N69-19031

CASE FILE COPY

THIRD QUARTERLY REPORT

STUDY OF RADIATION EFFECTS IN LI-DOPED SILICON SOLAR CELLS

14 February 1969

10971-6011-R0-00

R. G. Downing
J. R. Carter
W. K. Van Atta

N69-19031

Contract 952251

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

TRW Systems
One Space Park
Redondo Beach, California 90278

THIRD QUARTERLY REPORT

STUDY OF RADIATION EFFECTS IN LI-DOPED SILICON SOLAR CELLS

14 February 1969 10971-6011-R0-00

R. G. Downing
J. R. Carter
W. K. Van Atta

Prepared by:

R. G. Downing

Approved:

J. L. Rogers

J. L. Rogers

Contract 952251

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

TRW Systems
One Space Park
Redondo Beach, California 90278

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract 952251.

TABLE OF CONTENTS

ABSTRACT

Several groups of lithium doped float zone silicon solar cells have been irradiated at fluences of 3×10^{14} and 3×10^{15} 1 MeV e/cm^2 and stored at room temperature. Half recovery times of 0.5 hours and 2-3 hours are observed for the corresponding fluences. The maximum annealed values are higher for the lower irradiation fluences but do not exhibit complete annealing in this fluence range. Previous experiments conducted on lithium doped crucible silicon solar cells indicate that, although annealing times are considerably longer, both the initial outputs and the maximum annealed outputs are higher than this group of float zone cells. Further, storage of lithium doped crucible cells at 80-100°C produce annealing times comparable to that of this group of lithium doped float zone cells. Lithium diffused silicon with concentrations varying from 10^{15} to 10^{18} atoms/cc exhibit hall coefficients in agreement which arsenic doped silicon and silicon doped with lithium in the melt. Carrier removal studies of this float zone lithium diffused silicon indicate an exponential dependence on lithium concentration of the carrier removal rate as previously observed in silicon doped with lithium in the melt. This dependence implies a relationship of the form:

$$\frac{dn}{d\Phi} = -\frac{n}{\alpha}$$

Irradiations performed on lithium doped silicon as a function of carrier concentration indicate that α is not a constant but rather linearly dependent on the initial lithium donor concentration of the form $\alpha = n_o/2.2$, which is approximately equal to theoretically computed atomic displacement rates for 1 MeV electrons in silicon.

I. INTRODUCTION

This report covers activities during the second three months of performance on JPL Contract No. 952251. The work presented here includes the evaluation of float zone and Lopex lithium doped silicon solar cells irradiated at 3×10^{14} and 3×10^{15} e/cm^2 at an energy of 1 Mev and stored at room temperature. The results of these evaluations when compared with previous lithium doped crucible silicon solar cells indicate that, although the float zone lithium doped silicon anneals rapidly at room temperature, the crucible silicon exhibits higher initial and maximum annealed outputs after sufficient time at room temperature or storage at elevated temperatures. Float zone silicon doped with lithium to concentrations between 10^{15} and 10^{18} atoms/cc indicate, as found previously, that the carrier removal rate is an exponential function of instantaneous carrier concentration. Isochronal annealing experiments indicate annealing stages at about 100°C and 200°C. Annealing at higher temperatures seems to result in the redissolving of lithium precipitates formed in the silicon in the initial diffusion.

II. PROGRESS IN THIS REPORT PERIOD

A. Lithium Solar Cell Evaluation Program

Two different groups of lithium doped float zone silicon solar cells were received and evaluated in this report period. The first group of cells consisted of Heliotek fabricated cells using phosphorus doped 80-120 ohm-cm float zone material with a paint-on lithium source diffused at 425°C. The second group of cells consisted of Texas Instruments fabricated cells utilizing greater than 50 ohm-cm Lopex silicon with an evaporated source and diffused

---

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

at 400°C. Further details are given in Table 1. The principle difference in the two groups of cells is the comparison of float zone material with Lopex material and the slight difference in diffusion schedules.

The initial characteristics of the two groups of cells were quite different. The H-4 group exhibited rather low short circuit currents in the 35 ma. range whereas the T-3 group of cells exhibited remarkably high short circuit currents in the 52-55 ma. range. Cells fabricated in this fashion in the past normally exhibit short circuit currents in the 40-50 ma. range under illumination with our 2800°K tunsten light table. In addition, the open circuit voltage of the T-3 group of cells was quite good, ranging from 590-600 mv. Normal open circuit voltages have been observed to range from about 525-575 mv. These initial characteristics are included in the response data given in Table 2. In view of the high lithium concentration, as determined by capacitance measurements, the high short circuit currents for the T-3 group of cells made from Lopex silicon are inconsistent with previous observations and can not be explained at this time while the high open circuit voltages are consistent with low resistivity material.

Capacitance versus voltage data was acquired as shown in Figures 1 and 2 and from this data lithium concentrations were computed as given in Table 3*. The observed capacitance for the T-3 group of cells indicated a very heavy lithium concentration of about 4 x 10^{15} Li/cc relative to the more normal contemporary lithium concentrations in the 10^{14} Li/cc range. The H-4 group also had a relatively high lithium concentration of 1 x 10^{15} Li/cc. The lower than normal short circuit currents observed in the H-4 group is consistent with their relatively high lithium concentration; however, the extremely high short circuit currents exhibited by the T-3 cells with a

---

*In the prior Second Quarterly Report No. 10971-6008-R0-00 an error was made in Table 3. The donor concentration given as exponent 15 should be exponent 14. This error will be corrected in the final report.

lithium concentration four times higher than the H-4 cells is very interesting and worthy of further exploration. The capacitance versus voltage characteristics again exhibit close to -1/4 slopes with the T-3 cells having a slope of -0.24 and the H-4 cells having a slope of -0.29. Inasmuch as the -1/4 slope has been appearing regularly in contemporary lithium doped cells, the theoretical significance of the -1/4 exponent was explored in terms of fundamental principles. As discussed in previous reports, a -1/2 slope is indicative of a step junction with a uniform concentration of carriers in the depleted region at the junction. A -1/3 slope is indicative of a linear gradient of carriers in the depleted region. Some groups of lithium doped cells have exhibited a -1/3 slope. A -1/4 slope results if the carrier concentration profile near the junction is functionally of a quadratic form. Diffusion profiles normally exhibit an error function concentration dependence. Since functionally an error function is very similar to quadratic and further since some pertabation of the profile at the junction can be anticipated, the -1/4 slope normally observed can actually be anticipated from basic principles. This approach, however, is not meant to be a rigorous quantitative solution but rather only a qualitative description of the relationship between the -1/4 power dependence observed in capacitance voltage measurements and the anticipated lithium concentration profile in the vicinity of the junction where the experimental measurements are valid.

As in the previous experiments the cells were irradited at 3×10^{14} e/cm^2 and 3×10^{15} e/cm^2 at 1.0 Mev. The initial degradation was greater in the T-3 group of cells than in the H-4 group of cells which was expected due to their higher lithium doping and hence lower material resistivity. The recovery times for the two groups of cells were about the same; namely, about 1/2 hour for the lower level of irradiation and about 2-3 hours at the higher level of irradiation as shown in Figures 3 through 6 and as summarized in Table 2. The recovered levels, however, were significantly higher for the T-3 group relative to the H-4 group after 3 x 10^{14} e/cm^2, whereas the recovered levels were approximately the same for the 3 x 10^{15} e/cm^2 irradiation. After approximately 400 hours, redegradation, though not yet significant in magnitude, is beginning to occur in the T-3 cells. More time will be required to further define the magnitude of the degradation for the T-3 cells and the existence of any redegradation for the H-4 group of cells.

The subject of redegradation is of critical concern in the development of the lithium doped radiation resistant silicon solar cell. Previous observations of redegradation seem to have been limited to float zone silicon which is moderately to highly lithium doped. Due to the long times required to observe redegradation, i.e., months to a year, adequate data to describe this phenomena has been difficult to obtain. Recent measurments, although obtained with efforts supported on another program (funded by Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base under Contract No. F33615-68-C-1198), are pertinent to the objectives of this program. In February of 1968 a neutron experiment was conducted in which a variety of lithium doped cells were irradiated and studied for subsequent annealing characteristics. Measurements now accumulated over the span of one year indicate that serious redegradation of annealed short circuit current and open circuit voltage is occurring in float zone lithium doped silicon solar cells fabricated in a manner very similar to the float zone cells now under evaluation. The magnitude of the redegradation is at this time 10-20% in short circuit current, 3-6% in open circuit voltage, but with negligible effect on the shape of the I-V characteristic. The control cells, which were not irradiated, exhibited identical redegradation characteristics. From these data it would appear that the redegradation phenomena is at least in part a basic instability of lithium in silicon and is not particularly sensitive to the irradiation environment. It is not felt, however, that all of the redegradation observed to date can be classified in this fashion since in some cases redegradation is observed to initiate after only a post-irradiation storage of a few hundred hours, wherein the actual age of the cells is of the order of months. Additional long term data on storage of both irradiated and unirradiated lithium doped cells will have to be acquired to further identify the kinetics of redegradation in this apparently complex reaction.

For purposes of adequate comparison of lithium doped cells to conventional n/p 10 ohm-cm contemporary cells, a group of standard cells provided by Heliotek and Centralab have also been irradiated with 1 Mev electrons as shown in Figure 7. As is evident in the figure, which contains within the band data on 12 separate cells from both manufacturers, the reproducibility of the conventional cell within a group and between manufacturers is very good. It is observed that after 3×10^{15} e/cm^2 the standard cells exhibit a degraded short circuit current of 33-35 ma. In comparison with lithium doped p/n cells which also exhibit annealed short circuit currents of approximately 33 ma., it is clear that the annealed lithium cell is as good as, but not better than, the conventional cell under electron bombardment to these moderately high fluences. Under proton and neutron irradiation, however, it has also been shown that the lithium cell when annealed is clearly superior to the conventional cell. A similar comparison can be made for fluences of 3×10^{14} e/cm^2 where the conventional cell has an output of 46-49 ma. compared to the lithium doped T-3 group with an annealed output of about 45 ma. short circuit current. In this particular case the H-4 group was noticably lower but this is attributed to the lower initial short circuit currents. Previous Heliotek cells with lower lithium concentrations and higher initial short circuit currents compare favorably with the T-3 group of cells. Although all of the comparisons presented here are based on short circuit current, the open circuit voltage measurements correspond linearly, and no anomolous effects were observed in the shape of the I-V characteristic. It is concluded, therefore, that the observations reported here in terms of short circuit current would also be valid for maximum power or power at a given voltage. Furthermore, the use of tengsten illumination as opposed to solar illumination will accentuate the deep diffusion limited response which is affected by irradiation and hence, although the observations presented here would qualitatively be reproduced under solar illumination, the magnitudes of the differences in response between various groups of cells would most certainly be less under solar illumination. Due to the number of cells under evaluation, and in many cases the short time span required for evaluation, the use of a solar simulator for the measurements as presented here is impractical.

In comparing the float zone cells evaluated in this report period with the lithium doped crucible silicon solar cells evaluated in the prior report period, several observations of interest can be made. The crucible cells in the previous group in general had higher initial characteristics than the corresponding group constructed from float zone material. Secondly, the annealed outputs of the crucible grown cells were, for those cells which exhibited annealing, significantly higher than this group of float zone lithium doped cells and the standard n/p 10 ohm-cm cells. The only disadvantage of the crucible cells is the slower annealing times at room temperature which range from several months to a year for maximum annealing. As was reported in the previous progress report, however, the raising of crucible lithium doped cells to temperatures of only 80-100°C produced annealing times comparable with the room temperature float zone cells. When other non-radiation oriented factors are considered, such as the practicality and economics of producing large quantities of lithium doped solar cells from crucible material, the lithium doped crucible cell remains as an extremely attractive device in comparison with the lithium float zone cell.

B. Carrier Removal Studies

Our previously reported work in this area has involved silicon which was doped with lithium during crystal growth. Our recent efforts are concentrated upon similar studies in silicon doped by diffusion of lithium into the sample. Float zone silicon with an n-type resistivity of 75 ohm-cm is used for most studies. The lithium was diffused in a 600°C to provide uniform saturation. The sample is then allowed to approach equilibrium at a lower temperature. In this manner samples have been prepared with lithium donor concentrations between 10^{15} and 10^{18} atoms/cm^3. Table IV summarizes the various electrical properties of the samples prepared to date. The electrical properties of this material are typical of phosphorus or arsenic doped silicon in regard to hall mobility and hall coefficient variation with temperature. In Figure 8 the hall mobilities of these samples are compared to the published experimental and computed values of Morin and Maita for arsenic doped silicon. In nearly all cases the values found for our lithium doped specimens are very close to previously mentioned data. This would indicate that the scattering centers are largely the singly charged lithium donor atoms.

The electron irradiation results of this material are shown in Figure 9. Sample D-1, described in Table IV, was irradiated with 1 MeV electrons at room temperature in increments. When the irradiation was interrupted, the resistivity and hall coefficient were determined. The electron carrier concentration, as determined by the hall coefficient, is plotted as a function of electron fluence. Since the logarithm of the carrier concentration versus fluence yields a straight line, it appears that this material has again demonstrated the same exponential dependence of carrier concentration upon electron fluence which was previously found in float zone silicon doped with lithium in the melt. The results of these irradiations are described by the following equation:

$$n = n_o \exp(-\Phi/\alpha)$$

where: n_o = initial electron concentration

Φ = electron fluence

α = a constant

n = electron concentration after irradiation

Such a relationship indicates that the instantaneous removal rate ($dn/d\Phi$) is not a constant, as has been found in other cases, but is directly related to the instantaneous carrier concentration as follows:

$$\frac{dn}{d\Phi} = -\frac{n}{\alpha}$$

In the case of sample D-2 the constant $\alpha = 5 \times 10^{16}$ e/cm^2. This exponential relation was found in all our recent investigations. Although one might expect the same value of α in samples with different lithium concentrations, in fact this condition was not found. There was considerable variation in values found for the constant α. In Figure 10, the experimental values of α are plotted versus the lithium donor concentration (carriers) of the sample irradiated. The points on this log-log plot indicate α is a linear function of the initial lithium donor concentration of the specimen. The relationship appears to be:

$$\alpha = n_o/2.2$$

In this relationship is substituted into the instantaneous carrier concentration expression, the following expression results:

$$\frac{dn}{d\Phi} = 2.2 \frac{n}{n_o}$$

This would result in:

$$\frac{dn}{d\Phi} = 2.2$$

at the start of irradiation when $n = n_o$. The physical reasons for this relationship are not apparent at this time. If, as one might expect, α was independent of lithium concentration, and the value of α found for a 10^{16} Li/cm^2 were to apply for samples of 10^{17} Li/cm^3 and greater the value of $dn/d\Phi$ would initially exceed that of the displacement rate for 1 MeV electrons. Such a situation would be very difficult to account for theoretically. The value of the initial removal rate found here (2.2/cm) is roughly equal to the calculated displacement rate of 1 MeV electrons in silicon.

The annealing behavior of radiation damage in the subject specimens is in marked contrast to that previously reported in silicon. We previously reported an isochronal annealing stage at about 150°C in which about 40% of the carrier removal damage recovered in float zone silicon lithium doped in the melt. Sample A-1 was irradiated with 4 x 10^{16} e/cm^2 and isochronally annealed for 15 minutes at 75°C and other higher temperatures at 25°C intervals. The annealing data for sample A-1 is shown in Figure 11. In the vicinity of 100°C about 10% of the removal damage is recovered. At 200°C what appears to be a second annealing stage begins. After annealing for 15 minutes at

275°C the carrier concentration has increased to approximately the same value found in the specimen prior to irradiation. Isochronal annealing at temperatures above 275°C produce rather startling results. Each successive annealing step increases the carrier concentration. After the anneal at 350°C the carrier concentration is five times greater than that found prior to irradiation. The apparent explanation of this behavior lies in the comparison of the isochronal annealing data to the lithium solubility of Pell, which is also plotted in Figure 11. Since the specimen was originally saturated with lithium at 600°C and then held at 200°C, the lower temperature produced a precipitated second phase of lithium silicide rather than outdiffusion of lithium as expected. The annealing above 200°C allowed the silicon to redissolve the precipitate, with subsequent increase of lithium donor concentration. The annealing data show a tendency to approach the solubility data as temperature increases. Since that behavior was not found in our previous studies of lithium doped float zone silicon, we can only conclude that the present material had a much lower oxygen content, and therefore the lithium atoms are not captured by oxygen atoms and can exist as free atoms or a second phase. If the observed effect is indeed lithium redissolving, it may mask the annealing of the remaining 90% of removal damage after annealing at 175°C. Further work is necessary to clarify these effects.

A second view of the irradiation and annealing of sample A-1 can be seen in Figure 12. In this figure the hall mobility of the specimen is plotted versus the lithium donor concentration after various irradiations and anneals. In addition to the data points, the arsenic data of Morin and Maita is shown as a solid line. It can be seen that the irradiation of this sample results in an increase in the hall mobility in addition to the loss of lithium donors.

Even after an irradiation of 4×10^{16} e/cm^2 the hall mobility is equal to that of an unirradiated sample of the same donor concentration. Since hall mobility is not degraded, the irradiation results in no additional charged scattering centers, but rather a reduction of charged scattering centers. This conclusion rules out the production of charged acceptor type defects by the irradiation. Thus the irradiation appears to electrically resemble the precipitation process. The anneal has the exact opposite effect as irradiation, as each higher temperature increases the donor concentration and decreases the hall mobility. The redissolving of lithium donors to concentrations greater than the before irradiated values is also illustrated in Figure 12. The irradiation and annealing of this material appears to be identical to the precipitation and redissolving lithium.

III. FUTURE WORK

In addition to continuation of the annealing measurements now underway, a new group of both crucible and float zone lithium doped cells have been received for irradiation and subsequent evaluation. Additional work will be extended in carrier removal studies and junction capacitance studies in an attempt to obtain further information on the energy levels involved in the lithium-silicon system. Two other areas of interest which were initiated in this report period are diffusion length versus temperature measurements to identify the recombination center energy level and the production of laboratory n/p lithium doped cells. Although sufficient data has not yet been obtained in these later two areas, efforts will continue in the next report period.

	BASE MATERIAL		LITHIUM INTRODUCTION			
CELL GROUP	BASE GROWTH	RESISTIVITY (ohm-cm)	DOPANT	SOURCE	DIFFUSION (min/°C)	REDISTRIBUTION (min/°C)
T3	Lopex	>50	Phos.	Evaporated	90/400	None
H4	Float Zone	80-120	Phos.	Paint-on	90/425	60/425

TABLE I. LITHIUM SOLAR CELL MANUFACTURING PARAMETERS

CELL GROUP	INITIAL LEVEL (I_{sc} ma.)	DAMAGED LEVEL (I_{sc} ma.)	RECOVERED LEVEL (I_{sc} ma.)	TIME (hours) TO 1/2 RECOVERY POINT AT 25°C
For irradiation of $3 \cdot 10^{14}$ e/cm^2:				
T3	51-54	24	44-46	0.5
H4	33-37	25-28	34-36	0.5
For irradiation of $3 \cdot 10^{15}$ e/cm^2:				
T3	49-53	15	32-34	2
H4	32-35	21	33	3

TABLE II. LITHIUM SOLAR CELL RECOVERY CHARACTERISTICS

CELL	N_D (cm^{-3})	CELL	N_D (cm^{-3})
T3-1	4.00 x 10^{15}	H4-4001	1.45
2	4.08	4007	4.08
3	4.22	4020	1.07
4	3.26	4023	1.19
5	4.84	4025	1.33
7	5.09	4031	1.13

TABLE III. DONOR CONCENTRATION AT JUNCTION

Sample #	Silicon	Li Diffusion	$\rho(\Omega\text{-cm})$	$R(cm^3/coulomb)$	$\mu_H(cm^2/volt\text{-}sec)$	$Li(atoms/cm^3)$
B-1	75 Ω-cm,n,F.Z.	1 hr @ 600°C	0.012	2.18×10^0	180	3.4×10^{18}
D-2	75 Ω-cm,n,F.Z.	1 hr @ 600°C, 8 hr @ 200°C	0.078	6.35×10^1	815	1.2×10^{17}
A-1	75 Ω-cm,n,F.Z.	1 hr @ 600°C 60 hrs @ 200°C	0.26	2.72×10^2	1150	2.7×10^{16}
C-1	75 Ω-cm,n,F.Z.	1 hr @ 600°C 48 hrs @ 150°C	0.50	6.32×10^2	1280	1.6×10^{16}
E-2	1000 Ω-cm,n.F.Z.	1 hr @ 600°C 60 hrs @ 150°C	2.3	3.46×10^3	1500	2.14×10^{15}

TABLE IV. PROPERTIES OF LI DIFFUSED SILICON SPECIMENS

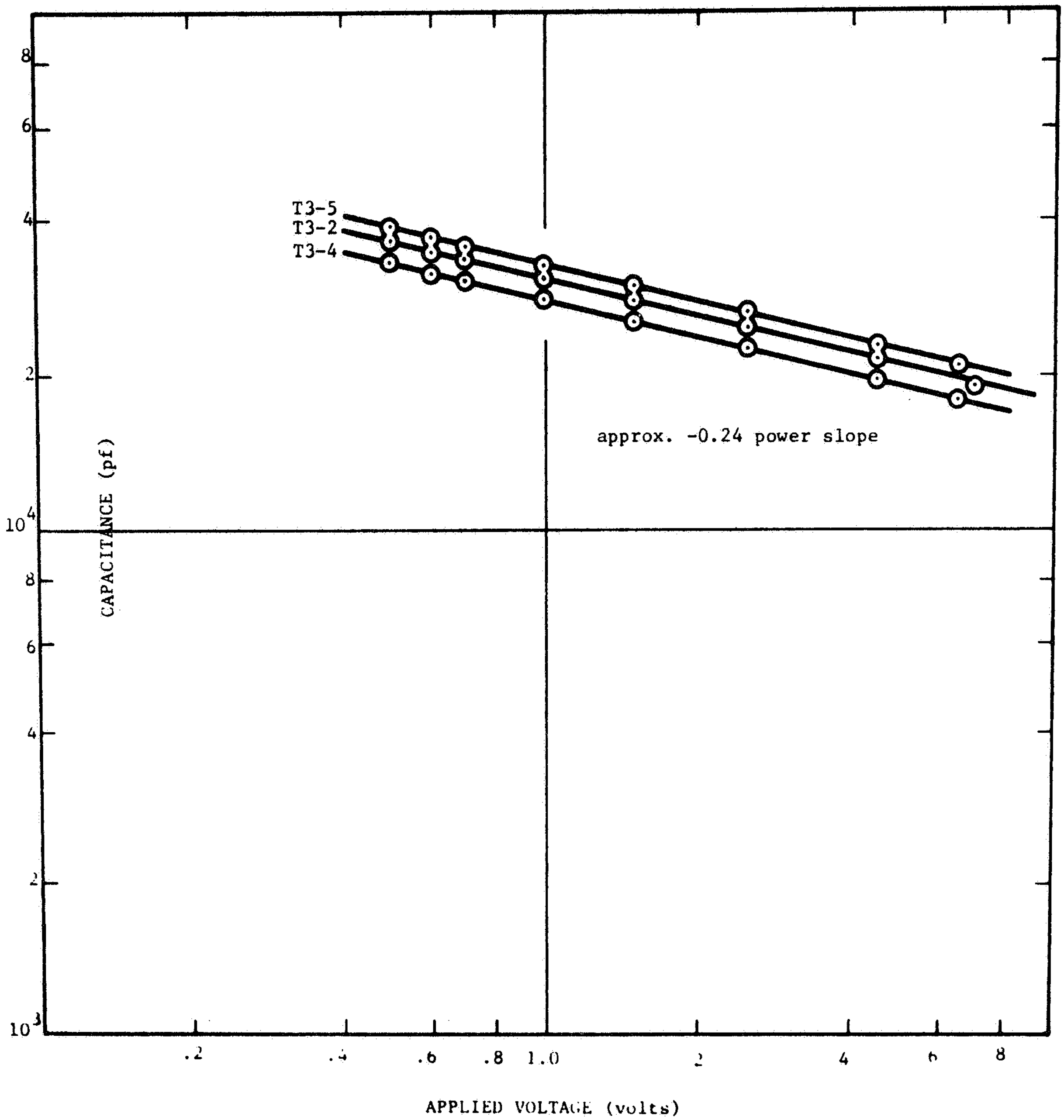

FIG. 1. CAPACITANCE VS. VOLTAGE FOR GROUP T3 LITHIUM SOLAR CELLS

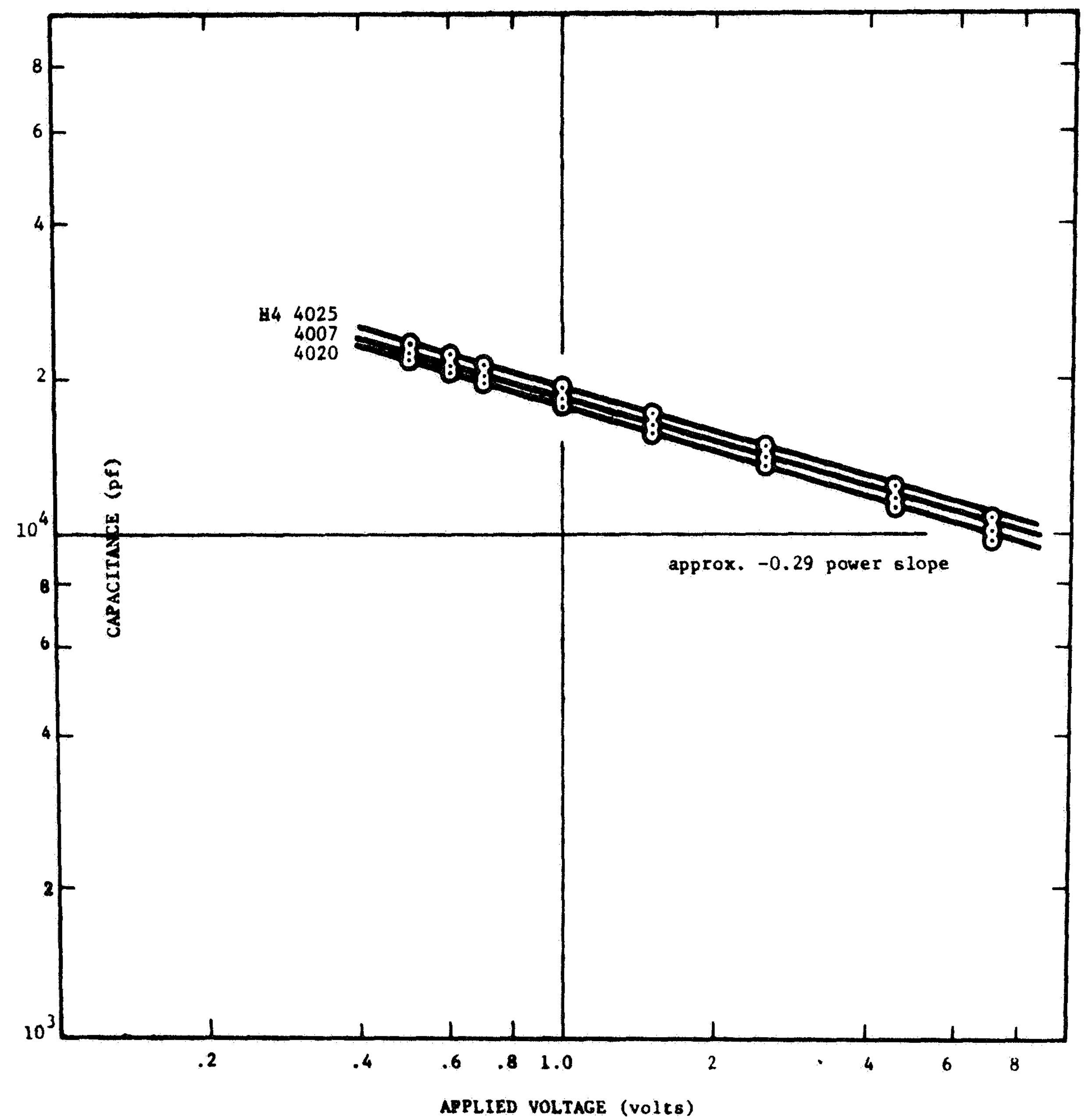

FIG. 2. CAPACITANCE VS. VOLTAGE FOR GROUP H4 LITHIUM SOLAR CELLS

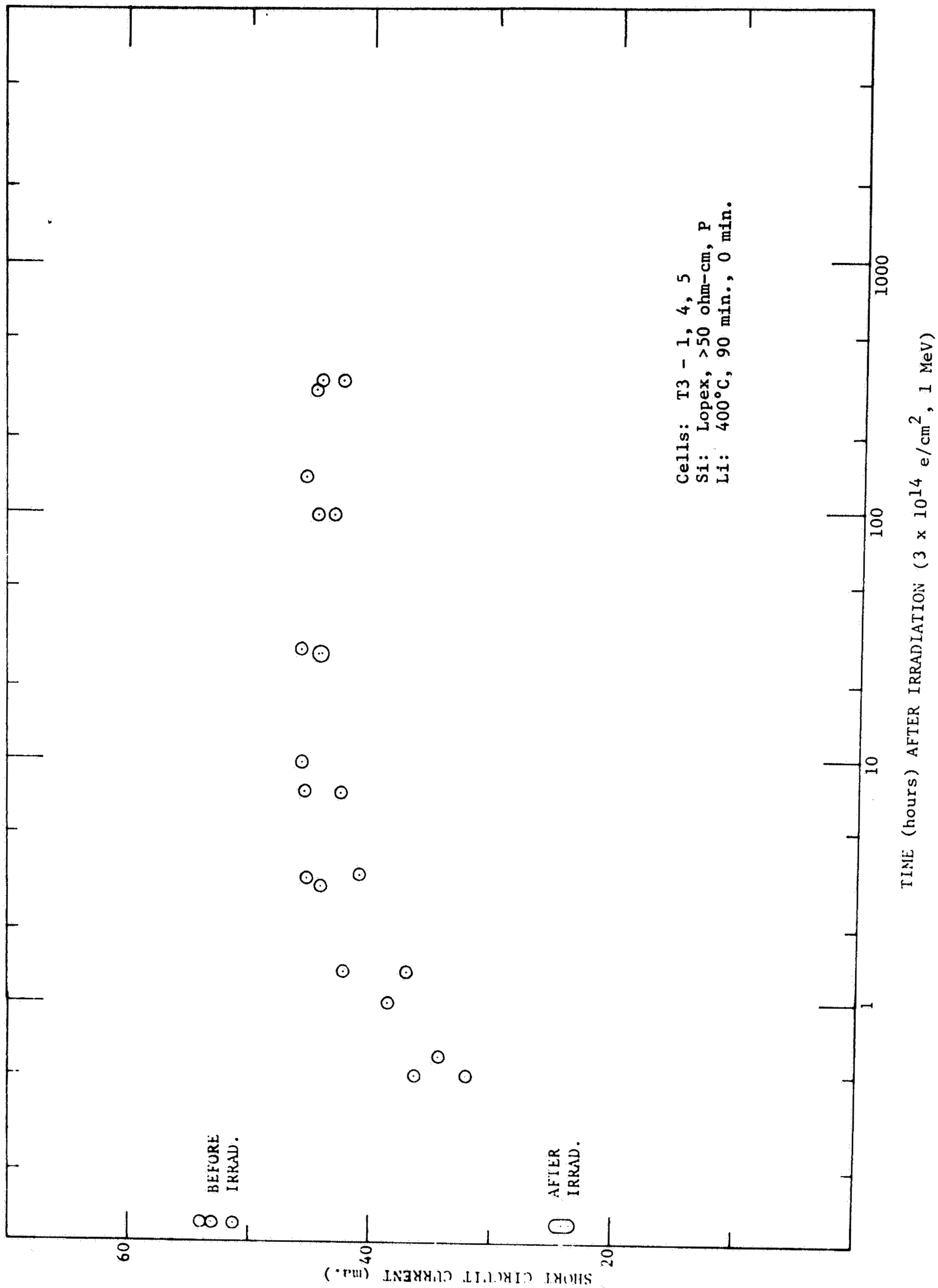

FIGURE 3. RECOVERY OF GROUP T3 LITHIUM SOLAR CELLS AT 25°C

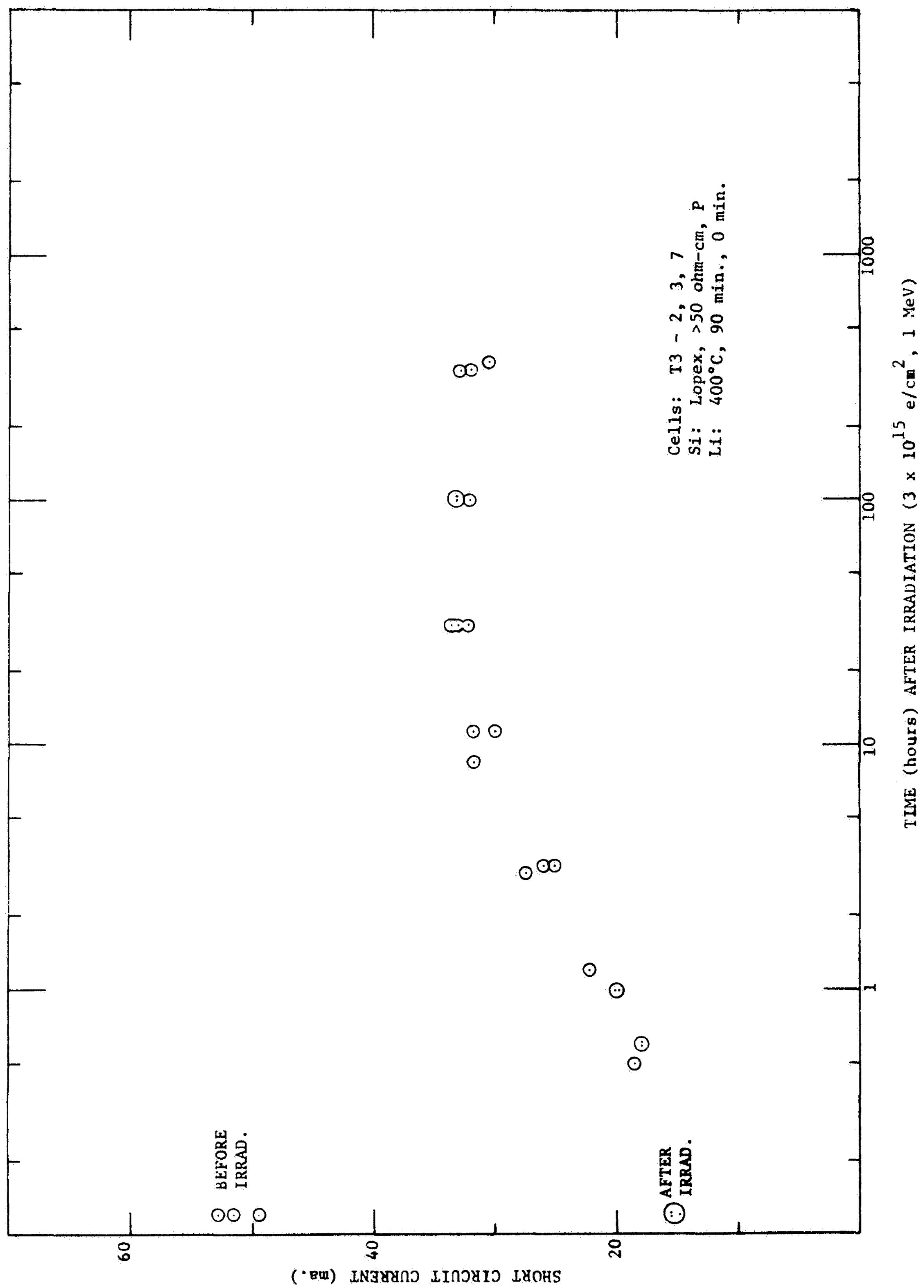

FIGURE 4. RECOVERY OF GROUP T3 LITHIUM SOLAR CELLS AT 25°C

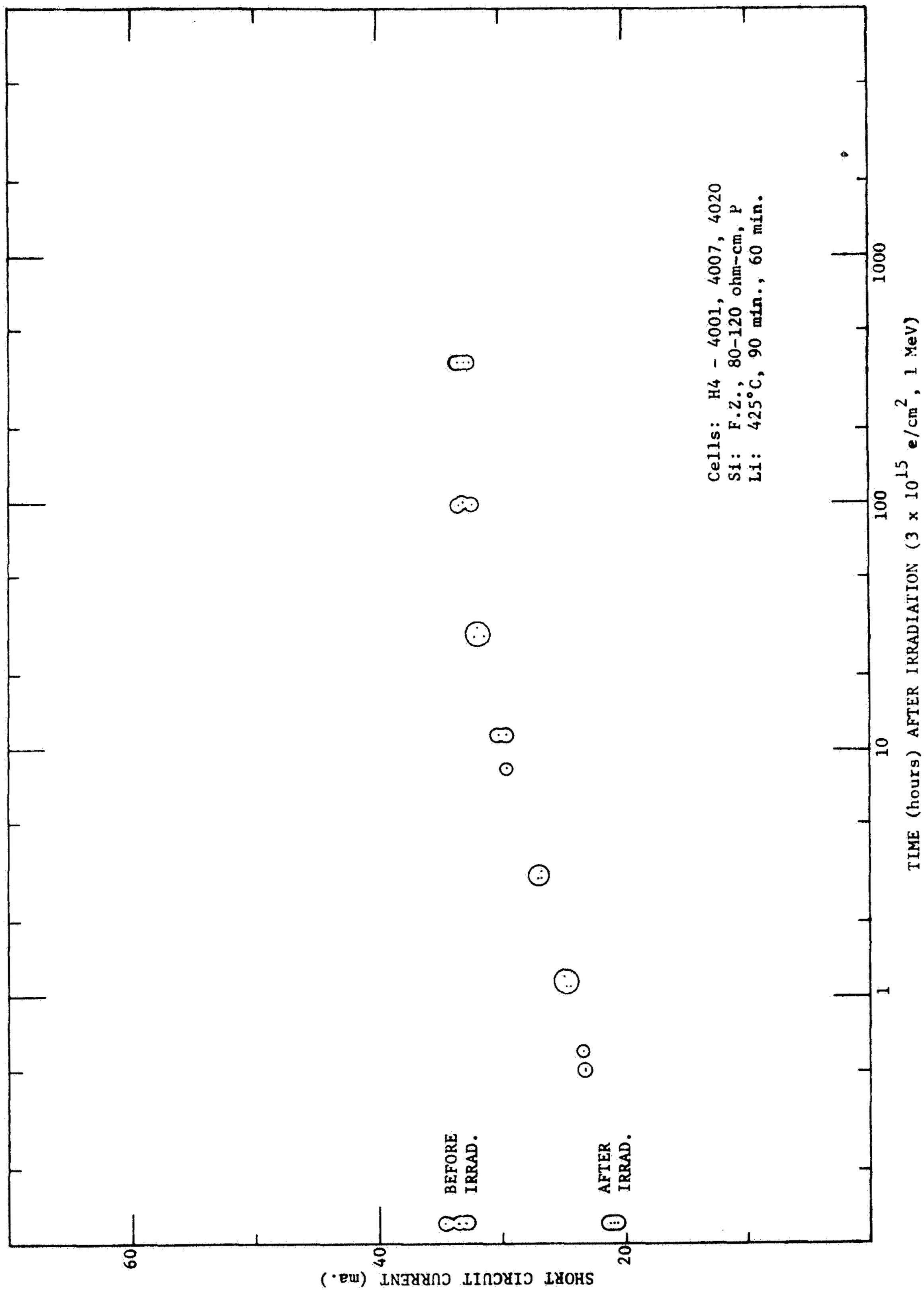

FIGURE 5. RECOVERY OF GROUP H4 LITHIUM SOLAR CELLS AT 25°C

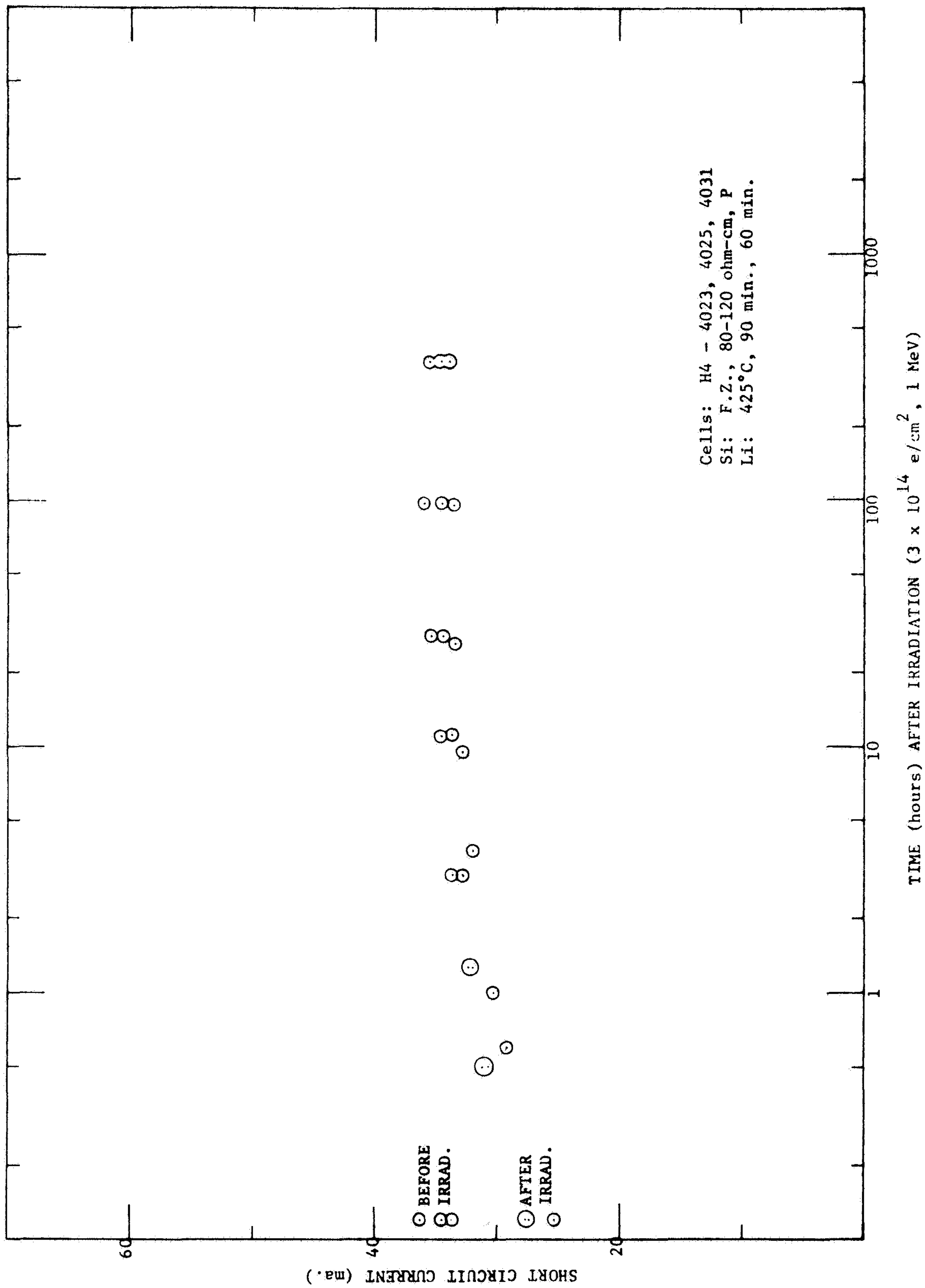

FIGURE 6. RECOVERY OF GROUP H4 LITHIUM SOLAR CELLS AT 25°C

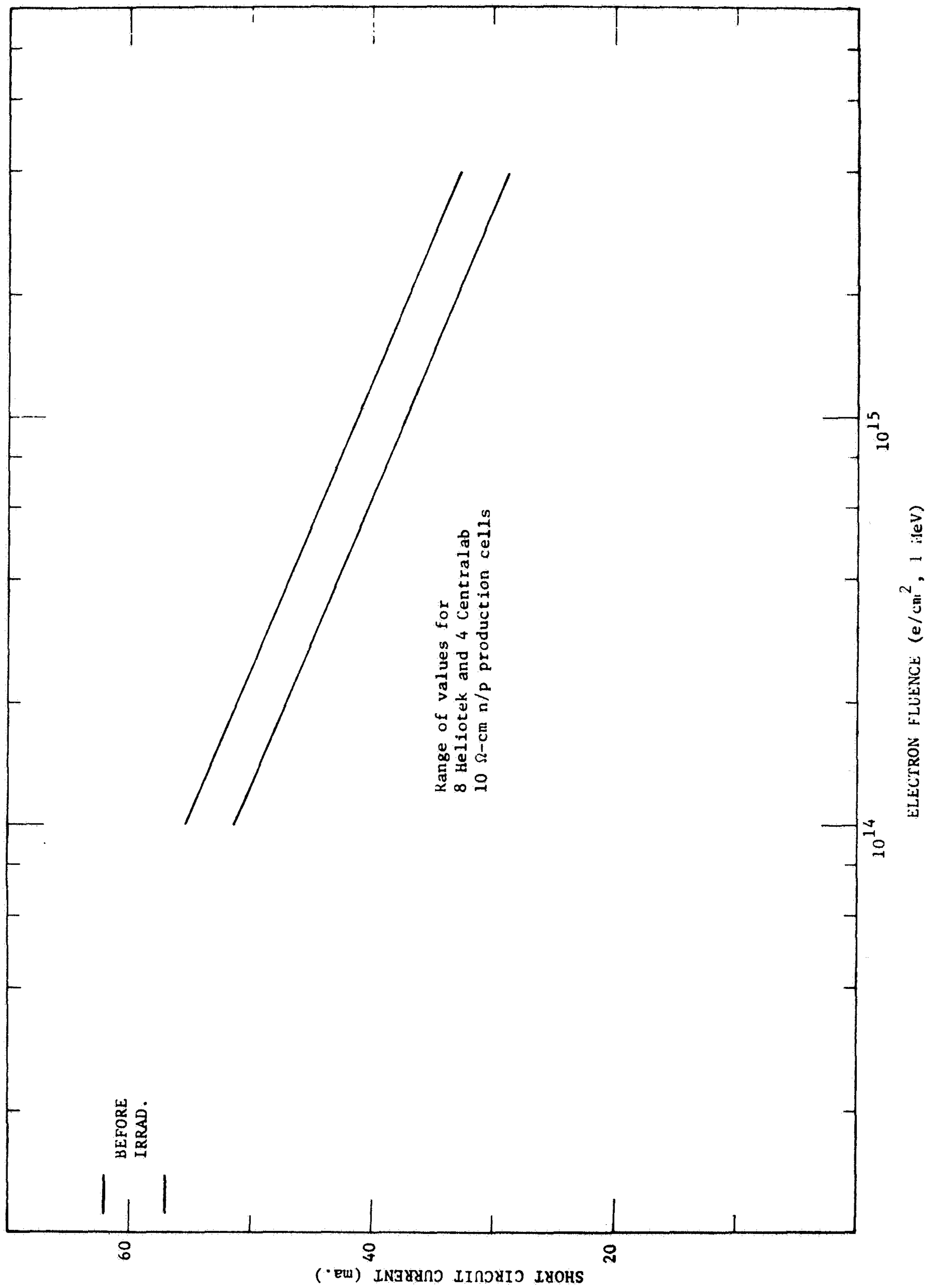

FIGURE 7. ELECTRON DEGRADATION OF CONTEMPORARY N/P SILICON SOLAR CELLS

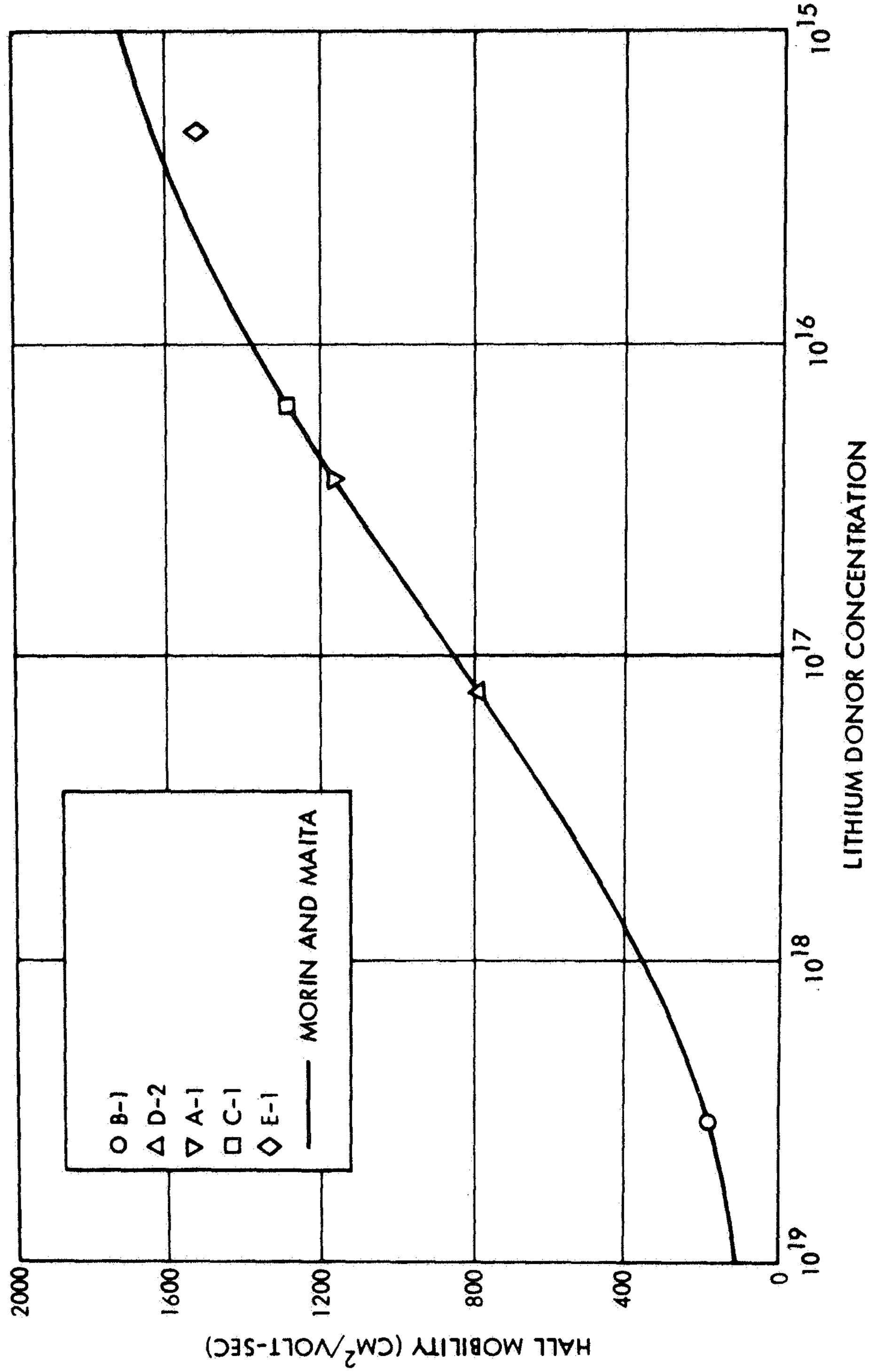

FIGURE 8. HALL MOBILITY FOR LITHIUM DOPED SILICON AS A FUNCTION OF LITHIUM CONCENTRATION

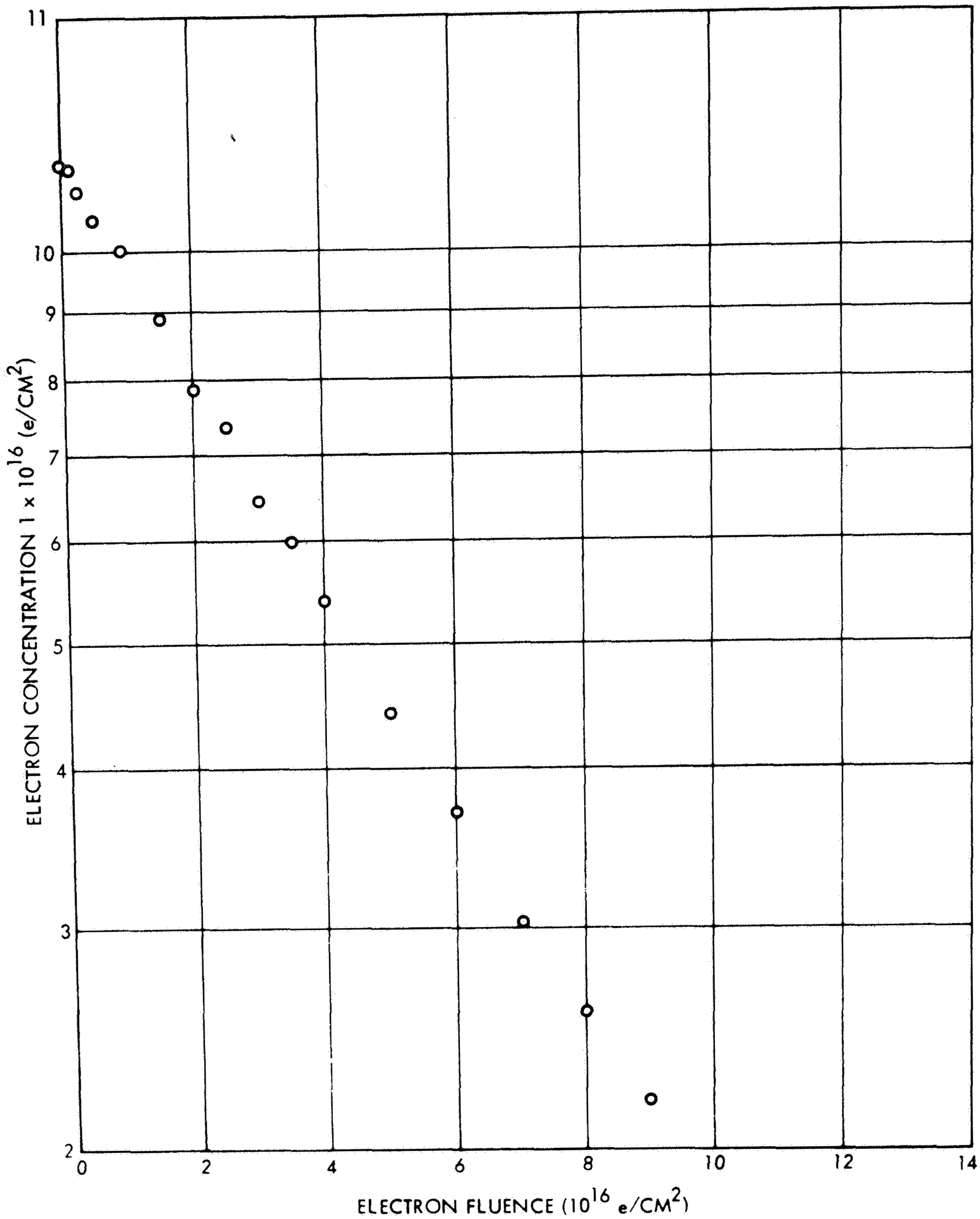

FIGURE 9. ELECTRON CONCENTRATION OF LITHIUM DOPED SILICON VERSUS ELECTRON FLUENCE

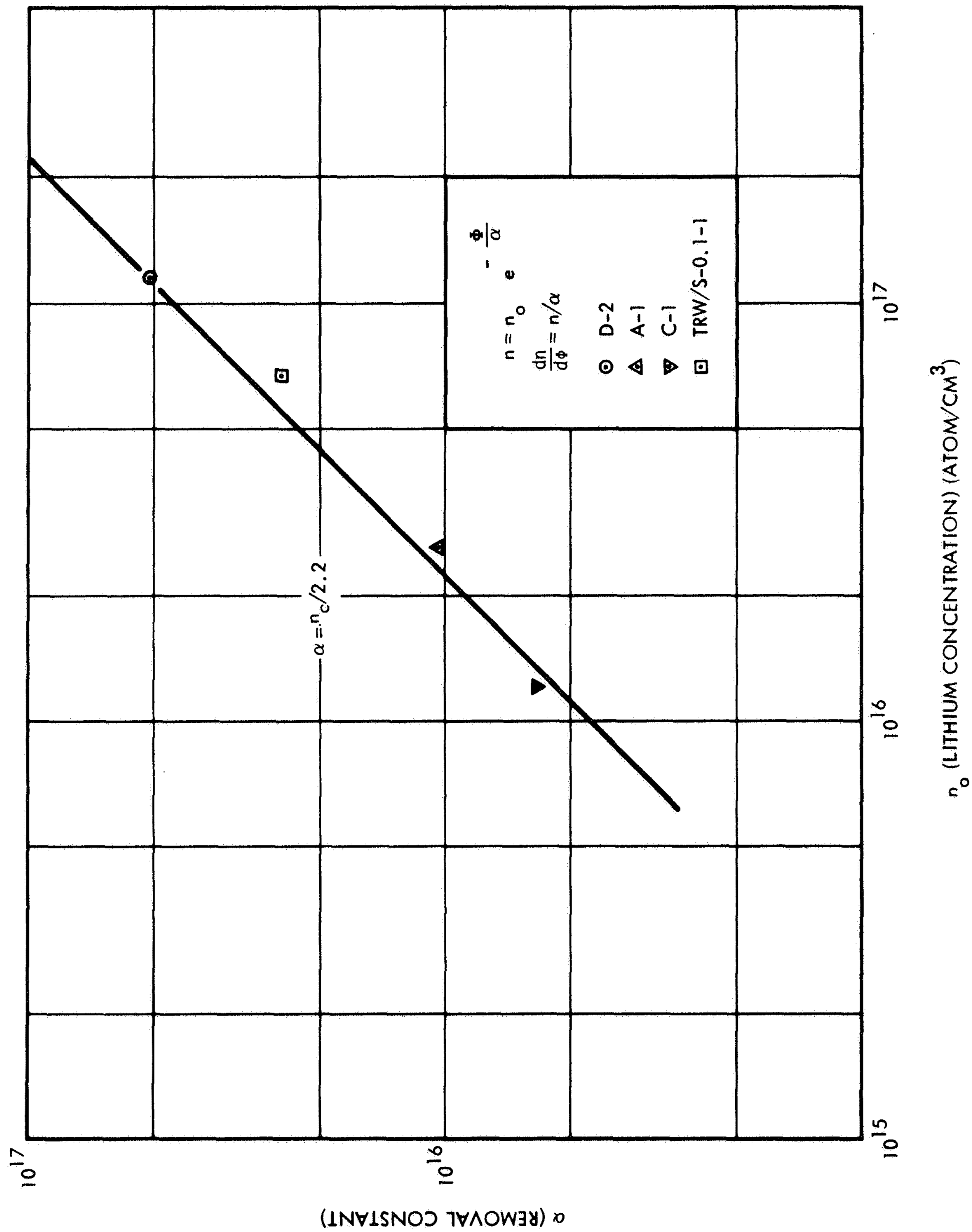

FIGURE 10. CARRIER REMOVAL CONSTANT AS A FUNCTION OF LITHIUM CONCENTRATION UNDER ELECTRON IRRADIATION

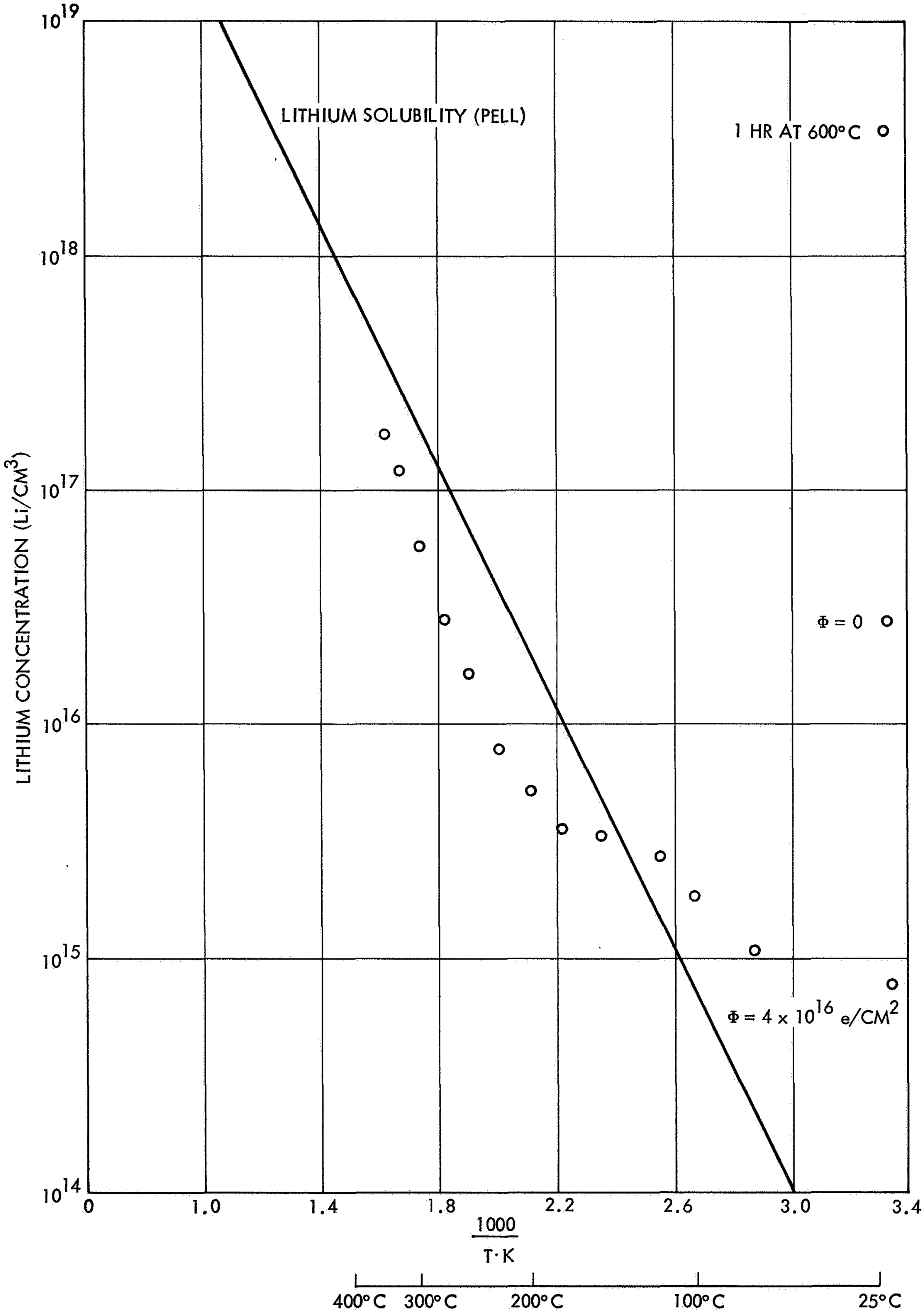

FIGURE 11. ISOCHRONAL ANNEALING OF LITHIUM DOPED SILICON

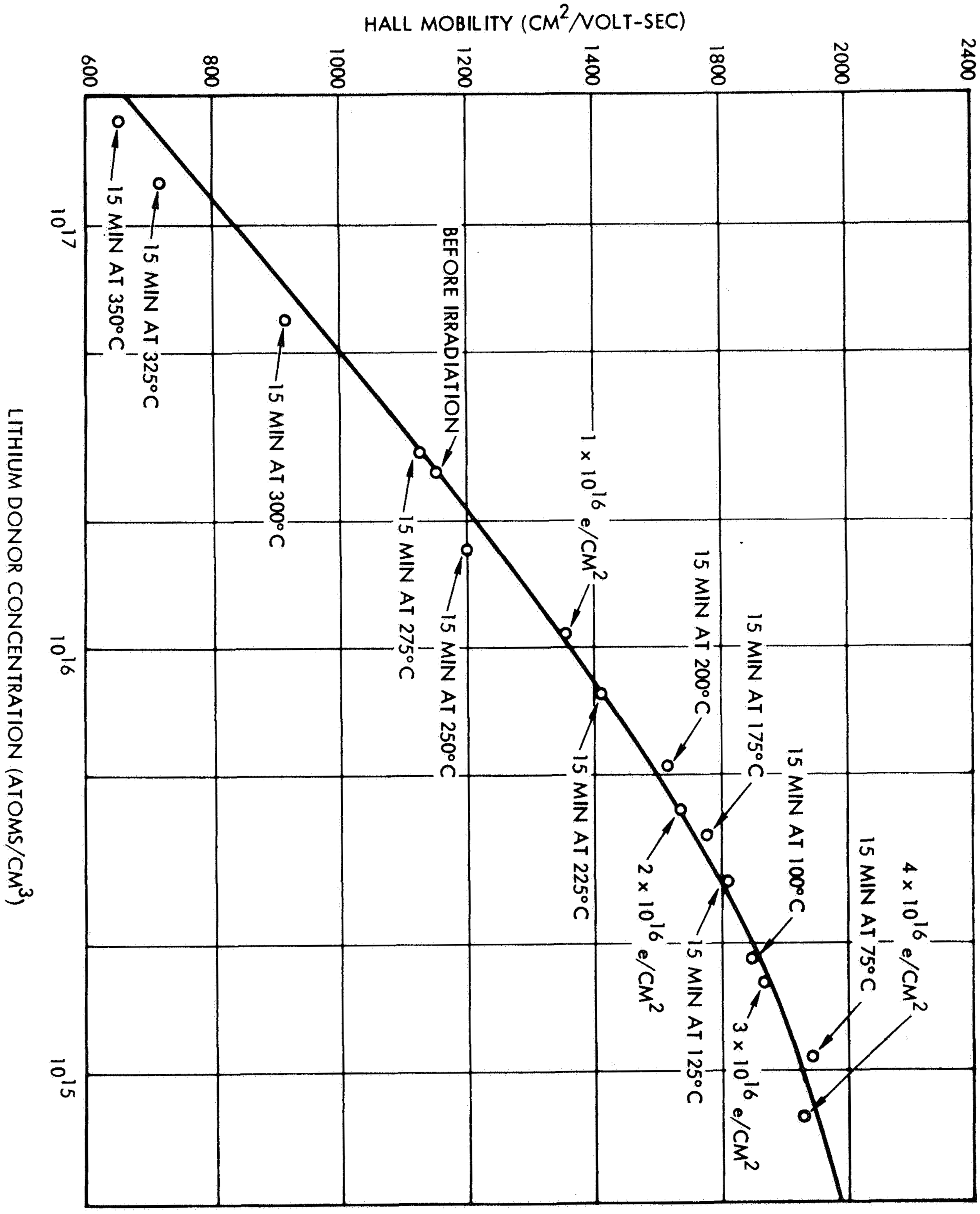

FIGURE 12. HALL MOBILITY VERSUS LITHIUM CONCENTRATION AS A FUNCTION OF IRRADIATION AND ISOCHRONAL ANNEALING