Gulf General Atomic
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RADIATION EFFECTS IN SILICON SOLAR CELLS

QUARTERLY REPORT

by

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Gulf General Atomic Incorporated
P. O. Box 608, San Diego, California

10 APRIL 1969

Prepared for
California Institute of Technology
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103

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ABSTRACT

The purpose of the contract is to ascertain the nature of the defect or defects responsible for the output degradation of silicon solar cells irradiated by space radiation. Present effort is concentrated on the effects of lithium on the production and annealing of damage in silicon.

Samples of high-purity silicon have been lithium diffused by the paint-on and lithium-tin bath techniques. Samples of various lithium content have been prepared, and the lithium content is being measured by room temperature resistivity and neutron activation analysis techniques. The first of a series of samples has been investigated. Resistivity and minority-carrier lifetime were measured as a function of temperature before and after irradiating the sample with 30-MeV electrons. During irradiation, the lifetime degradation and annealing rates were measured, at room temperature and above, as a function of fluence. Isothermal anneals were performed in an effort to determine the temperature dependence of the annealing rate.

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1. INTRODUCTION

This first quarterly report on National Aeronautics and Space Administration Contract NAS7-100, "Radiation Effects on Silicon Solar Cells," covers work performed during the period 1 January 1969 through 31 March 1969.

The purpose of this research is to investigate and diagnose the defects produced in lithium-diffused n-type silicon irradiated with 30-MeV electrons, which should produce defects of the same type as produced by high-energy protons. In a space-radiation environment, solar cell outputs degrade and anneal at various rates, depending, in part, on the lithium content of the cell. In general, lithium-diffused cells degrade more rapidly and anneal more completely than cells which contain no lithium. A knowledge of the defect or defects responsible for the degradation and the nature of the annealing mechanism is sought in order to develop analytical techniques for characterizing the radiation resistance of lithium-diffused silicon solar cells.

Our approach to the study of radiation-induced damage and its anneal in lithium-diffused solar cells concentrates on the study of these processes in bulk silicon. During the first quarter, efforts included:

1. Preparing silicon samples with lithium concentrations ranging from about 5×10^{14} cm^{-3} to 5×10^{16} cm^{-3}.
2. Determining the resistivity and resistivity profiles of such samples by four-point probe resistivity measurements.
3. Estimating the lithium content from resistivity and neutron activation analysis.
4. Fabricating lifetime samples of various lithium content.
5. Measuring preirradiation and postirradiation resistivity and lifetimes as a function of temperature.
6. Initiating measurements of the minority-carrier lifetime degradation and anneal rates as a function of fluence, using 30-MeV electrons as a radiation source.

2. TECHNICAL DISCUSSION

2.1 LITHIUM-DIFFUSION OF SAMPLES

In a previous contract with NASA/Goddard, lithium-diffused samples were prepared by NASA/Goddard, Centralab Semiconductor Products, and RCA. During the present contract, Gulf General Atomic is lithium-diffusing the samples in an effort to save time and insure that our sample requirements are met. A program to lithium diffuse silicon by two techniques, lithium paint-on and lithium-tin bath has been initiated.

In the lithium paint-on technique, a lithium mixture, consisting of a 10:1 volume ratio of lithium to Al_2O_3 blended to paste consistency with mineral oil, was applied to one large flat side of the sample. Samples of high-purity vacuum-float-zone n-type silicon, 10^4 ohm-cm and 1.5 x 1.5 x 0.23 cm, were diffused for up to 2 hours at 450°C. The lithium paste was removed and the lithium redistributed at 450°C.

Two lithium-doped tin baths were prepared by mixing approximately 1:1000 weight ratios of (99.9%) lithium metal powder with (99.98%) tin metal pellets (40 mesh) and melting the mixture. The "as-received" tin was somewhat oxidized, and this oxide was removed by dripping the melt through small glass orifices. Emission spectroscopy analysis indicated the baths contained 0.2 percent and 1 percent lithium by weight. These concentrations allow the application of published data[1] on lithium-diffusing of silicon. Vacuum-float-grown samples were prepared with resistivities of from 0.25 ohm-cm to about 10^3 ohm-cm corresponding to estimated lithium concentrations ranging from about 5×10^{14} cm^{-3} to about 5×10^{16} cm^{-3}. The 10^3-ohm-cm sample, however, exhibited nonuniform resistivity (high in the center and low at the surface of the sample) and will be discarded. Samples with $\rho \lesssim 11$ ohm-cm are uniform, and will be used. Additional samples will be produced as necessary.

2.2 NEUTRON ACTIVATION ANALYSIS

Using available techniques and equipment, the Activation Analysis Group at Gulf General Atomic quantitatively detects as little as 10^{-9} g of lithium.

Three samples underwent analysis. One 10^4 ohm-cm sample contained no lithium; a second sample, about 3×10^{-10} g of lithium; and the third sample, nearly 10^{-8} g of lithium. These samples were chosen to test the reliability of neutron activation analyses for small quantities of lithium and to start the program which will correlate the lithium content as determined by electrical conductivity with activation analysis measurements.

The activation analysis results on the first three samples indicate greater lithium content than that indicated by room-temperature resistivity measurements. The lithium content, determined by activation analysis, was about a factor of 3 greater than the resistivity measurements. Measurements of the 10^4 ohm-cm sample indicated small traces of lithium and this reading is being verified.

Three more samples will undergo activation analysis. Another 10^4 ohm-cm sample was included to test the reliability of the technique. The results have not yet been received.

2.3 ELECTRICAL MEASUREMENTS

Resistivity profiles for several lithium-diffused samples were determined with a four-probe technique. These measurements determined the uniformity of lithium diffused into the silicon. One of the lithium-diffused samples was originally 6.4 x 8.7 x 2 mm. The initial resistivity of each side was measured, then 0.25 mm was lapped off one side and the resistivity of both sides measured. This process was repeated, each time removing about 0.25 mm from the same side, until the sample thickness was reduced to about 1 mm. Our four-probe instrument has 1-mm probe spacing, so the measured resistivity was corrected for the diminishing sample thickness. Figure 1 shows the corrected resistivity versus sample thickness of the 11-ohm-cm sample.

Lifetime samples were fabricated from 11-ohm-cm, 4-ohm-cm, and 0.4-ohm-cm lithium-diffused, vacuum-float-zone-grown silicon. Sample dimensions were about 1.6 x 1.6 x 9.1 mm. The first 11-ohm-cm sample was mounted in the cryostat illustrated in Fig. 2 and cycled several times from about 100°K to about 400°K. The resistivity and preirradiation minority-carrier lifetime was measured with a 600-keV flash X-ray used to inject carriers.

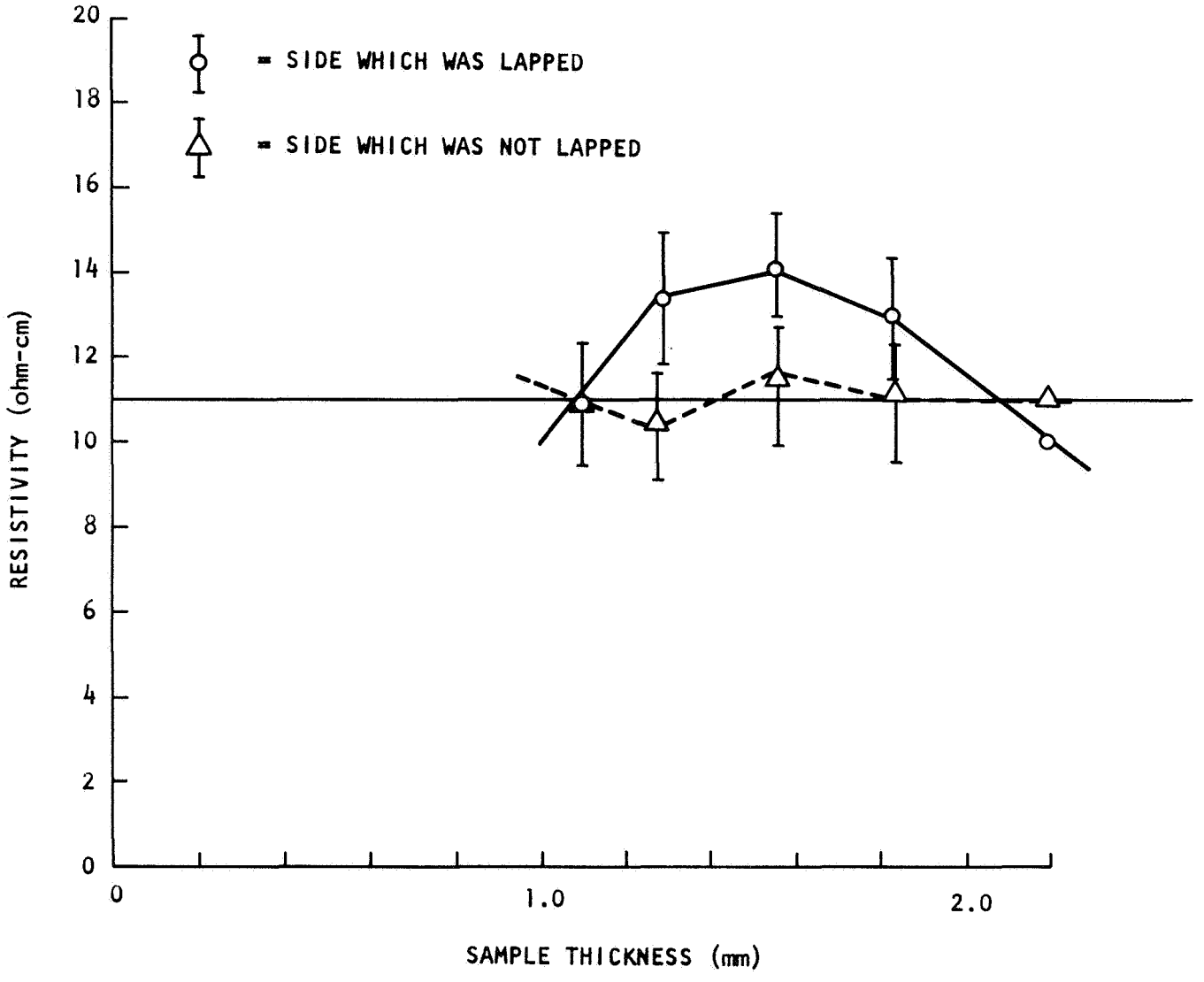

Fig. 1--Resistivity versus sample thickness for the 11-ohm-cm lithium-diffused silicon

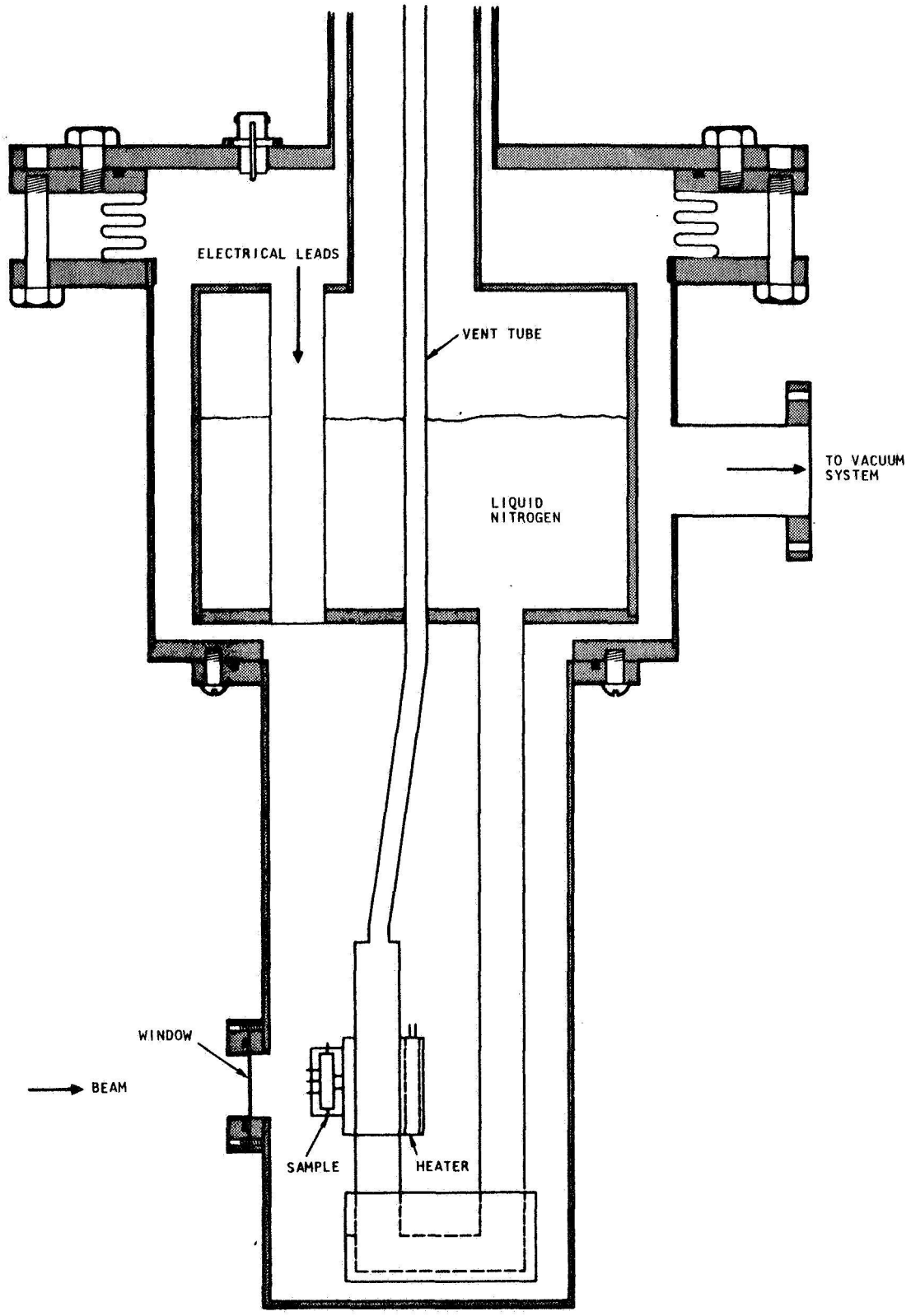

Fig. 2--Variable temperature (50 to 500 deg K) cryostat used to make electrical and optical measurements

Figures 3 and 4 exhibit temperature-dependence of conductivity and lifetime plotted as σ and τ versus (1000/T). The 11-ohm-cm sample had a relatively long preirradiation lifetime (τ = 50 ±10 μsec at 300°K).

After the preirradiation electrical measurements, the sample was irradiated at room temperature with 30-MeV electrons produced by the Gulf General Atomic linear accelerator. Damaging pulses were 4.5-μsec long with fluences of 2.5×10^{11} e/cm^2 per pulse. Low injection levels for lifetime measurements were accomplished by shortening the Linac pulse length to 0.4 μsec, defocusing the beam, and reducing the beam intensity. The detailed data reduction of this run is still in progress, but some preliminary conclusions can be drawn. The sample's initial lithium content was less than 10^{16} cm^{-3} and room-temperature minority-carrier lifetime τ_0 about 55 μsec. This lifetime was reduced to about 1.2 ±0.2 μsec by a net fluence Φ of about 2×10^{13} e/cm^2. The degradation constant K, defined by the equation $1/\tau = 1/\tau_0 + K\Phi$, was approximately 5×10^{-8} (cm^2/e-sec), near that observed in 10-ohm-cm nonlithium-diffused silicon and a factor of 2 less than was previously observed in samples diffused with lithium to between 10^{16} and 10^{17} cm^{-3}.

Isothermal anneals were attempted at 360°K and 380°K. After an hour at 360°K and a half hour at 380°K, the room-temperature lifetime recovered to about 10 μsec. Further irradiation with 30-MeV electrons indicated a degradation constant of about 3×10^{-8} (cm^2/e-sec) and preliminary analysis of the data indicates that, after redegrading the lifetime to about 1.5 μsec, little further annealing was observed at about 420°K even though the sample resistivity was 15 ohm-cm.

Figure 3 also shows postirradiation conductivity as a function of temperature between 160°K and 400°K. (Below 160°K, high contact resistance made measurements unreliable.) These data are presented in a rough form. The raw data will be reduced with a computer program and semiautomatic readings of the raw data, which should result in more accurate measurements.

The minority-carrier lifetime was measured as a function of time during the isothermal anneals at 360°K and 380°K. The reduction of these data is not complete.

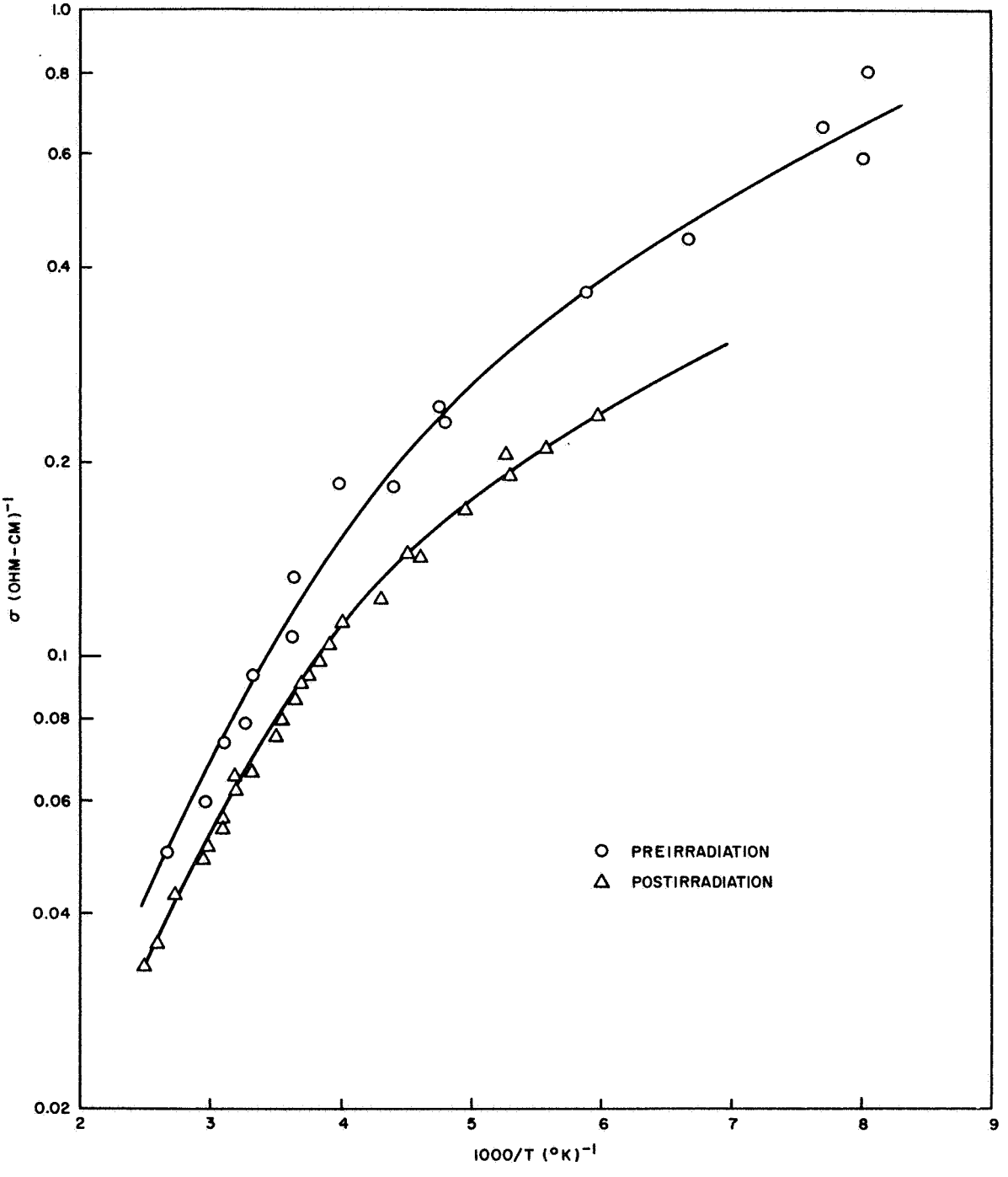

Fig. 3--Electrical conductivity as a function of 1000/T for lithium-diffused n-type silicon

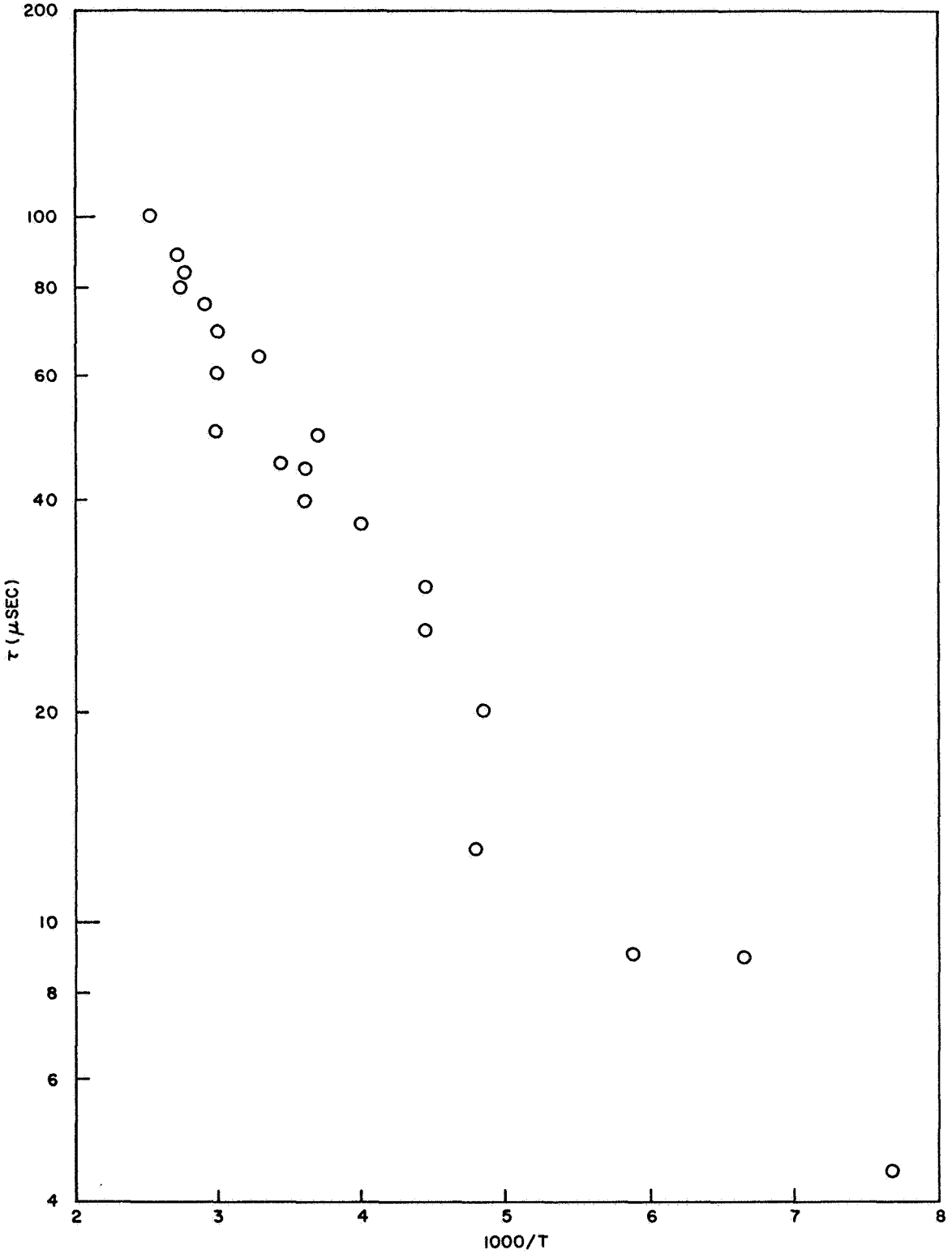

Fig. 4--Preirradiation minority-carrier lifetime versus 1000/T for lithium-diffused n-type silicon

After the second isothermal anneal, we observed a trapping center. This center did not anneal at temperatures up to $420^{\circ}K$.

3. ANALYSIS AND CONCLUSIONS

Using both the techniques of lithium paint-on and lithium-tin bath, we can uniformly diffuse lithium into n-type silicon. The donor concentrations of these diffused samples range from 5×10^{14} cm^{-3} to 5×10^{16} cm^{-3}. These diffusing techniques will be used to produce the samples for the experimental program.

All previous work has assumed that the lithium concentration is equal to the donor concentration. The results of the activation analysis studies indicate that the amount of lithium is greater than the donor concentration, implying the existence of large quantities of electrically inactive lithium. The lithium, present as free lithium, may also be present in large complexes. These large complexes, if they can be broken up, may be a source of free lithium.

The initial electrical measurements on the 11-ohm-cm lithium-diffused n-type sample are presented in Figs. 3 and 4. The variation of electrical conductivity as a function of 1000/T (Fig. 3) can be explained by the changes in carrier mobility. These data indicate no donor level in the region from $160^{\circ}K$ to $400^{\circ}K$, which is equivalent to the nonexistence of a level in the region from 0.1 eV below the conduction band to 0.40 eV below the conduction band. The temperature dependence of the minority-carrier lifetime data is evident in the data presented in Fig. 4. No attempt has been made to fit this dependence to the Shockley-Read recombination theory using the recombination capture cross sections of Lax. This fit will be attempted with the computer as soon as the lifetime values in Fig. 4 are determined with greater accuracy. When these lifetime data are analyzed, further information on the band-gap position of the recombination center in lithium-diffused silicon will be made available.

The 11-ohm-cm sample was selected for investigation because of its relatively low lithium content. We hoped to observe the effect of lithium

depletion during the irradiation experiment, and it appears that we may have. The lifetime degradation constant approximates that of nonlithium-diffused silicon, and, while partial annealing was observed when the sample was heated to 360°K, only partial annealing was observed for temperatures as high as 420°K after further irradiation, indicating that the mobile lithium had been depleted.

Revised and more accurate information on this sample will be included in future reports, following completion of detailed data reduction.

We plan to irradiate samples estimated to contain between 2 and 30 times more lithium, in anticipation that additional information will clarify our present observations.

4. FUTURE WORK

The next irradiations of lithium-diffused n-type silicon will be performed on 0.4-ohm-cm material. The effects of lithium depletion and the mechanisms of defect production will be given more intense study. Electron spin resonance to observe the production and annealing of the divacancy in lithium-diffused silicon will also be initiated in the near future.

5. NEW TECHNOLOGY

No new technology is currently being developed or employed in this program.

REFERENCE

1. H. Reiss and C. S. Fuller, Journal of Metals, February 1956, pg. 276.