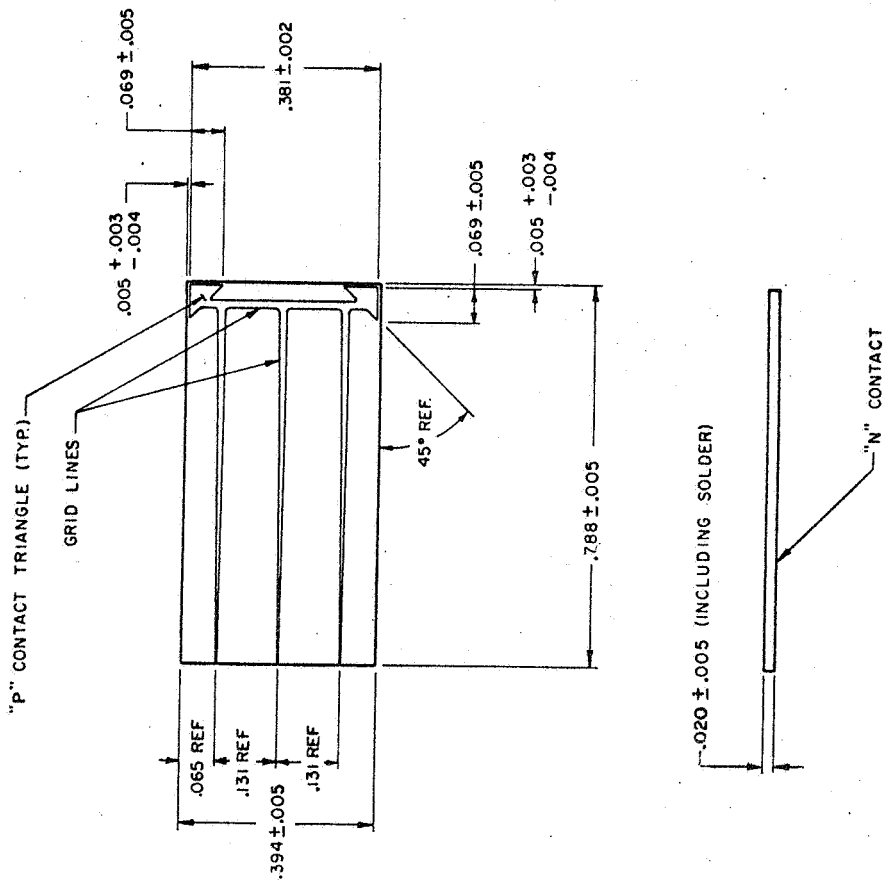
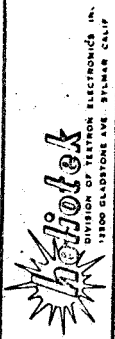
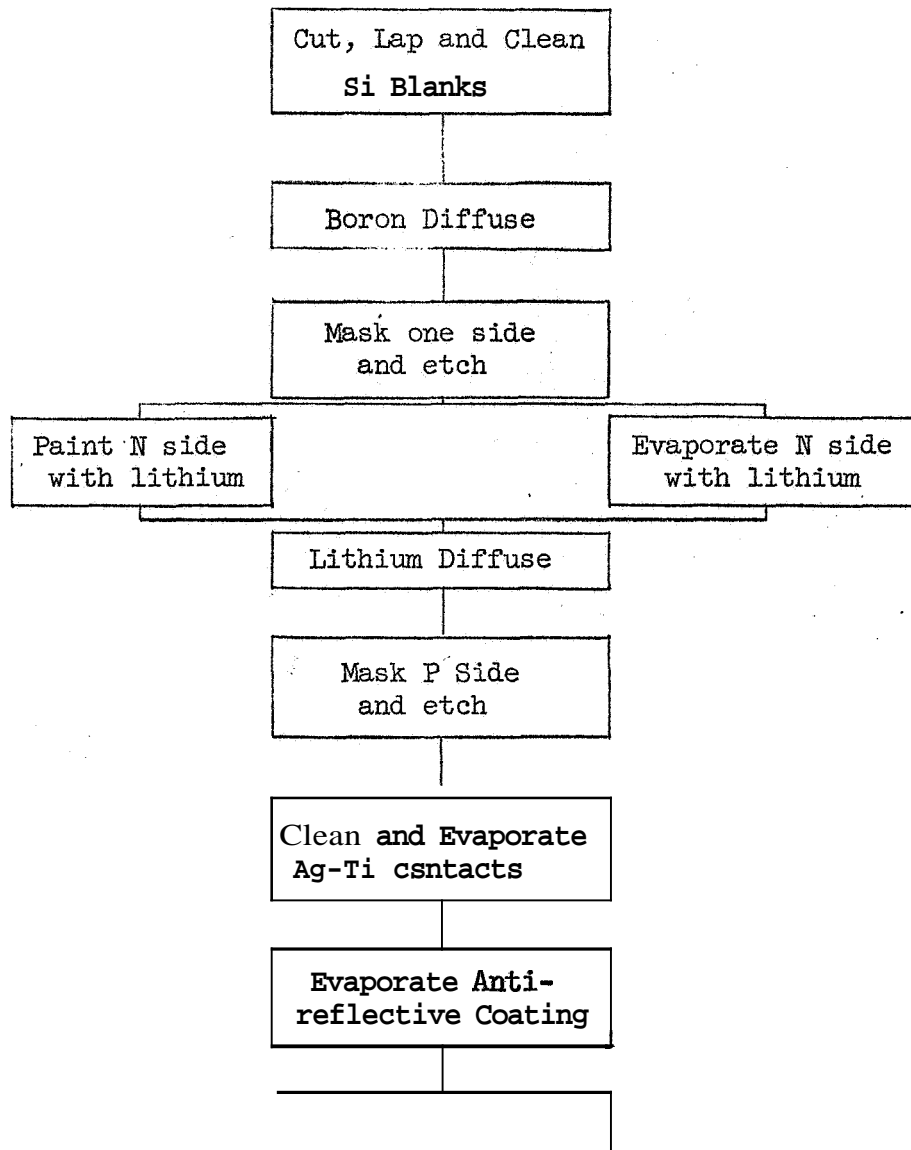


Fig. 1

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Flow Chart of Lithium Doped P<sup>+</sup>/N Process

Figure 2.

N-type silicon ingots of a particular resistivity, impurity type, lifetime, oxygen content, and growing process were used as the raw material input. Typically, N-type ingots for solar cells have been grown by the Czochralski (crucible grown) technique. For the lithium-diffused solar cell- both float zone low oxygen content material and Czochralski material have been used. The ingots were slabbed and sliced into cells blanks, using conventional silicon cutting techniques. A shallow 0.3 micron deep P-N junction was formed by the high-temperature diffusion of boron into the N-type silicon blank. A  $BCl_3$  source was used. The  $BCl_3$  source was in the liquid form under pressure and was vaporized at room temperature and atmospheric pressures. The vapor was carried to the silicon blanks, which were heated to the diffusion temperature in a multizoned furnace, by means of a slow constant flow of high purity nitrogen carrier gas. The entire diffusion operation took place within a quartz tube located within the multizoned furnace. After diffusion, the cell blanks were boiled in nitric acid. The acid attacked the boron source layer that was deposited during diffusion on the surface of the cell blanks and formed a loosely adhering residue. The residue was then brushed off the surfaces of the cell blanks, leaving a blue-black surface characteristic of this type boron diffusion. Surface concentrations were calculated from sheet resistivity and junction depth measurements using the Backenstoss<sup>4</sup> technique and Irvin's curves<sup>5</sup>.

After visual inspection the more perfect surface was masked with acid-resistant tape, and the less perfect surface was etched in a nitric-hydrofluoric acid mixture. This exposed the N-base material. The tape was then removed and the slices cleaned to insure complete removal of the tape residue.

The cells were then prepared for lithium diffusion, The lithium was applied to the surface of the N side of the cell blank in one of two ways: either a suspension of fine lithium particles in mineral oil was painted on with a brush in such a way that the lithium particles were distributed uniformly over the entire N surface, or, as an alternate procedure, lithium pellets were evaporated in a vacuum environment and a thin layer of lithium deposited onto the N surface,

After the lithium had been applied to the surface of the cells, the lithium was then diffused a prescribed length of time at a preset temperature. The various the-temperature values used are described in the diffusion experiment discussion. The diffusion took place within a quartz tube located within a constant temperature region of a single-zoned furnace, A slow constant flow of high purity nitrogen gas was maintained throughout the diffusion process to remove vapors, insure a controlled environment, and prevent rapid depletion of the lithium source by oxidation. Immediately after the diffusion, the excess unreacted lithium was removed from the surfaces of the cells by immersing them in DI water which violently reacted with the lithium.

Once the excess lithium had been removed from the surfaces of the cells, the P (boron-diffused) side of the cell was again masked with acid-resistant tape and the N surface re-etched in a nitric-hydrofluoric acid mixture. This removed excess lithium from the surface, thus making it possible to make good electrical contact to this material, Also, as a result of this etch, the P-N junction interface was cleaned so that the likelihood of low cell shunt resistance had been eliminated. The tape was removed, and the slices were again cleaned to insure complete

removal of the tape residue. The slices were then cleaned in hydrofluoric acid and placed in a mechanical mask so that the silver-titanium metal contacts could be selectively deposited onto the N and P type material surfaces in the desired contact configuration.

The cells were then cleaned, and a silicon monoxide coating having an optical thickness of about 1400 Å (a physical thickness of about 700 Å, assuming an index of refraction of 2) was deposited onto the active surface (the boron-doped layer) to provide increased light collection through minimization of the surface reflection. Subsequently, the cells were electrically tested and categorized according to conversion efficiency. This procedure was used for making all the standard Ag-Ti contact lithium-diffused P/N-type solar cells during this reporting period. Special phosphorous-diffused cell designs will be described in a separate section,

## Material Studies

All the experiments and the lithium diffused solar cells made in this program were made using single crystal silicon ingots as the starting material. In order to better understand the influence of the starting material on the resulting solar cell characteristics, several material parameters were varied. One of these variables was a comparison of the crystal growing process, Both float zone and Czochralski grown ingots were used. Also, the effect of various bulk resistivities was looked at. The dopant used in the float zone material was phosphorus and this was kept constant for all the float zone material. The Czochralski material was doped to the proper resistivities with arsenic. Various silicon supplier's material was used, in order to be able to see if the crystal growing facility had any significant effect on the material properties.

Previous studies had indicated that lithium solar cells made with float zone silicon would exhibit radiation damage annealing at room temperature while lithium solar cells made from Czochralski grown silicon would not. <sup>3)</sup> Czochralski grown silicon was used in this study to confirm these results and to possibly show a way in which Czochralski grown material could be used. For economic reasons, it would be desirable to use Czochralski (crucible grown) material in preference to the float zone material,

Czochralski grown silicon ingots with starting resistivities in the range of .2-1.2  $\Omega$  cm with arsenic dopant and undoped virgin silicon ingots  $\approx$  200  $\Omega$  cm were investigated. Float zone silicon ingots with starting resistivities of 15-25, 80-120, and  $>1000$   $\Omega$  cm, all with phosphorus dopant were also used. These different resistivities were used to evaluate the importance of resistivity as a variable in lithium cell fabrication.

Previous work on lithium doped solar cells indicated that the important factor for achieving room temperature radiation damage annealing was the oxygen content in the silicon crystal. It is well known in the semiconductor field that Czochralski (crucible grown) silicon crystals dissolve a great deal of  $\text{SiO}_2$  from the crucible during the crystal growth process. The oxygen content level is dependent on the particular process used, however, it is commonly at the  $10^{18}$  atoms/cc level. Float zone material, on the other hand, does not have molten silicon in contact with a  $\text{SiO}_2$  container during the crystal growth process. Therefore the oxygen content levels for this type material is typically about  $10^{15}$  atoms/cc. In order to try to evaluate the oxygen content in some of the silicon material being studied, samples were sent out to be analyzed by the fast neutron activation analysis technique,

Samples of both Czochralski grown and float zone silicon were analyzed. Each sample was irradiated along with an oxygen standard for 10 seconds in a 14 Mev neutron flux of approximately  $10^8$  neutrons/cm<sup>2</sup>-second, and counted for  $\text{N}^{16}$  induced activity on a single channel pulse-height analyzer, using a pair of 5" x 5" NaI (Tl) scintillation crystals. The oxygen concentration was determined by comparing the intensity of the 6.13 Mev gamma ray photopeak of  $\text{N}^{16}$  from the sample with that from the oxygen standard. (Oxygen forms  $\text{N}^{16}$  by interaction with 14 Mev neutrons via the  $^{16}\text{O}(n,p)^{16}\text{N}$  reaction,) The results of these analyses, given in Table 2-1, indicate that this type of analysis was inadequate since all the measurements were on the order of  $10^{18}$  atoms/cc and float zone silicon should have an oxygen content of approximately  $10^{15}$  atoms/cc. Furthermore, duplicate samples (#5 and 6) did not yield duplicate results, so it is questionable whether the Czochralski grown silicon with an oxygen content of approximately  $10^{18}$  atoms/cc was analyzed accurately.



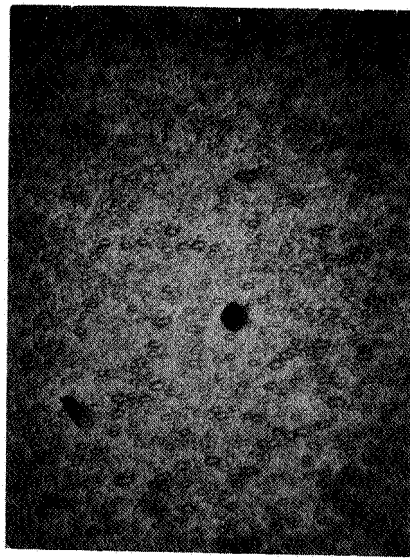
Table 1 Results of Oxygen Analysis

Sample No.	Crystal Growth Method	Starting Resistivity (ohm cm)	Weight of Sample (g)	Oxygen (atoms/cc)
1	Float zone	15-25	4.11	$\approx 2.92 \times 10^{18}$
2	Czochralski grown	200	3.50	$5.88 \pm 1.99 \times 10^{18}$
3	Float zone	15-25	2.98	$5.54 \pm 2.25 \times 10^{18}$
4	Float zone	80-120	4.76	$6.40 \pm 1.38 \times 10^{18}$
5	Float zone	16-24	3.53	$\approx 3.36 \times 10^{18}$
6	Float zone	16-24	3.70	$5.04 \pm 1.76 \times 10^{18}$

No other oxygen content analysis techniques were readily available that promised better accuracy at the  $10^{15}$  atoms/cc level, so no further work was done this period. A technique that has been considered which might give better results and may be considered in the future, is the thermal annealing technique. In this technique the oxygen is changed from a donor state to an electrically inactive state by thermal processes. The change in resistivity would then be a direct indication of the oxygen content.

Work has been initiated to determine the dislocation density in the materials being used. Dislocations, being imperfections, may produce electrical consequences in solar cells, since they produce scattering of carriers, act as recombination sites, and can generate excess carriers. Therefore, cells made from float zone silicon, which typically has a very high dislocation density, might be expected to be affected significantly

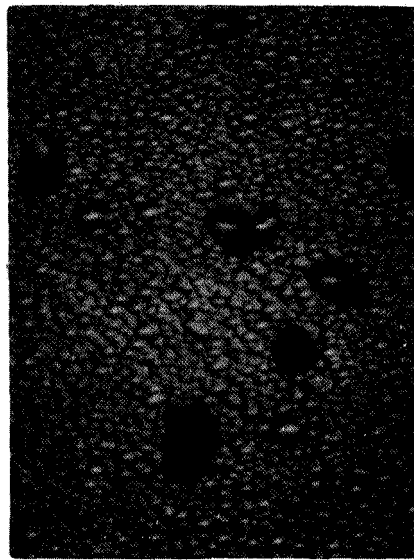
by the number of dislocations in the silicon, Preferential etching techniques were used to produce etch pits in the silicon slice, that corresponded with the dislocation, and these pits were then counted to determine the density. The cell slices were first polish-etched in HF-HNO<sub>3</sub> acid mixture and then were put in HF-HNO<sub>3</sub>HAC acid mixture to bring out the etch pits, Figures 3 through 6 are pictures of some of the material. The area shown in each picture is approximately  $4.3 \times 10^{-4} \text{ cm}^2$  at a magnification of 500 X, Figure 3 shows the etch pit pattern on a 1 ohm cm slice of Czochralski grown silicon, This region was equivalent to a dislocation density of about 2000 pits/cm<sup>2</sup>. This count was found in only certain regions of the slice. The more typical etch pit pattern for this material is illustrated by Figure 4 which is equivalent to about 16000 pits/cm<sup>2</sup>. Typical etch pit patterns for 20 and 100 ohm cm float zone silicon are shown in Figures 5 and 6, respectively, They have much higher dislocation counts than the Czochralski grown silicon. There are about 120,000 pits/cm<sup>2</sup> in the sample represented by Figure 5, and about 420,000 pits/cm<sup>2</sup> in Figure 6.



.01 cm

Dislocations in 1 cm Czochralski grown silicon  
This represents some regions of the slice

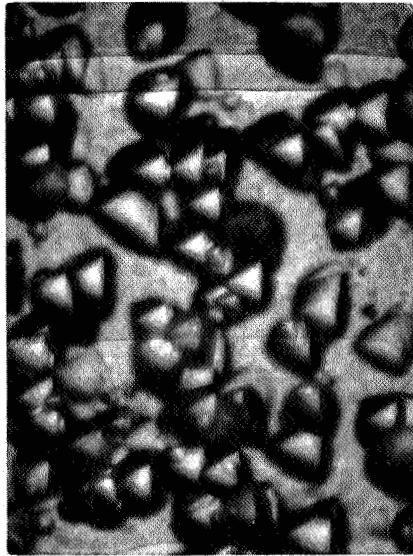
Fig. 3



| .01 cm |

Typical number of dislocations in 1 ohm cm Czochralski grown silicon

Fig. 4



| .01 cm |

Dislocations in 20 ohm cm float zone silicon

Fig. 5



$.01 \mu m$

Dislocations in 100 ohm cm float zone silicon

Fig. 6

## Diffusion Studies

A diffusion furnace was set up and a method for applying the lithium source determined. Initially, diffusions were made into nominal 10-ohm cm P-type blanks at 425°C. P-type blanks were used so that junction depths and concentration profiles of the lithium could be evaluated. A 15-minute diffusion was first used, and, by lapping through the lithium-diffused N region to the P region, it was determined that the lithium had diffused through approximately 8 mils of silicon. In a 30-minute diffusion the lithium diffused through 18 mils of silicon. In a 90-minute diffusion it diffused throughout the blank and converted it to N-type material. Incremental lapping of these lithium-diffused P-type blanks was combined with sheet-resistance measurements to give an analysis of the lithium distribution by the method used by Iles and Leibenhaut<sup>6</sup>. This method was used for evaluating the lithium concentration profile in blanks diffused for 30 and 90 minutes at 425°C.

The conductance,  $I/V$ , was plotted against the depth into the lithium-diffused region, see figure 7. From this plot the change in  $I/V$  was calculated for each .001-inch increment and plotted against the depth into silicon as  $d(I/V)/dx$  vs.  $x$ , see figure 8. At every .001-inch the  $d(I/V)/dx$  value was used to calculate  $\bar{N}\mu$ , see figure 8, according to the following equation:

$$\frac{d(I/V)}{dx} = Aq N\mu$$

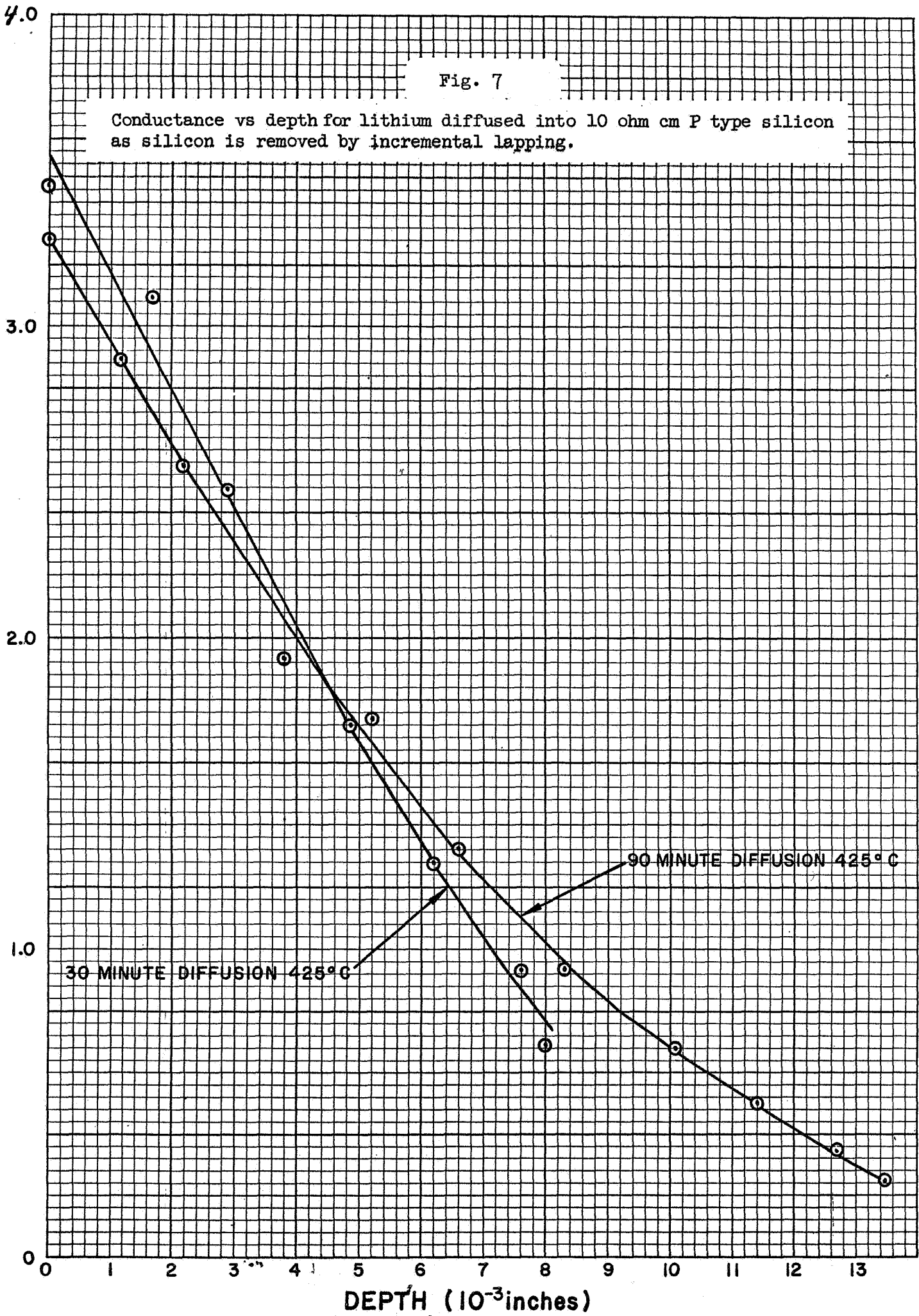
where

$d(I/V)/dx$  = change in  $I/V$  over interval  $x$ ;

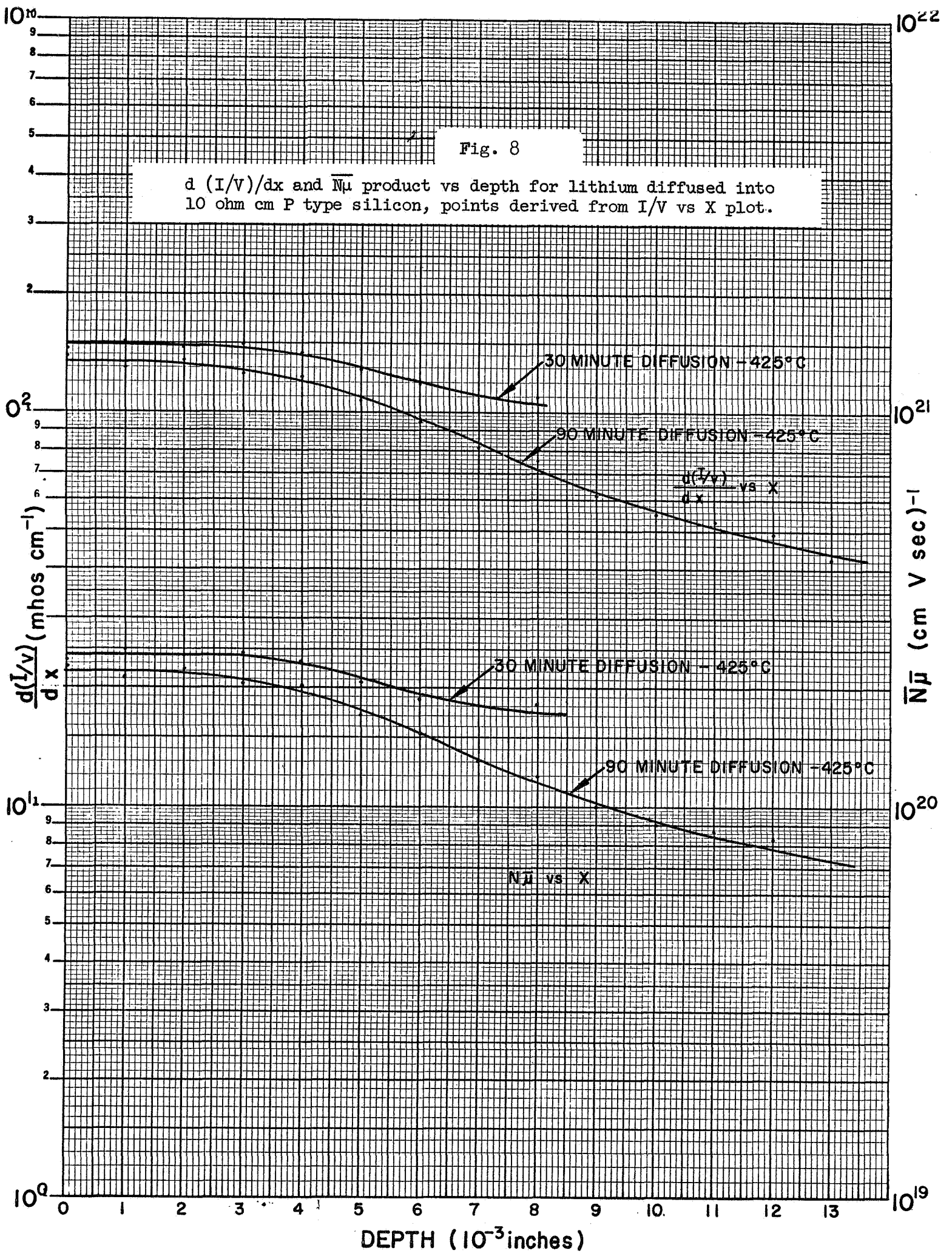
$A$  = conversion factor from Smits<sup>7</sup> for converting  $V/I$  readings to sheet resistance;

$q$  = electronic charge;

$N$  = average values of carrier concentration and mobility in the layer  $dx$ .



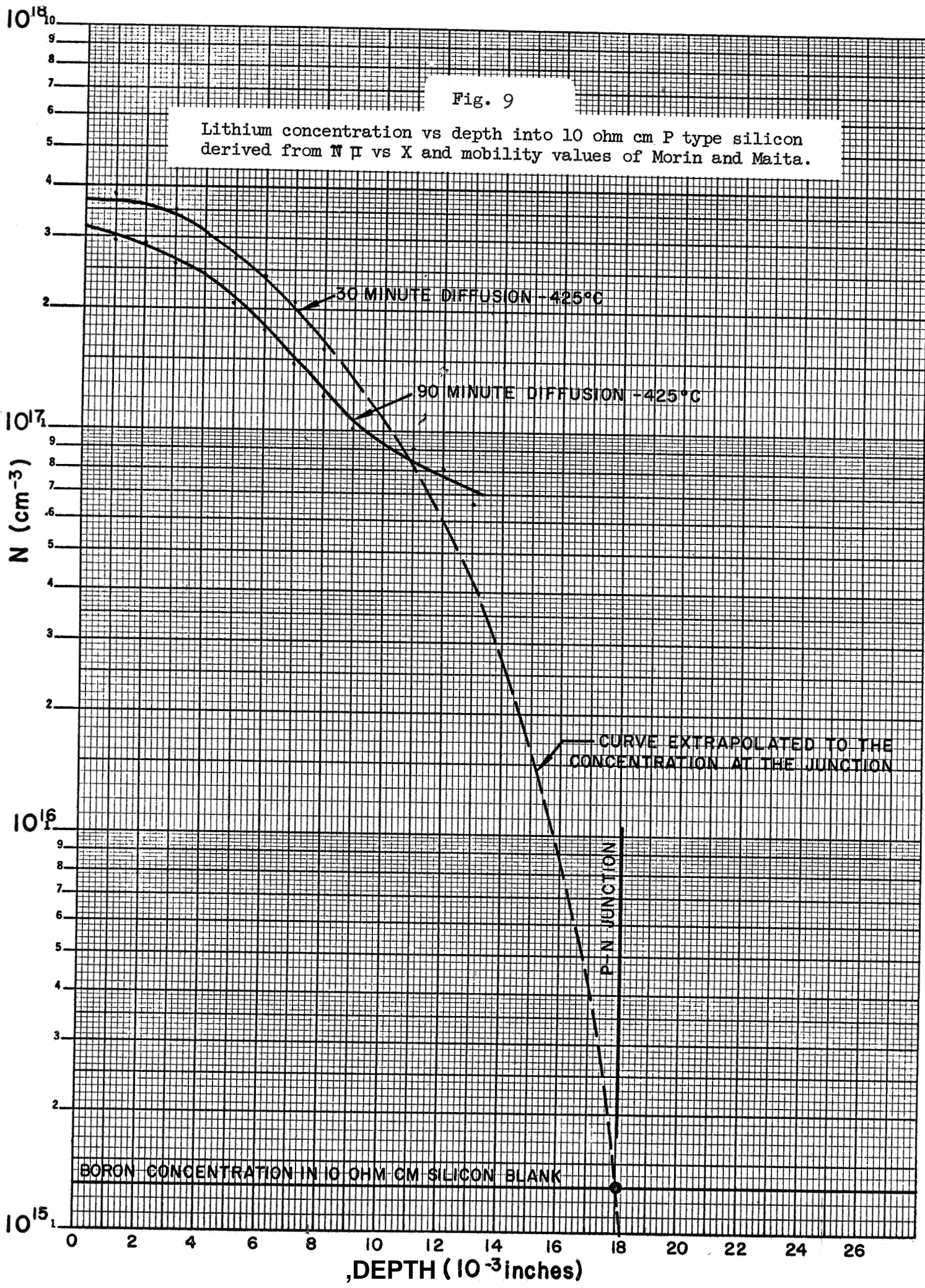




Using mobility values from Morin and Maita<sup>8</sup>, the lithium concentration,  $N$ , was then calculated, see figure 9.

The surface concentration from both diffusions was approximately  $3 \times 10^{17}$  atoms/cc. The concentration values obtained from the P-type blank which was diffused 30 minutes were actually slightly higher than those obtained from the blank which was diffused 90 minutes. This could be due to more outgassing in the longer diffusion or could be just variations in measurements since, for the same diffusion, measurements will vary this much from cell to cell. The presence of a junction of known depth in the 30-minute diffused blank made it possible to extrapolate the curve to the concentration of the background material. This was not possible in the case of the concentration curve for the 90-minute diffusion because there was no junction. The absence of a junction shows that the 10-ohm cm P-type blank was completely overcompensated indicating that the lithium concentration was much higher than  $10^{15}$  atoms/cc at the back of the diffused blank. There was a similar concentration gradient after both the 30-minute and the 90-minute diffusions near the surface; however, the longer diffusion time did result in a higher concentration at the back of the slice.

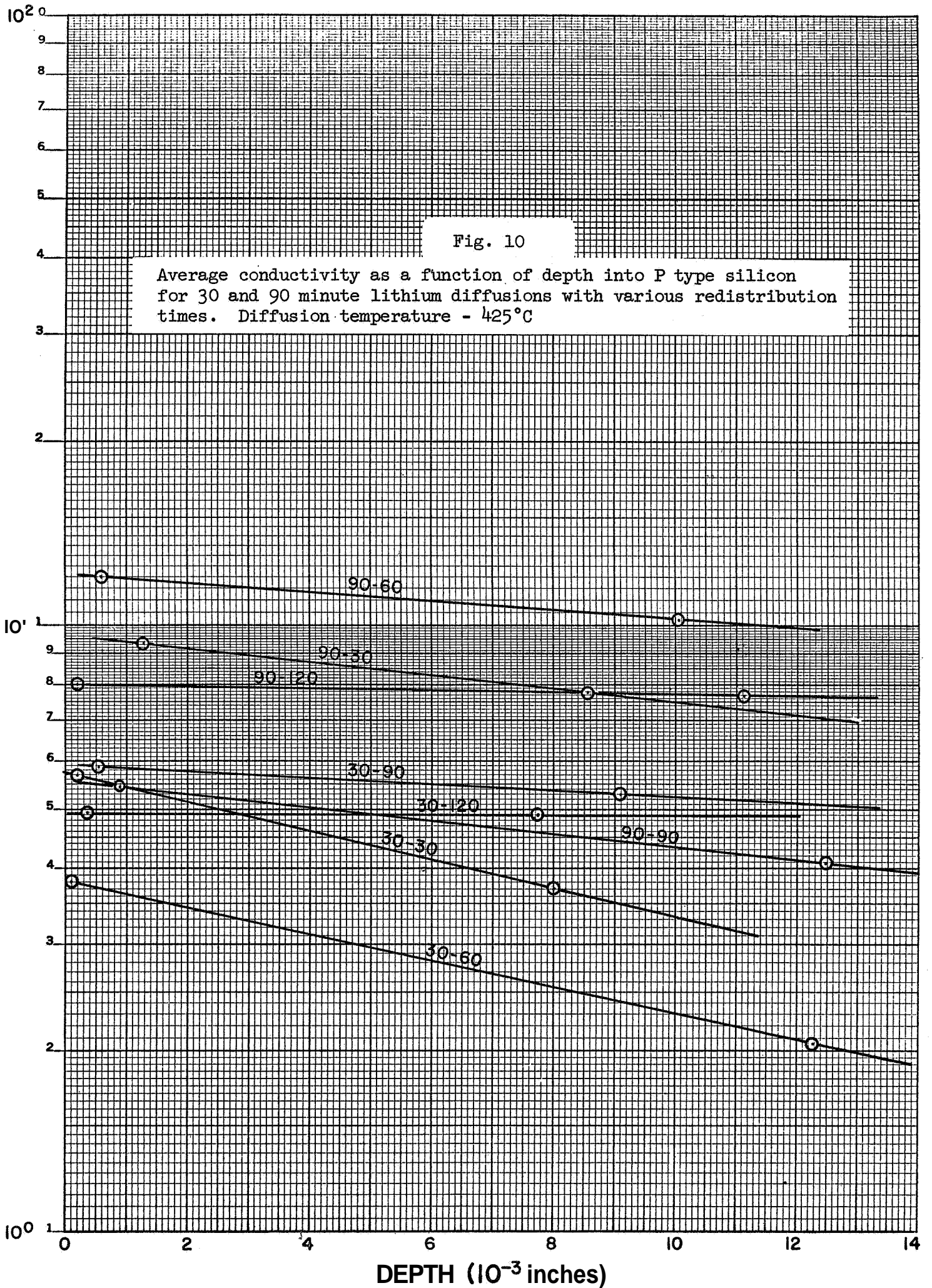
A flatter distribution of lithium was expected to be more desirable because a higher concentration of lithium in the junction region should increase the open circuit voltage. For this reason, a redistribution step was included in the lithium diffusion process. This involved removing the excess lithium from the cells after diffusion and then placing them back into the diffusion furnace for a period of time. In order to determine



what combination of diffusion and redistribution times would give the best distribution, two groups of P-type blanks- *one* diffused 30 minutes, the other diffused 90 minutes - were redistributed 30, 60, 90 and 120 minutes. Incremental lapping and V/I measurements were too time consuming for such a large experiment so, to facilitate this process, measurements were made at only two points. One was taken at the surface after slight lapping, and the second was taken at approximately the half-way point through the slice. This technique was limited because it did not show the complete shape of the concentration profile, but it did give a good indication of any changes in average conductivity and, therefore, the average lithium concentration at a particular depth into the slice, see figure 10. The blanks which had been diffused 30 and 90 minutes and redistributed 30 minutes, when compared with blanks with no redistribution, showed a slight increase in the lithium concentration half-way through the slices, but a substantial gradient was still present, The 60 and 90 minute redistributions showed more flattening of the concentration gradient, The 120-minute redistribution for both the 30 and 90 minutes showed the greatest degree of flattening, but the lithium concentration was typically lower indicating that outgassing occurred. The effect of any particular redistribution time was similar for both the 30 and the 90 minute diffusions, but the lithium concentration in the 30 minute diffused blanks was lower. The information obtained from this study indicated that a 90-minute diffusion with a 60 or 90 minute redistribution would give the best lithium redistribution without excessive lithium depletion due to outgassing,

Fig. 10

Average conductivity as a function of depth into P type silicon for 30 and 90 minute lithium diffusions with various redistribution times. Diffusion temperature - 425°C

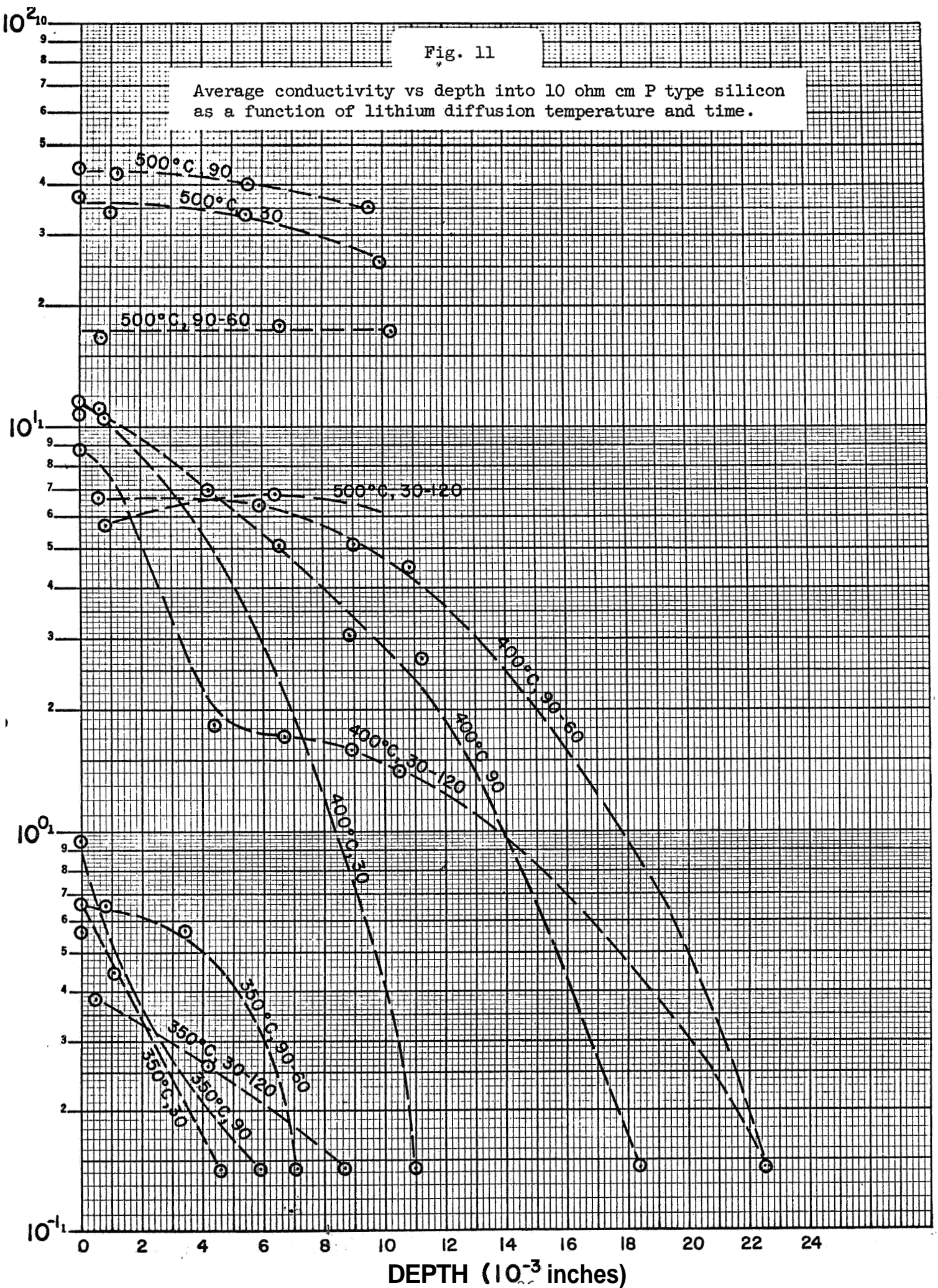


Cells fabricated using a 90-minute lithium diffusion with redistribution times of 60, 90 and 120 minutes were analyzed with respect to open circuit voltage. Redistribution generally raised the open circuit voltage approximately 10 mV, but there were no appreciable differences resulting from variations in the redistribution time.

All the above work with diffusion and redistribution times was done at a constant temperature of 425°C. The next step in the study of the diffusion process was to investigate the effects of temperature. Nominal 10-ohm cm P-type blanks were again used in the analytical work, Two diffusion processes, namely 90-minute diffusion with 60-minute redistribution, and 30-minute diffusion with 120-minute redistribution, were used at 350°, 400°, and 500°C. Incremental lapping and V/I measurements were used to calculate the average conductivity (proportional to the average lithium concentration) versus the depth into the diffused silicon as shown in figure 11. The average conductivity or concentration was a relative calculation, It did not indicate the precise lithium concentration at a known depth into the diffused slice; it was merely used as a method of evaluating relative differences in the lithium concentration. Average conductivity calculations indicated the concentration of lithium for diffusions made at 400°C was more than ten times higher than the lithium concentration for diffusions made at 350°C. Blanks diffused at 500°C had lithium concentrations about five times higher than blanks diffused at 400°C. Diffusions at 350°C drove lithium into the P-type silicon only a short distance and formed a junction at 4.6 mils depth for the 30-minute diffusion and 5.9 mils for the 90-minute diffusions, During redistribution the lithium continued to diffuse deeper into the P-type blank. The result was a deeper N region and reduced surface concentration

Fig. 11

Average conductivity vs depth into 10 ohm cm P type silicon as a function of lithium diffusion temperature and time.



values which were only slightly higher than the initial boron concentration of  $10^{15}$  atoms/cc.

The lithium concentration in the blanks diffused at  $400^{\circ}\text{C}$  was considerably higher than the concentration in those diffused at  $350^{\circ}\text{C}$ , but the lithium behaved in a similar way. After the 30 and 90 minute diffusion, junctions were again present and the redistribution process resulted in deeper junctions and slightly reduced surface concentrations. Reduction of the surface concentration can be attributed to two things: 1) the lithium diffusing deeper into the slice after the infinite source removal, and/or 2) outgassing. It appears that at  $400^{\circ}\text{C}$  the predominant movement of the lithium was into the cell rather than outgassing, This was shown by the deeper junctions and the higher lithium concentrations in the back half of the blanks. At  $500^{\circ}\text{C}$  much more outgassing seemed to occur, particularly in the 30-minute diffusion with 120-minute redistribution, After the redistribution the concentration in the first 10 mils of silicon had decreased by a factor of approximately six. The occurrence of increased outgassing was further substantiated by the electrical characteristics of fabricated cells which had been diffused and redistributed at  $500^{\circ}\text{C}$ . This will be further discussed in the next section. Outgassing also occurred in the blanks which were diffused 90 minutes and redistributed 60 minutes at  $500^{\circ}\text{C}$ . Even so, the lithium concentration was higher than the concentrations obtained in diffusions done at  $400^{\circ}\text{C}$ .

For many of the above diffusion experiments N-type silicon blanks of various resistivities and growth method were included in the diffusion runs. These blanks were used to make up lithium-doped P on N solar cells for subsequent electrical performance analysis, Resistivity measurements



were made on all the slices which were ultimately made into lithium P/N cells. Using these measurements, the average conductivity of the cells was calculated for various diffusion and redistribution times at 350°, 400°, 425°, and 500°C. A summary of this data is presented in figure 12, These measurements showed essentially the same concentration trends as those illustrated in figure 11: an increase in the lithium concentration was obtained with higher temperatures and longer diffusion times, and a decrease in the concentration was obtained when a redistribution time was added to diffusions.

These investigations of the effect of temperature and time upon the diffusion process revealed, as one would expect, that temperature was a far more important variable than time, Any significant changes in the characteristics of lithium-diffused solar cells will depend primarily upon the diffusion temperature unless the diffusion time is varied considerably.

### Electrical Characteristics

The primary method of evaluating the electrical characteristics of the solar cells fabricated was the measurement of I-V curves in an air-mass-zero solar simulator set to light level of 140 mW/cm<sup>2</sup>. The open circuit voltage normally would be expected to be a direct indication of the amount of lithium in the junction region, Consequently, this was one of the first Characteristics considered in the investigation of the effects of lithium on the finished cell. The open circuit voltage for cells made from 20-ohm cm float zone material diffused at 425°C for 30 minutes was typically between 565-570 mV which was 10-15 mV higher than

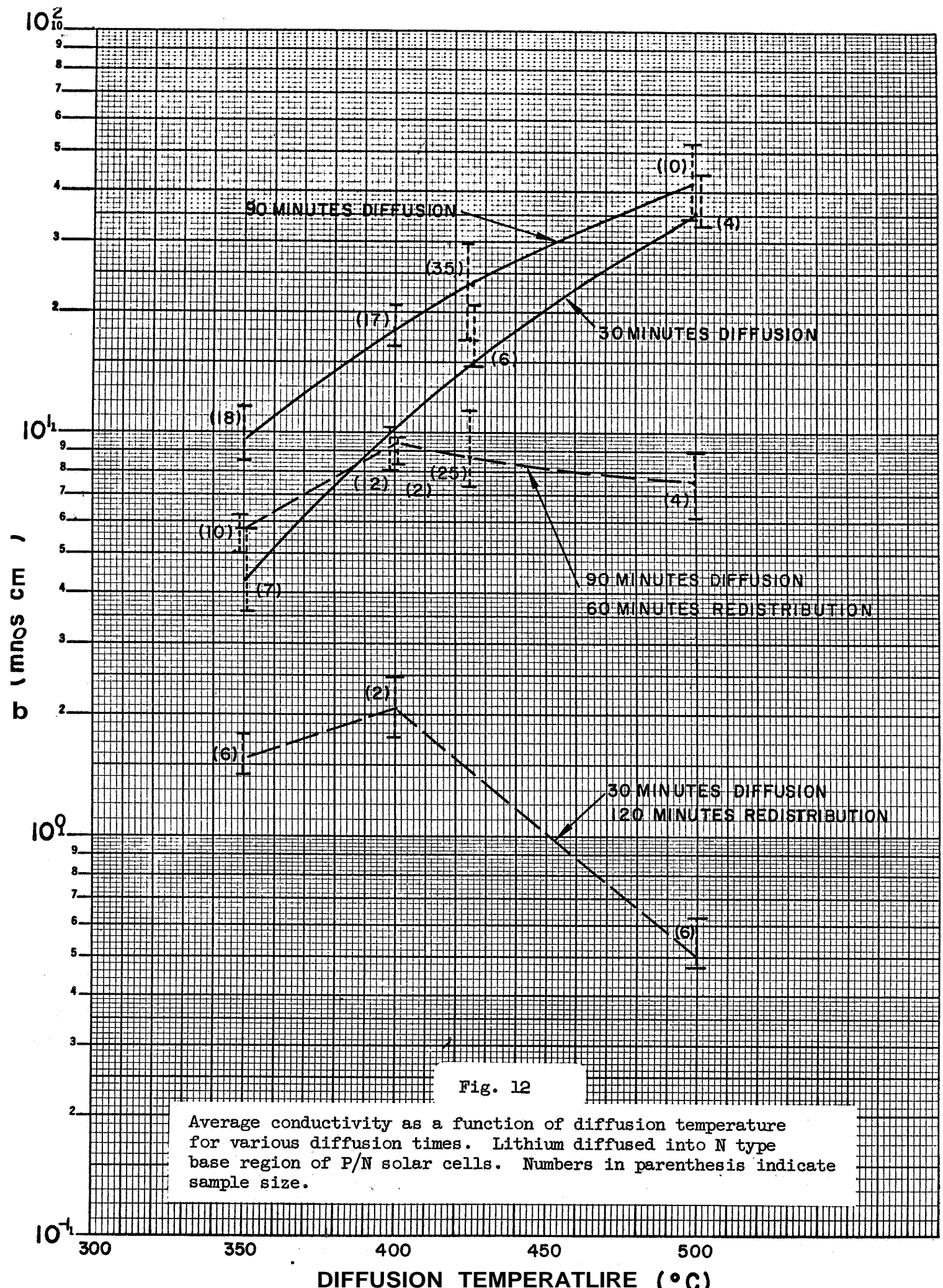


Fig. 12

Average conductivity as a function of diffusion temperature for various diffusion times. Lithium diffused into N type base region of P/N solar cells. Numbers in parenthesis indicate sample size.

similarly processed cells with no lithium, This definitely indicated that the lithium was reaching the P/N junction, decreasing the resistivity in this region, and causing the open circuit voltage to increase, A 90-minute diffusion at the same temperature increased the open circuit voltage to 570 mV, showing that more lithium was reaching the junction region. A redistribution time added to the 425°C diffusions resulted in the average open circuit voltage increasing to 581 mV.

As the redistribution time was increased from 60 to 90 or 120 minutes, the open circuit voltage showed no significant increase, A double diffusion in which the entire diffusion and redistribution process was performed twice on the same cells showed through resistivity measurements that a higher concentration of lithium was present, but there was no corresponding increase in the open circuit voltage. This effect of saturating at some open circuit voltage irrespective of the lithium concentration suggested that there was a trade-off mechanism present. The increased lithium concentration caused a decrease in minority carrier diffusion length (as short-circuit current values indicated), which is important in determining open circuit voltage, The effect of both the lithium atom concentration (donor atoms  $N_n$ ) and lifetime  $\tau$  on open circuit voltage  $V_{oc}$ , can be seen in the equations below:

$$V_{oc} = \frac{AkT}{q} \ln \frac{I_L}{I_o}$$

$$I_c = 2.25 \times 10^{20} \sqrt{qkT} \left( \sqrt{\frac{\mu_p}{\tau_p}} \cdot \frac{1}{n_n} + \sqrt{\frac{\mu_n}{\tau_n}} \cdot \frac{1}{p_p} \right) ;$$

where:

- $q$  = charge on electron
- $\mu_p$  = hole mobility in n-type region
- $\mu_n$  = electron mobility in p-type region
- $n_n$  = density of ionized excess donor atoms in n-region
- $p_p$  = density of ionized excess acceptor atoms in p-region
- $\tau_p$  = hole minority carrier lifetime in n-region
- $\tau_n$  = electron minority carrier lifetime in p-region

Increasing the lithium atom concentration indefinitely will consequently not continue to increase the  $V_{oc}$ . Another mechanism that may be involved here may be that the lithium near the junction reached a saturation point, When more lithium was pushed into the junction region by longer redistribution times or higher temperature, it did not remain there but was swept away by the built-in electrostatic field at the junction, It was not until cells were fabricated at  $350^{\circ}\text{C}$  that there was any further increase in the open circuit voltage. In these cases the lower temperature probably preserved the minority carrier diffusion length more than the high temperatures did.

The result of the lithium concentration buildup in the bulk region was a decrease in the minority carrier lifetime and, consequently, a decrease in both the short circuit current and the open circuit voltage. The diffusions at  $500^{\circ}\text{C}$  were good examples of this problem. Resistivity measurements indicated that a 90-minute diffusion at  $500^{\circ}\text{C}$  gave a higher lithium concentration than any other process investigated, yet there was little or no improvement in the open circuit voltage, and the short circuit

current was much lower than usual, When a redistribution was added to the 90-minute diffusion, resistivity measurements showed a substantial drop in the concentration. There was no corresponding drop in open circuit voltage, but the short-circuit current did increase. This would indicate that the short-circuit current rather than the open circuit voltage was the best characteristic for electrical evaluation of the concentration and effects of lithium.

Figure 13 shows the short circuit current decrease that is experienced as the diffusion temperature and lithium concentration is increased. This means that to produce a high efficiency solar cell it is undesirable to have the maximum lithium concentration. The converse is not the most desirable situation either as the radiation analyses will show. Since radiation recovery increases with the lithium concentration, it appears that a compromise between initial output and radiation recovery will have to be made, The maximum power was found to be affected by the lithium concentration in the same manner as the short circuit, i.e., the cells with the highest power were those with the highest short circuit current.

In addition to looking at the effects of various diffusion parameters, the effects of various starting materials were investigated. A comparison of the maximum power of cells made from 20-ohm cm and 100-ohm cm float zone silicon showed no significant differences between the two. In the case of the two types of Czochralski-grown silicon used, the starting resistivity did influence the maximum power output. Lithium cells were made from nominal 1-ohm cm and approximately 200-ohm cm Czochralski-grown silicon. The maximum power of 1-ohm cm cells in which lithium

SHORT CIRCUIT CURRENT MA (NASA 100 MW/cm<sup>2</sup>)

Effect of lithium diffusion time on short circuit current  
Diffusion temperature 425°C, 1 x 2 cm P/N lithium solar cells  
active area 1.94 cm<sup>2</sup>, first and second experimental cell groups

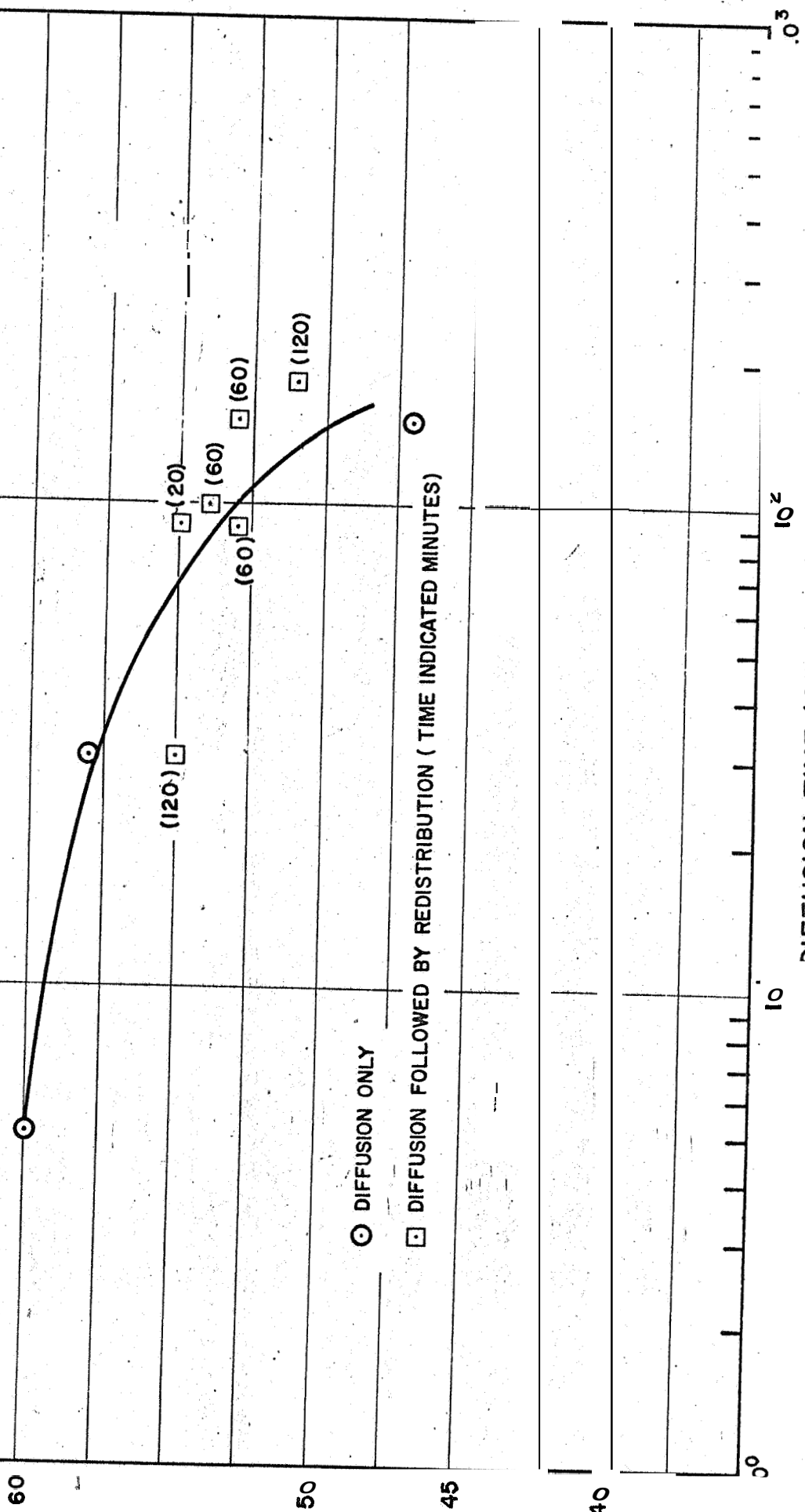


Fig. 13

had been diffused at  $425^{\circ}\text{C}$  was typically 29-30 mW in  $m = o$  simulated sunlight, while the maximum power of those made under the same conditions using 200-ohm cm starting material was approximately 22 mW due to the lower  $I_{sc}$  and  $V_{oc}$ .

Lithium cells made from .2-1.2 ohm cm Czochralski-grown arsenic doped silicon had the highest maximum power and open circuit voltage of any of the lithium cells, The high voltage was typical of the voltages obtained with standard P/N cells without lithium present. It appears that lithium alone cannot dope the silicon to a high enough level to obtain these high voltages. The lithium limitation may be due to the built-in field present or the degradation in lifetime with high lithium concentrations. More probably, the arsenic can be used to dope to the levels needed to obtain a high  $V_{oc}$  without damaging the lifetime, whereas the lithium cannot.

In order to better understand and analyze the lithium-doped P on N solar cell, a test of the cell electrical performance in simulated sunlight at various temperatures was made. The IV characteristic curves for a wide range of temperatures is shown in figure 14. An evaluation of the short-circuit current and open-circuit voltage temperature coefficients was made. The coefficient for both was constant over the complete temperature range which is not typical for standard N/P cells. (N on P cells typically deviate from a linear relationship below  $-40^{\circ}\text{C}$ .) The short-circuit current increased at a rate of  $49 \mu\text{A}/^{\circ}\text{C}$  with increasing temperature, while the open-circuit voltage decreased  $2.00 \text{ mV}/^{\circ}\text{C}$  with increasing temperature, These coefficients are the same as those obtained with P on N cells with no lithium present. The IV curves were normal at all temperatures and no distortions or anomalous behavior was observed.

In fabricating the majority of the lithium cells, the lithium was painted on in the form of a lithium-mineral oil suspension. Application of the lithium by evaporation of metallic lithium was also experimented with and used in the fabrication process for some of the cells. In general, there did not seem to be much difference in the short-circuit current or open-circuit voltages; however, the evaporated lithium cells usually had higher series resistance.

Sintering experiments done on the lithium-doped P/N solar cells have shown that the performance of the unsintered and sintered cells is essentially the same, This indicates that in contrast to the case of the N/P cell which must be sintered to obtain a good ohmic contact, sintering is unnecessary for good ohmic contact on the lithium-doped P/N cell, Contact pull tests have shown equivalent: contact strengths, and series resistance measurements also are similar, The superfluity of sintering is further substantiated by figure 14 which shows an unsintered P/N lithium-doped cell curve that exhibits a good ohmic contact even at low temperatures. Poor ohmic contacts would be expected to distort the IV curve near open-circuit voltage at very low temperatures.

### Radiation Effects

Although the primary purpose of the contract was to provide experimental lithium doped solar cells to NASA for radiation testing and analysis, it is desirable to include some discussion of the radiation effects on these cells and to provide some empirical data on the significance of the various cell designs, The introduction of lithium into P on N solar cells made from low oxygen content silicon has caused a radiation damage recovery process to exist. The lithium combines with radiation induced defect



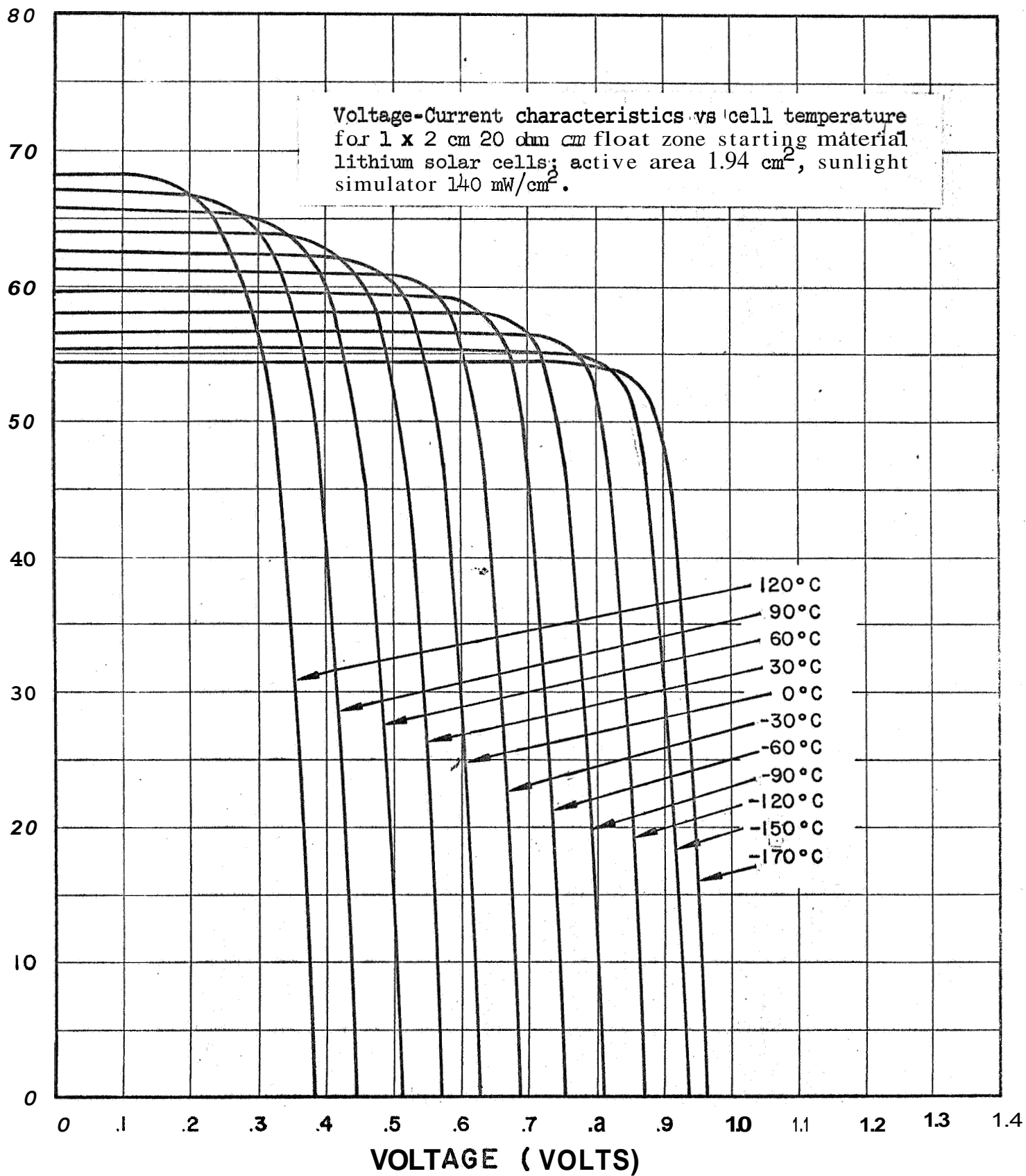


Fig. 14

centers at room temperature, thus making the defect center inactive. Studies on lithium doped P/N cells described in the preceding sections show that the higher the lithium concentration, the faster and more complete is recovery after irradiation. The investigation has also revealed, however, that fabrication of high efficiency P/N lithium diffused solar cells involves much more than getting the highest possible concentration of lithium into the solar cell.

Irradiation of lithium doped P/N solar cells by 1 Mev electrons to an integrated flux of  $1 \times 10^{14}$  e/cm<sup>2</sup> caused both the  $I_{sc}$  and the  $V_{oc}$  to degrade in a manner and degree similar to a standard P on N cell with no lithium present. When these cells were kept at room temperature for some length of time (sometimes hours or days) subsequent measurements of the electrical output showed that annealing of the radiation damage was occurring. Although cells with a very high lithium concentration had complete  $I_{sc}$  recovery, the recovery of the  $V_{oc}$  was never complete,

The first two groups of cells sent to NASA/GSFC were part of the diffusion and resistivity studies. The experiments and cells are described in detail in the Appendix, The radiation recovery of cells in each group are summarized in Figure 15.

Cells were fabricated from both float zone and Czochralski grown silicon, Thus far no way has been found for making a lithium diffused P/N cell made from Czochralski grown silicon which has room temperature radiation damage recovery after irradiation. Only lithium diffused cells made from float zone silicon show a room temperature recovery.

Effect of 1 Mev Electrons on maximum power of Heliotek lithium doped P/N solar cells. Integrated flux of  $1 \times 10^{14}$  e/cm<sup>2</sup>, cell temperature 28°C float zone silicon  $1 \times 2$  cm.

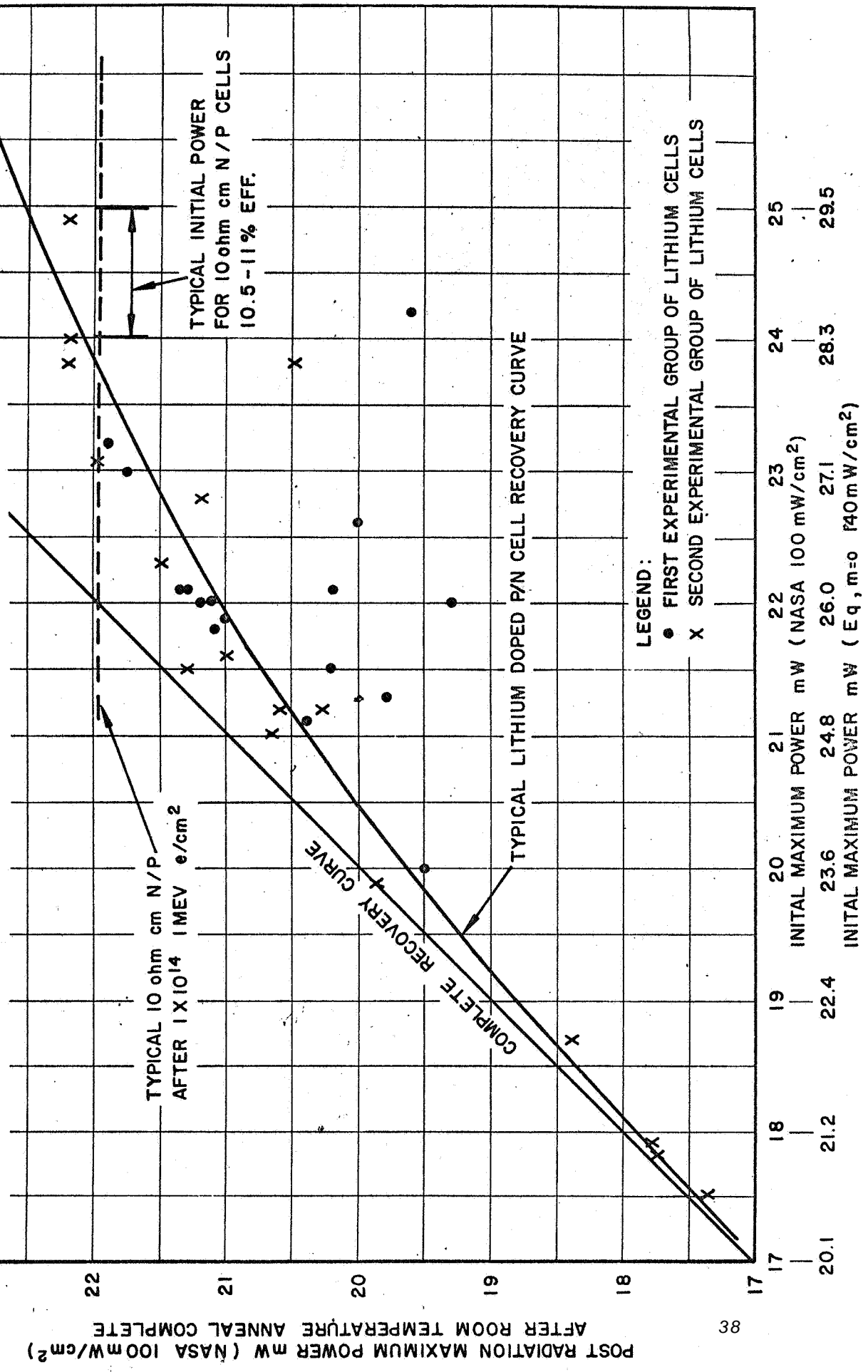


Fig. 15

All cells were irradiated with 1 Mev electrons to an integrated flux of  $2 \times 10^{14}$  e/cm<sup>2</sup> by NASA/GSFC and measurements of the cell I-V characteristic curves were made periodically over a period of about one week. Within this time period the annealing process was essentially completed and the room temperature recovery was assumed to have reached its maximum. The NASA measurements were made in a tungsten light source that was set to an intensity equivalent to 100 mW/cm<sup>2</sup> of sunlight. The correlation of the initial maximum power output in the NASA source to the Hellotek sunlight simulator set up to an equivalent intensity of 140 mW/cm<sup>2</sup> of M = 0 sunlight, is shown along the abscissa. Each lithium doped cell was plotted showing the correlation of the initial power output to the power output after irradiation and complete room temperature anneal. Although there was much scatter in the data due to the wide range of diffusion process variables used, it becomes apparent that the initially lower output cells come much closer to achieving complete recovery than do the higher output cells. Further correlation to the diffusion process shows that the lower output cells always had higher lithium concentration and the higher output cells contained less lithium. A similar analysis of these same cells at various flux levels has not been made, however, this would be very informative since a picture of the relative usefulness of all cell types would then emerge.

The first diffusion studies investigated the effect of time at a constant temperature. The sample cells made in these studies showed the following radiation recovery characteristics. The cells diffused 5 minutes did not recover indicating that not enough lithium was present. The cells diffused 30 minutes had initial maximum powers varying from 21.3-24.2 mW (NASA 100 mW/cm<sup>2</sup>), but they all recovered to approximately the same maximum power of 19.5-20 mW after irradiation (see Figure 15). The cells diffused 90 minutes

and redistributed 60 minutes started with maximum powers ranging from 21.8-23.2 mW. After irradiation they recovered to maximum powers between 21.0 and 21.9 mW. This was somewhat higher than the power recovery of cells diffused 30 minutes and indicated that the presence of additional lithium was increasing the amount of recovery. The effect of lithium concentration on the rate and amount of recovery was seen to a small degree in the cells diffused for varying lengths of time, but it became more obvious when the diffusion temperature was varied. Those cells diffused at 500°C had a very high lithium concentration and recovered almost 100% after irradiation. Those cells diffused at 350°C recovered approximately 92% of their initial power at a much slower rate. It should be noted, however, that the initial power output was much higher for the cells diffused at 350°C than for those diffused at 500°C. These recovery characteristics indicate that the optimum lithium doped cell design will require a trade-off between the initial efficiency and the radiation recovery. If the lithium concentration is very low reduced radiation damage annealing is obtained, however, the initial  $I_{sc}$  values are very good. As the lithium concentration is increased there is a corresponding increase in the room temperature annealing characteristics, but the initial efficiency of the cell is damaged by the lower minority carrier lifetime resulting from a high lithium concentration,

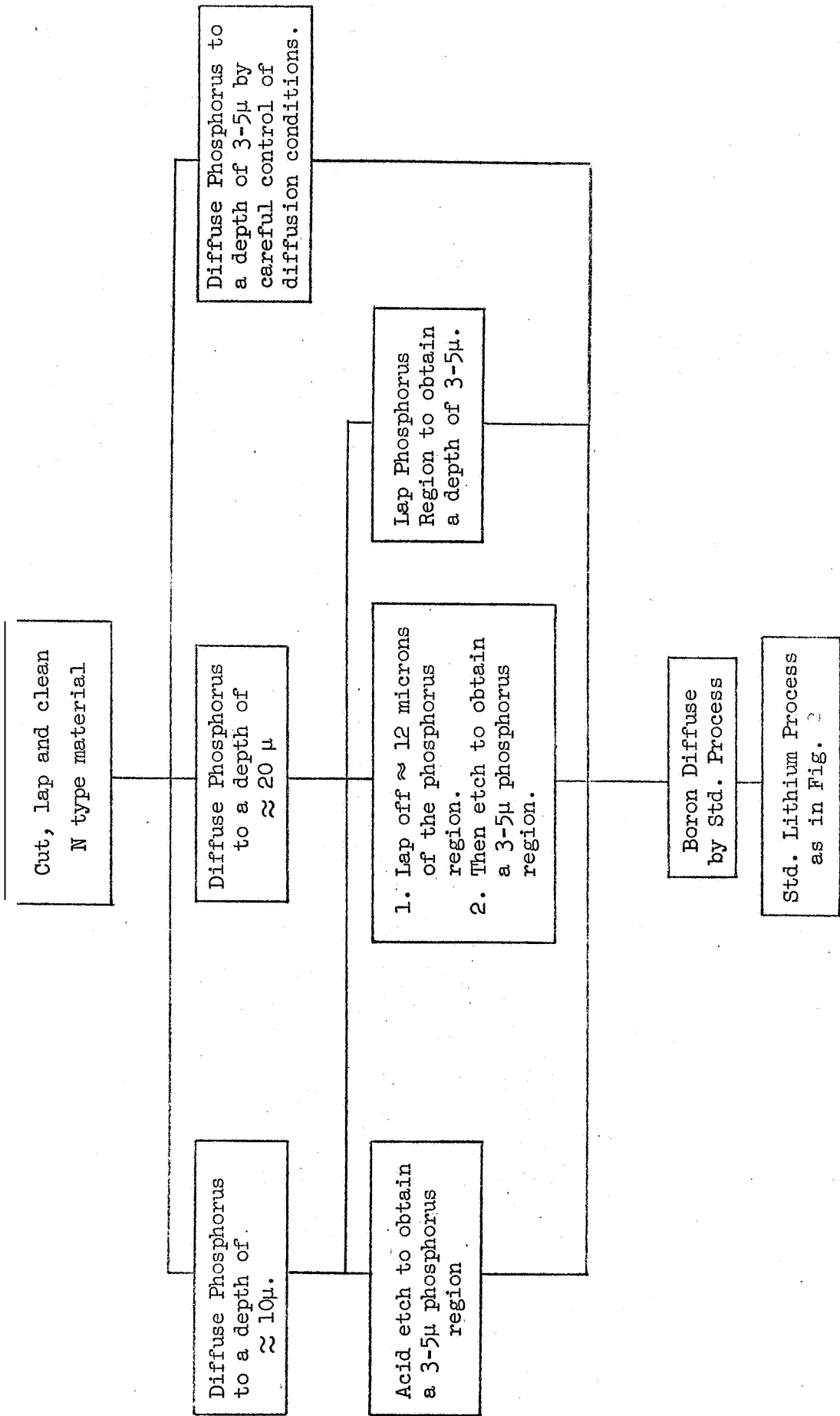
These radiation studies seem to indicate that there will not be just one kind of lithium doped solar cell which will best meet the requirement of radiation resistant high efficiency solar cells. A high lithium concentration will optimize the radiation resistance for a very high flux environment at the expense of initial power. A low concentration will provide high initial efficiencies and be optimum for a low flux environment, but the radiation

resistance is limited. A comparison of the lithium doped cells to typical 10 ohm cm, N/P cells also is made in Figure 15. The N on P cells typically start with an initial power of 28.3-29.5 mW (Eq. M = 0 140 mW/cm<sup>2</sup>) which corresponds to 24 to 25 mW in the NASA 100 mW/cm<sup>2</sup> source. After irradiation to a flux of  $1 \times 10^{14}$  e/cm<sup>2</sup>, the 10 ohm cm N on P cells would have a power output of 22 mW. Several of the lithium cells (which were diffused at 350°C) have a higher power output than 22 mW after the same flux indicating that they withstood the radiation better than the N/P cells. The initial power of these cells was high enough that even with the low lithium concentration and the lower percentage recovery the cells were able to recover to a higher power output than the N/P cells after the same flux.

#### Special Designed Lithium Cell

A special designed lithium cell was worked on that differed from the standard lithium cell in that a phosphorus region was diffused into the region near the junction. The objective of incorporating the phosphorus in the cell design was to provide a stable majority carrier concentration near the junction. This would be expected to maintain the open circuit voltage as the lithium atoms were depleted during irradiation. The phosphorus would maintain the P-N junction characteristics while the lithium would be only required for annealing out the radiation defects and preserving the minority carrier diffusion length.

The process used in making this type cell is shown in Figure 16. The phosphorus was first diffused into the silicon blank. The desired design required that a very thin phosphorus region of about 3 microns depth was to be diffused into the cell surface. Depending on the diffusion process used, a thickness alteration step was used. Boron was then diffused into the phosphorus region to form the P-N junction and from there on the process remained the same as used for the standard lithium cell.



Process Diagram for Fabrication of the Special Design Lithium Cell with Phosphorus in the Junction Region

Fig. 16

Several phosphorus diffusion processes were evaluated. In one process a standard solar cell phosphorus diffusion ( $\approx 0.3$  micron penetration) was made and then the diffusion was extended for 24 hours at  $1055^{\circ}\text{C}$ . After the 24-hour phosphorus diffusion the junction depth was measured and determined to be  $\approx 10$  microns. Since the cell design goal was about a three-micron phosphorus region it was necessary to remove some of the silicon at the surface. This resulted in a reduced surface concentration as well as reducing the phosphorus region to the desired thickness. This approach seemed desirable for two reasons: 1) too high a phosphorus concentration being present could create too many recombination centers and therefore decrease the diffusion length in the region where the junction was to be formed, and 2) with a lower phosphorus surface concentration the boron could more easily overcompensate and form a good P-N junction.

Several P-type blanks along with the material to be used in making the special cells, were always included in each phosphorus diffusion. They were used for analytical tests and were etched in increments to determine the proper etching procedure and time needed to obtain a phosphorus region depth of approximately 3 microns. This process proved to be very critical and difficult to control because of the difficulty in getting reproducible etching from slice to slice. The resulting phosphorus region depths ranged from 3 to 8 microns. These variations resulted in concentrations ranging from  $10^{17}$  to  $10^{19}$  atoms/cc and the phosphorus region was occasionally completely removed, thus destroying the cell.



It was decided that the above problems could be minimized by using a deeper diffusion. A deep diffusion made the phosphorus concentration gradient more gradual making it easier to etch to a specific phosphorus concentration. At the same time variations in the depth of the region would be less critical and slight errors in the amount of material removed would not cause large cell design changes. For the special lithium cells made by this method phosphorus was diffused into 1000 ohm cm float zone, 200 ohm cm and 10 ohm cm P type Czochralski grown slices to a depth of  $\approx 20$  microns. After the diffusion some of the cells were etched in a solution of HF-HNO<sub>3</sub>-HAC acids. This acid solution etched the edges of the cells faster than the center, thus leaving a higher concentration of phosphorus in the center of the cell and little or none at the edges. Hot NaOH was found to be superior for etching since it produces a more uniform etch. This worked particularly well for the P type control blanks and the 200 ohm cm Czochralski grown slices. In the case of the 1000 ohm cm float zone slices some difficulty was experienced since the faces etched very slowly while the edges of the slices etched down more rapidly. The variation in the etch rates was a result of the different crystal orientation. The Czochralski grown material was cut in the  $\langle 100 \rangle$  plane and float zone material in the  $\langle 111 \rangle$  plane. The  $\langle 111 \rangle$  plane etched much slower than any other plane. The NaOH etch was therefore not suitable since much of the material to be investigated had  $\langle 111 \rangle$  orientation.

An alternate method investigated for removing the proper portion of the phosphorus diffused region was to lap about 12 microns off both sides of the cells. The purpose of lapping was to obtain better control of the amount of material removed and at the same time maintain flatness. Following the lapping an acid etch was used to remove a small amount of material to

clean up the surface and **remove the damaged** silicon region. This process gave **limited** success since the acid did not always etch the lapped surface evenly. **As** a result the etching **time** had to be determined by the regions which etched fastest and the etching was stopped before all the phosphorus diffused region was **removed** in these areas. The result was a higher **con-**centration **than** desired ( $10^{19}$ - $10^{20}$  atoms/cc) **over most** of the cell, with **same** areas of **low** concentration.

**On** several cells the phosphorus region depth was reduced **to** approximately 5 microns by lapping and **no** etch was used, The phosphorus concentration ranged **from**  $10^{17}$ - $10^{20}$  on these lapped cells.

Since the phosphorus concentration and depth were **so** difficult **to** control when lapping and/or etching methods were used, **a** third approach was used. **In** the case **no** material was removed, and **instead** the phosphorus diffusion **was** controlled such that **a** phosphorus region thickness **of** about 3-1/2 microns was obtained. This method resulted **in** higher phosphorus concentration, but **did** provide **a** reproducible process and a consistent phosphorus region thickness. Once the **proper** depth of phosphorus was obtained the cells were boron diffused, The boron diffusion **did** overcompensate the phosphorus and **formed** a good junction **contrary to** the original concern in this regard. Lithium was then diffused **90 minutes** and redistributed **60 minutes** at  $425^{\circ}\text{C}$  and the cell **processed in** the **normal** manner **from** this **point on.**

Whether the phosphorus was diffused **to** exactly the proper depth **or** diffused deeper and then lapped and/or etched **to** the proper depth **did not seem to** affect the short circuit current significantly. But the open circuit voltage **of** the lapped and etched cells was **sometimes** 10-40 mV lower than that **of** the cells **in** which the phosphorus had been diffused to exactly 3-1/2 microns. The yield of good power output cells was also much better for those cells which **did not** have **to** be lapped and/or etched.

The **phosphorus** concentration was very critical in determining electrical characteristics of these special cells. In order to evaluate the effect of the presence of the phosphorus region, three types of cells were made from the 1000 ohm cm float zone silicon for comparison with the special designed phosphorus cells. Type 1 cells were made just as any P/N cell, N type 1000 ohm cm slices were boron diffused, then contacts were applied, Type 2 cells were made by diffusing **phosphorus** to a 3-1/2 micron depth following this with a boron diffusion: then **contacts** were applied. Type 3 cells were made **like** the normal lithium cell, The N type slices were first boron diffused, then lithium diffused and **contacts** were applied. Comparison of Type 1 and 2 cells showed that the presence of the phosphorus region in a P/N cell without lithium improved the  $I_{sc}$  by 4.5 mA and the  $V_{oc}$  by 30 mV. Type 3 cells, P/N lithium cells of 1000 ohm cm float zone silicon, differed **from** the special design cells in that they did not have a phosphorus region, yet the  $V_{oc}$  of the two types was the same (559 mV). The  $I_{sc}$  of the special design cells with both phosphorus and lithium present was approximately 5 mA lower than those **lithium** cells without the phosphorus region. This indicated that between the lithium and phosphorus, the Concentration of N type donor was too high and was decreasing the diffusion length, the  $I_{sc}$  and possibly the  $V_{oc}$ . This could be the reason why the  $V_{oc}$  of the special design cell was no better than that of the type 3 cell which had **no phosphorus region**.

Irradiation of these special design cells has shown some interesting results. The special cells fabricated from 1000 ohm cm float zone silicon and irradiated to a flux of  $10^{15}$  e/cm<sup>2</sup> recovered to less than 75% of their

initial power output, however, they did maintain their curve shape. In comparison, a standard lithium doped P/N cell would lose its sharp knee and the curve shape would be very poor under the same conditions. Those cells made from the same material which were irradiated to a flux of  $10^{14}$  e/cm<sup>2</sup> recovered to 95% of their original power output. The cells made from 200 ohm cm Czochralski grown silicon, when irradiated to a flux of  $10^{14}$  e/cc showed negligible recovery of the  $I_{sc}$ , as would be expected for Czochralski grown material, but the  $V_{oc}$  did show recovery which was comparable to that of cells made from float zone silicon,

## PROGRAM FOR NEXT REPORT INTERVAL

**Work** will continue on analysis of the materials being used **and various** diffusion parameters. **Lopez** silicon will also be included in the diffusion studies, More extensive work will be done on various diffusion temperatures, Work will also continue on the special design lithium cell with phosphorus in the junction region, This will include investigating methods **of** lowering the phosphorus concentration in order **to** minimize lifetime damage,

Fabrication of sample cells will **continue!** and these will be sent: to **NASA/GSFC** for radiation analysis,

## CONCLUSIONS

The experience during this reporting period has **shown** that high efficiency lithium doped P on N solar cells can be made. These cells can be made by processes that are straightforward, controllable and reproducible. A wide range of variables have been investigated and experimental solar cells representative of these variables have been fabricated and submitted to NASA/GSFC for radiation testing and analysis.

The radiation studies to date have shown several **significant** things, **some** of which are verifications of previous knowledge while others **bring** new knowledge. The comparison between Czochralski (crucible grown) and float zone (low oxygen) material has reconfirmed the need for using low oxygen content material in making lithium doped solar cells in order **to** see the **room** temperature annealing effect. A special, design lithium cell (containing a phosphorus diffused region) made from Czochralski material has shown the unusual behavior of annealing **so** that the  $V_{oc}$  improves (not the  $I_{sc}$ , however) after irradiation. Comparisons of the resistivity of the starting material shows no preference in all cases where the predominant donor atom in the finished cell **is** the lithium. Radiation studies have shown that the  $I_{sc}$  can be **completely** recovered to its original value if enough lithium has been placed **in** the crystal to **compensate for the number** of defect centers formed. The  $V_{oc}$  does **not completely recover, however**, which would indicate that lithium atoms (donor atoms that determine the resistivity and consequently the  $V_{oc}$  in this device) are being used up in defect center reactions, thus resulting **in** a gradual increase in the base region resistivity and consequently a decrease in  $V_{oc}$ . Increasing the

lithium concentration **to high** levels **has** reduced the initial short circuit current output **so** that the net effect **is** a **self limiting situation**. That **is**, **as** the radiation recovery **properties** are improved **with** increased lithium concentrations, **there is** a decrease **in I<sub>s</sub>**, associated with it. This indicates that a **trade-off** study must be made **to optimize the two** before the true value of the lithium doped P on N cell can be determined,

For the fairly low flux level of  $1 \times 10^{14}$  e/cm<sup>2</sup> that has been evaluated thoroughly, the experiments to date indicate that there are several P on N lithium cell designs that have comparable or improved cell output over that expected from a standard 10 ohm cm N on P solar cell,

Although the work on the special design cell containing a phosphorus diffused region has not been very comprehensive to date, it has been shown that at very high flux levels (about  $10^{15}$  e/cm<sup>2</sup> or greater) this type cell preserves its I-V curve shape while the standard lithium cell curve is badly degraded even to the point of appearing as a straight line due to the lithium removal process.

## BIBLIOGRAPHY

1. NASA Contract Report, "Radiation Damage in Silicon," N. Almeleh, et al, RCA Laboratories, Final Report, 15 October 1963 to 15 October 1964, NAS5-3788, NASA Goddard Space Flight Center,
2. Wysocki, J.J., et al, "The Effect of Lithium on Radiation Damage in Solar Cell Devices," Proc ■ Fifth Photovoltaic Specialists Conference, Vol. II, 19 October 1965,
3. NASA Contract Report, "Analysis of Radiation Damage in Silicon Solar Cells and Annealing or Compensation of Damage by Impurities," B. Golstein, et al, RCA Laboratories, NAS5-9131, Final Report, 7 January 1964 to 21 April 1966, NASA Goddard Space Flight Center.
4. Backinstoss, G., "Evaluation of the Surface Concentration of Diffused Layers in Silicon," Bell System Technical Journal, Vol. 37, p 699-718, May 1958.
5. Irvin, J., "Effective Conductivity of Diffused Layers," Bell System Technical Journal, 1962.
6. Iles, P. A., and (the late) B. Leibenhaut, "Solid State Electronics," 5, p 331-339, 1962,
7. Smits, F.M., "Bell System Technical Journal: 37, p 13-20, 1958,
- 8, Morin, F.J., and 3,P ■ Maita, Physical Review, 97, p 1521-1525, 1955,



APPENDIX

Description of Experiments Studied in First Group of  
Solar Cells Sent to NASA/GSFC

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Diffusion Temperature = 425°C

Diffusion Experiment 1

Purpose: To study effects of various diffusion times on 20 ohm cm float zone material.

1. F. Z.	20 ohm cm	5 minute diffusion	41, 42
2. F. Z.	20 ohm cm	30 minute diffusion	30, 106
3. F. Z.	20 ohm cm	150 minute diffusion	73

Diffusion Experiment 2

Purpose: To study effects of redistribution on varying diffusion times.

1. F. Z.	20 ohm cm	30 min. diff.	120 min. redist.	52
2. F. Z.	20 ohm cm	90 min. diff.	60 min. redist.	58, 60
3. F. Z.	20 ohm cm	90 min. diff.	120 min. redist.	53
4. F. Z.	20 ohm cm	100 min. diff.	60 min. redist.	61
5. F. Z.	20 ohm cm	150 min. diff.	60 min. redist.	76

Diffusion Experiment 3

Purpose: To look for any changes resulting from repeating of the entire diffusion and redistribution process, i.e., the lithium diffusion and redistribution process was performed twice on the same cells.

1. F. Z.	20 ohm cm	90 min. diff. (twice)	60 min. redist. (twice)	100, 103
2. F. Z.	20 ohm cm	90 min. diff.	60 min. redist.	95, 97

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Resistivity Experiment 1

Purpose: To study the effect of starting material resistivity when no redistribution is used.

1. F. Z.	20 ohm/cm	30 min. diff.	106
2. F. Z.	100 ohm cm	30 min. diff.	107, 109

### Resistivity Experiment 2

Purpose: To study effect of starting material resistivity when diffusion and redistribution are used.

1. F. Z.	20 ohm cm	90 min. diff.	60 min. redist.	89,90
2. F. Z.	100 ohm cm	90 min. diff.	60 min. redist.	87,88

### Resistivity Experiment 3

Purpose: To study effect of starting material resistivity of Czochralski grown material when both diffusion and redistribution are used.

1. C. G.	1 ohm cm	90 min. diff.	60 min. redist.	56, 47
2. C. G.	200 ohm cm	90 min. diff.	60 min. redist.	91,92
3. F. Z.	20 ohm cm	90 min. diff.	60 min. redist.	95,97

### State-of-the-art cells

F. Z.	20 ohm cm	90 min. diff.	60 min. redist.	49, 55, 59, 78, 96
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LITHIUM DIFFUSED P/N SOLAR CELLS

Cell No.	Starting Material Resistivity Nominal (ohm cm)				Crystal Growth Method		Diffusion Time Minutes					Redistribution Time	
	1	20	100	200	F.Z.	C.G.	5	30	90	100	150	60	120
30		x			x			x					
41		x			x		x						
42		x			x		x						
47	x					x			x			x	
49		x			x				x			x	
52		x			x			x					x
53		x			x				x				x
55		x			x				x			x	
56	x					x			x			x	
58		x			x				x			x	
59		x			x				x			x	
60		x			x				x			x	
61		x			x					x		x	
73		x			x						x		
76		x			x						x	x	
78**		x			x				x			x	
87			x		x				x			x	
88			x		x				x			x	
89		x			x				x			x	
90		x			x				x			x	
91				x		x			x			x	
92				x		x			x			x	
95		x			x				x			x	
96		x			x				x			x	
97		x			x				x			x	
100		x			x				x*			x*	
103		x			x				x*			x*	
106		x			x		x						
107			x		x		x						
109			x		x		x						

\*Diffusion and redistribution process performed twice on same cell.

\*\*Cell at  $\approx 200^{\circ}\text{C}$  for 105 minutes prior to diffusion.

DESCRIPTION OF EXPERIMENTS STUDIED IN SECOND  
GROUP OF SOLAR CELLS SENT TO NASA/GSFC

Diffusion Experiments

Purpose: To study effects of various oven temperatures on several diffusion processes.

Diffusion temperature - 350° C

1. F.Z.	20 ohm cm	90 min diff., 60 min. redist.	134, 135
2. F.Z.	20 ohm cm	30 min diff., 120 min. redist.	114, 144

Diffusion temperature - 400° C

1. F.Z.	20 ohm cm	90 min. diff., 60 min. redist.	116, 118
2. F.Z.	20 ohm cm	30 min diff., 120 min. redist.	119, 120

Diffusion temperature - 500° C

1. F.Z.	20 ohm cm	90 min diff., 60 min. redist.	124
2. F.Z.	20 ohm cm	30 min diff., 120 min. redist.	125
3. F.Z.	20 ohm cm	90 min diff.	152, 153

Resistivity Experiments

Purpose: To compare 20 and 100 ohm cm F.Z. material at various temperatures using several diffusions.

Diffusion temperature - 350° C

1. F.Z.	20 ohm cm	90 min diff., 60 min. redist.	137, 138
2. F.Z.	100 ohm cm	" "	140, 141
3. F.Z.	20 ohm cm	30 min diff., 120 min. redist.	142, 144
4. F.Z.	100 ohm cm	" "	146

Diffusion temperature - 500° C

1. F.Z.	20 ohm cm	90 min diff., 60 min. redist.	124
2. F.Z.	100 ohm cm	" "	121, 122
3. F.Z.	20 ohm cm	30 min diff., 320 min. redist.	125
4. F.Z.	100 ohm cm	" "	328
5. F.Z.	20 ohm cm	90 min diff	152, 153
6. F.Z.	100 ohm cm	"	149, 150

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LITHIUM DIFFUSED P/N SOLAR CELLS

Second, Group of Cells Sent to NASA/GSFC

Cell no.	initial Resistivity (ohm cm) and Crystal Growth Method			Diffusion Time Minutes		Redistribution Time Minutes		Oven Temperature °C		
	20	100	F.Z.	30	90	60	120	350	400	500
14	X		X	X			X	X		
16	X		X		X	X			X	
18	X	**	X		X	X			X	
19	X		X	X			X		X	
20	X		X	X			X		X	
21		X	X		X	X				X
22		X	X		X	X				X
24	X		X		X	X				X
25	X		X	X			X			X
28		X	X	X			X			X
34	X		X		X	X		X		
35	X		X		X	X		X		
37	X		X		X	X		X		
38	X		X		X	X		X		
40		X	X		X	X		X		
41		X	X		X	X		X		
42	X		X	X			X	X		
04	X		X	X			X	X		
46		X	X	X			X	X		
49		X	X		X					X
50		X	X		X					X
52	X		X		X					X
53	X		X		X					X





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EMpire 5-6301, Area Code 213

TWX No. 213 464-5978

12500 GLADSTONE AVE., SYLMAR, CALIFORNIA

*Manufacturer of Space Age Solid State Devices*

### Description of Fourth Group of Cells

sent: to NASA/GSFC

4 January 1967

These cells were diffused with phosphorus to a depth of approximately 10 microns and then etched down to reduce the junction depth and the surface concentration. Boron was diffused in on top of the phosphorus and then lithium was diffused into the back for 90 minutes and redistributed 60 minutes at 425°C.

Cells 210 and 211 were fabricated from 200 ohm cm Czochralski grown material and cells 213, 214, 216 and 218 from 1000 ohm cm float zone material.



LITHIUM DIFFUSED P/N SOLAR CELLS

Cell No.	Starting Material Resistivity Nominal (ohm cm)				Crystal Growth Method		Diffusion Time Minutes					Redistribution Time Minutes	
	1	20	100	200	F.Z.	C.G.	5	30	90	100	150	60	120
	30		X			X			X				
41		X			X		X						
42		X			X		X						
47	X					X			X			X	
48		X			X				X			X	
52		X			X			X					X
53		X			X				X				X
55		X			X				X			X	
56	X					X			X			X	
58		X			X				X			X	
59		X			X				X			X	
60		X			X				X			X	
61		X			X					X		X	
73		X			X						X		
76		X			X						X	X	
78		X			X				X			X	
87			X		X				X			X	
88			X		X				X			X	
89		X			X				X			X	
90		X			X				X			X	
91				X		X			X			X	
92				X		X			X			X	
95		X			X				X			X	
96		X			X				X			X	
97		X			X				X			X	
100		X			X				X			X	
103		X			X				X			X	
106		X			X			X					
107			X		X		X						
109			X		X		X						

\*Diffusion and redistribution process performed twice on same cell.  
 \*\*Cell at  $\approx 200^{\circ}\text{C}$  for 105 minutes prior to diffusion.

HELIOTEK

Description of Experiments  
for

Date: 2/8/67

Fifth Group of P/N Li Cells Sent to NASA/GSFC

1. Cells with a deep diffused phosphorus region ( $\approx .7$  mil) which was then lapped and etched to approximately 3 microns. 1000 ohm cm float zone 90 minute diffusion, 60 minute redistribution  $-425^{\circ}\text{C}$ , 220
2. Cells in which phosphorus was diffused to depth of 3-5 microns:  
1000 ohm cm float zone, 90 minute diffusion, no redistribution  $-425^{\circ}\text{C}$  235, 236, 237, 240, 241.  
1000 ohm cm float zone, 90 minute diffusion, 60 minute redistribution  $-400^{\circ}\text{C}$  244, 245.  
1000 ohm cm float zone, 90 minute diffusion, 60 minute redistribution  $-350^{\circ}\text{C}$ , 247, 249, 251, 252 .

Study of Li evaporation instead of paint-on technique;

1. 20 ohm cm float zone, 90 minute diffusion, 60 minute redistribution  $-425^{\circ}\text{C}$  305, 307, 312
2. 100 ohm cm float zone, 90 minute diffusion, 60 minute redistribution  $-425^{\circ}\text{C}$  314, 316, 317, 319, 321, 322
3. 20 ohm cm float zone, 90 minute diffusion, 60 minute redistribution  $-400^{\circ}\text{C}$  327, 330, 331
4. 100 ohm cm float zone, 90 minute diffusion, no redistribution  $-400^{\circ}\text{C}$  347, 349, 351, 352
5. 100 ohm cm float zone, 90 minute diffusion, no redistribution  $-400^{\circ}\text{C}$  356, 357

Extended study of the effects of various Li diffusion temperatures:  $400^{\circ}\text{C}$

1. 100 ohm cm float zone, 90 minute diffusion, 60 minute redistribution 337, 344
2. 20 ohm cm float zone, 90 minute diffusion, 60 minute redistribution, 345, 358, 359, 361, 363

350°C

1. 20 ohm cm float zone, 90 minute diffusion, no redistribution, 364, 366
2. 100 ohm cm, float zone, 90 minute diffusion, no redistribution, 367
3. 1000 ohm cm float zone (no phosphorus), 90 minute diffusion, 60 minute redistribution, 370, 371
4. 20 ohm cm float zone, 90 minute diffusion, 60 minute redistribution 372, 373

HELIOTEK

Lithium Diffused PN Solar Cells

Fifth Group of Cells Sent to NASA/GSFC

2/8/67

Cell No.	Initial Resistivity (ohm cm) (all F.Z. silicon)			Method of Li Application		Diffusion 90 min.	Redistribution 60 min.	Li Diffusion Temp. °C		
	100	100	20	Eva	Paint on			350	400	425
	220	x				x	x	x		
235	x				x	x				x
236	x				x	x				x
237	x				x	x				x
240	x				x	x				x
241	x				x	x				x
244	x				x	x				x
245	x				x	x	x		x	
247	x				x	x	x		x	
248	x				x	x	x	x		
249	x				x	x	x	x		
251	x				x	x	x	x		
252	x				x	x	x	x		
305			x	x		x	x	x		
306			x	x		x	x			x
307			x	x		x	x			x
312			x	x		x	x			x
313		x		x		x	x			x
316		x		x		x	x			x
317		x		x		x	x			x
319		x		x		x	x			x
321		x		x		x	x			x
322		x		x		x	x			x
327			x	x		x	x			x
330			x	x		x	x		x	
331			x	x		x	x		x	
337		x			x	x	x		x	
338		x			x	x	x		x	
339		x			x	x	x		x	
340		x			x	x	x		x	
341		x			x	x	x		x	
342		x			x	x	x		x	

HELIOTEK

Lithium Diffused PN Solar Cells

Fifth Group of Cells Sent to NASA/GSFC

2/8/67

Cell No.	Initial Resistivity (ohm cm) (all F.Z. silicon)			Method of Li Application		Diffusion 90 min.	Redistribution 60 min.	Li Diffusion Temp. °C		
	1000	100	2c	Evap.	Paint-on			350	400	425
343		x			x	x	x		x	
344		x			x	x	x		x	
345			x		x	x	x		x	
347		x		x		x			x	
349		x		x		x			x	
351		x		x		x			x	
352		x		x		x			x	
353		x		x		x			x	
356		x		x		x	x		x	
357		x		x		x	x		x	
358			x		x	x	x		x	
359			x		x	x	x		x	
361			x		x	x	x		x	
362			x		x	x	x		x	
363			x		x	x	x		x	
364			x		x	x		x		
365			x		x	x		x		
366			x		x	x		x		
367		x			x	x		x		
370	JK				x	x	x	x		
371	JK				x	x	x	x		
372			x		x	x	x	x		
373			x		x	x	x	x		

Note: All cells numbers in the "200's" have phosphorus in the vicinity of the junction.