

FIRST QUARTERLY REPORT

STUDY OF RADIATION EFFECTS IN LI-DOPED  
SILICON SOLAR CELLS

15 August 1968

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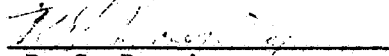
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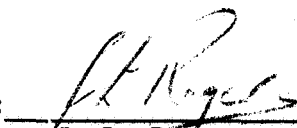
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ABSTRACT

This report covers the initial three months of effort on JPL Contract No. 952251 concerning radiation effects in Li-doped silicon. Inasmuch as considerable additional work remains to be performed, the data and conclusions presented herein are considered tentative. Initial efforts utilizing  $\text{LiAlH}_4$  as a diffusion source are promising, but to date have failed to yield surface lithium concentrations in excess of  $10^{17}$  atoms/cm<sup>3</sup>. Lang x-ray topography has been attempted to determine whether lithium instabilities at higher temperatures are due to precipitation, outdiffusion, or some other mechanism. Results to date indicate that lithium precipitation producing strained regions greater than 0.1 mm are not observed. Removal rate studies indicate exponential carrier removal as a function of electron fluence in Li-doped float-zone silicon, but a linear dependence on electron fluence in crucible grown silicon. Finally, isochronal annealing studies indicate a variety of material dependent effects including relatively low temperature annealing stages and reverse annealing stages. Sufficient data on these annealing phenomena have not yet been obtained to determine their dependence on material parameters.

## I. INTRODUCTION

This report covers activities during the first three months of performance on JPL Contract 952251. This work has included studies of new methods of diffusing lithium into silicon, thermal stability of lithium doped silicon, radiation caused carrier removal in lithium doped silicon, annealing of carrier removal damage, and recovery kinetics studies. As this period covered the start of the contract, considerable effort was expended on preparation, planning and equipment maintenance.

## II. PROGRESS IN THIS REPORT PERIOD

Recent studies have been directed at a better understanding of the behavior of lithium in silicon. More knowledge is needed regarding the thermal stability of lithium doped silicon and the role of lithium in the radiation damage processes. The results reported here are intermediate in nature and will be further elaborated before drawing significant conclusions.

### A. Diffusion Sources

A series of diffusion experiments have been performed to evaluate the usefulness of  $\text{LiAlH}_4$  as a diffusion source. The material was used in the form of a 5 molar solution in diethyl ether. The silicon wafers were painted with a thick coating of solution. The first problem involved in use of this material is the evaporation of the solvent to obtain a uniform coating of the hydride. There is a strong tendency for the coating to bubble in some areas. A second problem is the tendency of the hydride to easily oxidize. The oxidation problem was eliminated by evacuating the diffusion furnace before heating. Use of an inert atmosphere would probably also suffice. The one clear advantage of this material is lack of physical attack

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of the silicon surface which is common with a lithium-mineral oil paste. The surface of the hydride diffused wafers remained flat with no pitting and the residue is easily removed. So far it has not been possible to produce any surface concentrations in excess of  $10^{17}$  Li atom/cm<sup>3</sup>. Additional work should improve this problem.

#### B. Stability Studies

When lithium doped silicon is raised to temperatures above 300°C and cooled to room temperature, the resistivity increases. Such a change could be caused by precipitation or outdiffusion of lithium. The times and temperatures involved suggest outdiffusion. To further investigate this behavior lithium doped float zone silicon wafers were annealed at various temperatures and slow cooled to room temperature. The resistivities of these wafers were measured with a four point probe after sufficient material was removed to insure uniform lithium distribution. The resistivity results are shown below:

|               |            |                                         |
|---------------|------------|-----------------------------------------|
| As received   | 0.035 Ω-cm | $5.1 \times 10^{17}$ Li/cm <sup>3</sup> |
| 1 hr @ 200°C  | 0.035 Ω-cm | $5.1 \times 10^{17}$ Li/cm <sup>3</sup> |
| 1 hr @ 300°C  | 0.035 Ω-cm | $5.1 \times 10^{17}$ Li/cm <sup>3</sup> |
| 18 hr @ 400°C | 21.2 Ω-cm  | $2.4 \times 10^{14}$ Li/cm <sup>3</sup> |

These wafers were examined by the Lang x-ray topography technique after all treatments. This x-ray technique uses Bragg reflection from a given set of crystal planes to give an unmagnified image of the crystal. Stressed areas of the crystal reflect the X rays more strongly and appear darker on a photographic plate, or lighter on a positive print such as those shown. Figures 1 and 2 are 9x enlargements of (220) topographs of the as-received and 18-hrs-at-400°C specimens, respectively. The topographs are taken in transmission through the specimens, using Mo characteristic radiation, and show a projection of the structural defects throughout the volume of the specimens, not just the surface. Instrumental resolution is less than 10 microns in the direct specimen image, which is less than 0.1 mm on the enlargements.

The highly dislocated structure normally associated with float-zone silicon is clearly shown in Figures 1 and 2. Individual dislocations are easily seen in many parts of the topographs. The spot at the edge nick is distortion associated with a zone spill during zone-refining of the crystal. The small white spot in Figure 1 is spurious, and is probably due to a scratch during handling of the photographic plate. The light area in Figure 2 near the edge and 90 degrees from the zone spill is due to the specimen mounting post, which did not appear in Figure 1 because that specimen was mounted at the unseen edge. The prominent white spot in Figure 2 appeared with the first heat treatment and is due to improper handling by tweezers.

No separate precipitate particles which might be integrated as lithium metal precipitates are seen. If present, such particles should be visible because of the extremely high strain sensitivity of this technique. However, it is entirely possible that lithium may precipitate at existing dislocations, causing very little change in specimen appearance. This specimen will be analyzed for lithium by atomic absorption spectrometry to check for outdiffusion of lithium. It is planned to repeat this experiment using Lopex silicon, which is relatively free of dislocations.

### C. Removal Rate Studies

Recent work has indicated that there are significant differences in the nature of the carrier removal process during irradiation of floating zone and crucible grown lithium doped silicon. One difference is in the annealing behavior and a second is found in the irradiation removal rate for majority carriers. We have previously discussed the manner in which the majority carrier concentration changes exponentially with electron fluence in heavily lithium doped floating zone silicon. This effect is again shown in Figure 3. It can also be seen in this figure that the situation is very different in similarly doped crucible grown silicon. In such material the decrease of carrier concentration is linearly related to the electron fluence. The removal rate constant for this material appears to be  $1.8 \text{ cm}^{-1}$ . This indicates that the production rate of these defects is constant and independent of the lithium concentration. This observation

is in contrast to that of float zone material which is proportional to the remaining ionized lithium concentration. Since the oxygen concentration in the crucible silicon is much higher than the lithium concentration, it is likely that the defects forming do not consume lithium but rather involve some combination of displacement products with oxygen. More work is necessary to clarify the data and allow a proper interpretation of these effects.

#### D. Annealing

As previously mentioned, the study of annealing of carrier removal damage has indicated some significant differences in various lithium doped silicon crystals. The results of the isochronal (15 min.) annealing of various irradiated lithium doped crystals are shown in Figure 4. One interesting phase of this data is the low temperature annealing stage in the 0.1 ohm-cm lithium doped float zone silicon. This stage occurs rapidly at 175°C and appears to be a discrete chemical reaction. Data from two such samples with different electron fluence are shown in Figure 4. In both cases it was possible to fit the data to a theoretical function which describes the isochronal anneal of a first order process, the time constant of which is limited by an activation energy of 0.32 eV. A different value of the pre-exponential constant was required for each of the samples, since this sample with a 3 fold higher fluence annealed at a slightly higher temperature. It is interesting to note that, in both cases, this stage restores roughly 40% of the carrier removal damage and the remainder is stable to 350°C. Attempts to continue the annealing at higher temperatures are nullified by the previously discussed "outdiffusion" effect which rapidly removes carriers at 400°C. The annealing is similar in temperature range to that of the Si-E center, but that center anneals with an activation energy of 0.94 eV. It is also unlikely that Si-E centers would be produced because phosphorus concentration of this material (approx.  $10^{14} \text{ cm}^{-3}$ ) is not sufficient to produce the required defects. The activation energy of 0.32 eV is curiously low. Interestingly this value is half that of the activation energy for lithium diffusion. This value is even smaller than the energy of solution of lithium in silicon (0.54 eV). Further work is necessary to confirm the data.



The 0.07 ohm-cm quartz crucible silicon and the 2 ohm-cm float zone silicon both exhibited similar annealing behavior after irradiation despite their very different impurity concentration. Both samples are characterized by a "negative annealing" stage at 100°C. This in effect is the formation of additional carrier removal defects from other incipient or latent defects which were prevented from forming a more stable defect by some thermally activated limiting process. The second point of interest is an annealing stage observed in both materials after heating to 150°C. In the 2 ohm-cm float zone the annealing stage removes approximately all of "reverse anneal" damage produced at 100°C. In the quartz crucible silicon the 150°C annealing stage removes over 10% of the original carrier damage in addition to the "reverse anneal" damage. The reason for the different behavior in these two samples may be related to the relative lithium and oxygen concentrations which are more nearly equal in the case of the last described samples.

### III. FUTURE WORK

We have received enough lithium solar cells to start the applied portion of the program. Evaluation studies will be performed and additional studies will be made to support theoretical work on the model for the kinetics of recovery. In addition, gold barrier diodes now being studied will be analyzed for use in these studies.

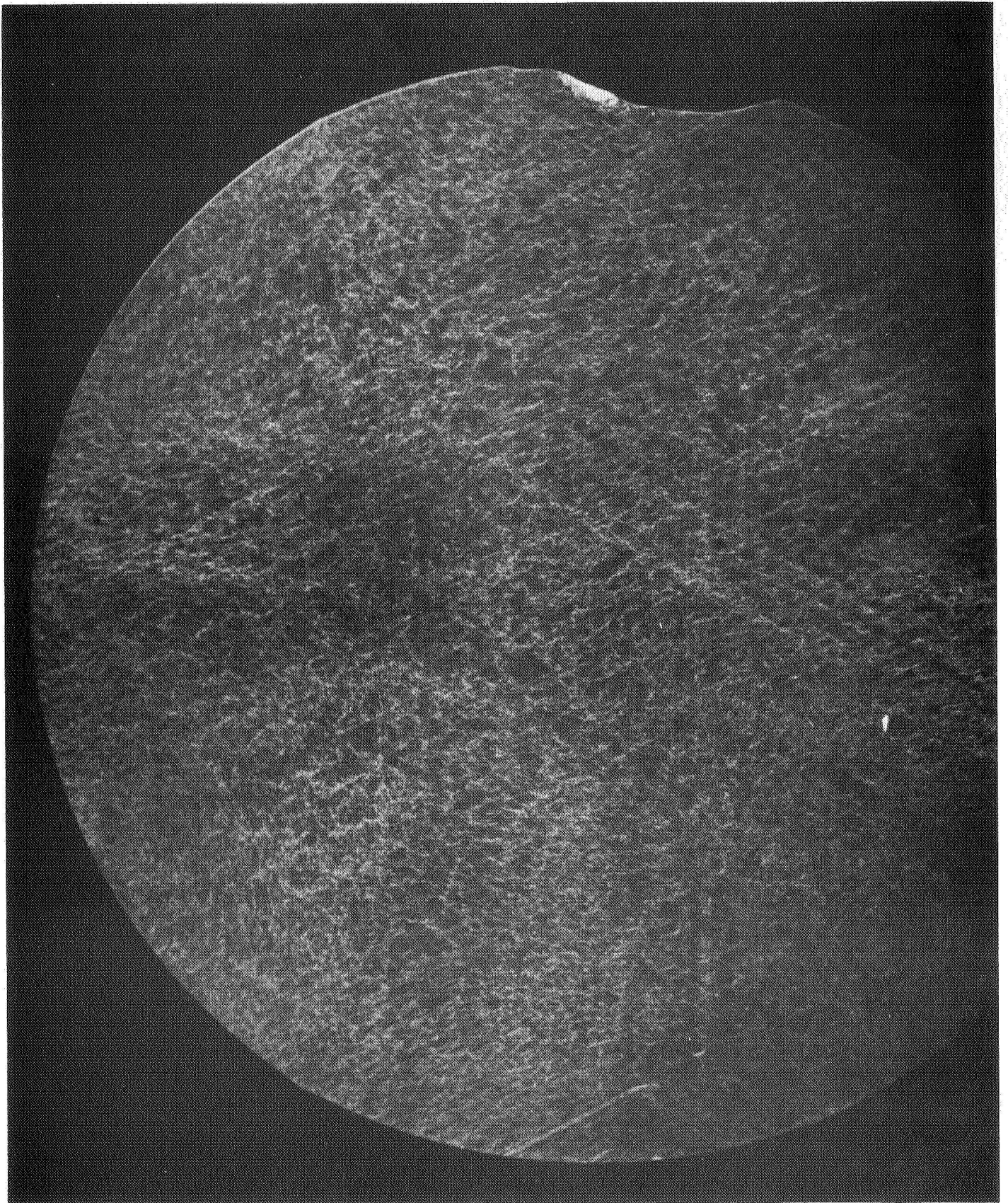


FIG. 1 TOPOGRAPH OF LITHIUM DOPED FLOAT ZONE  
SILICON (0.1 ohm-cm), AS RECEIVED



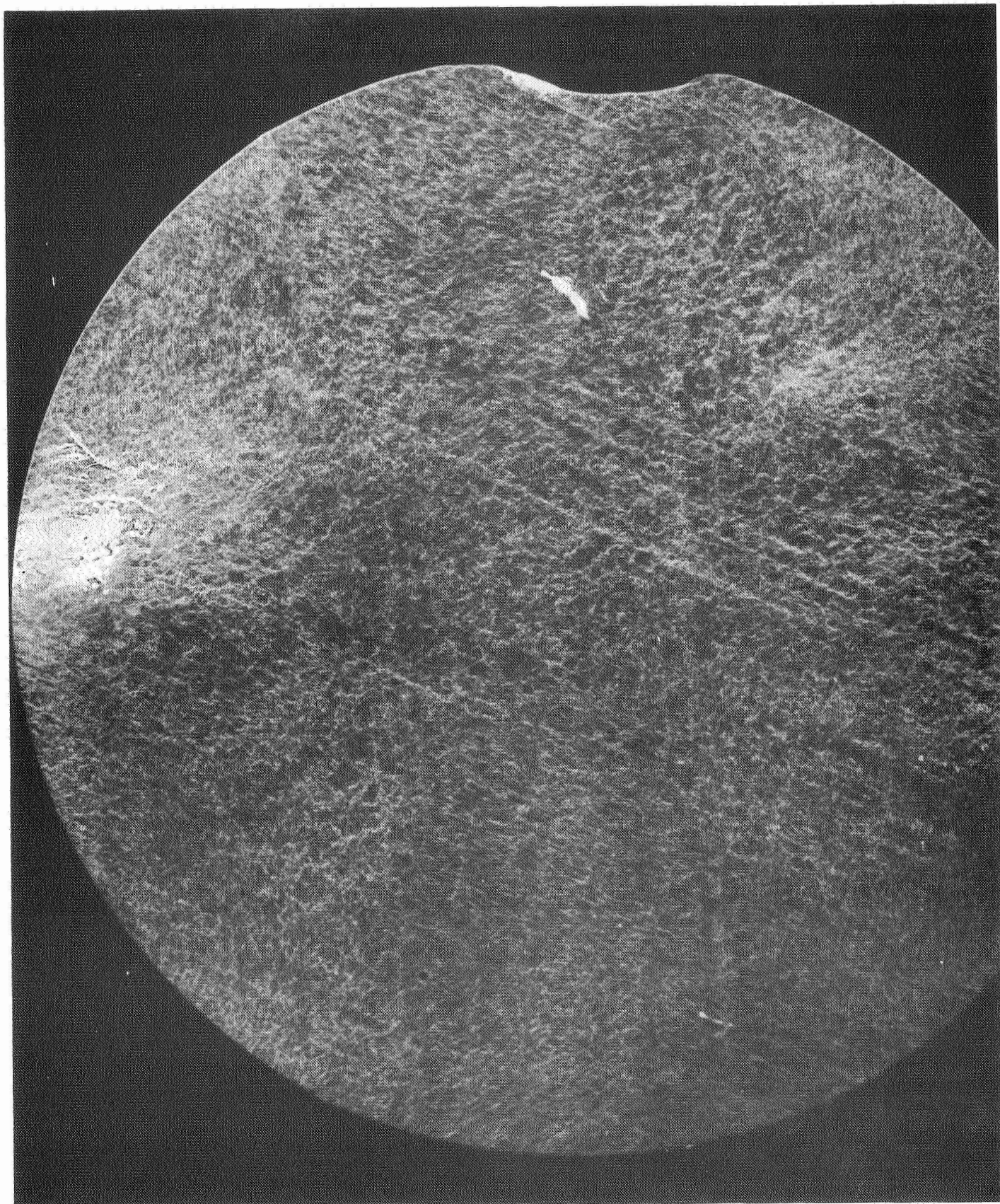


FIG. 2 TOPOGRAPH OF LITHIUM DOPED FLOAT ZONE SILICON  
(21 ohm-cm), AFTER 18 HRS. AT 400°C, SLOW COOLED

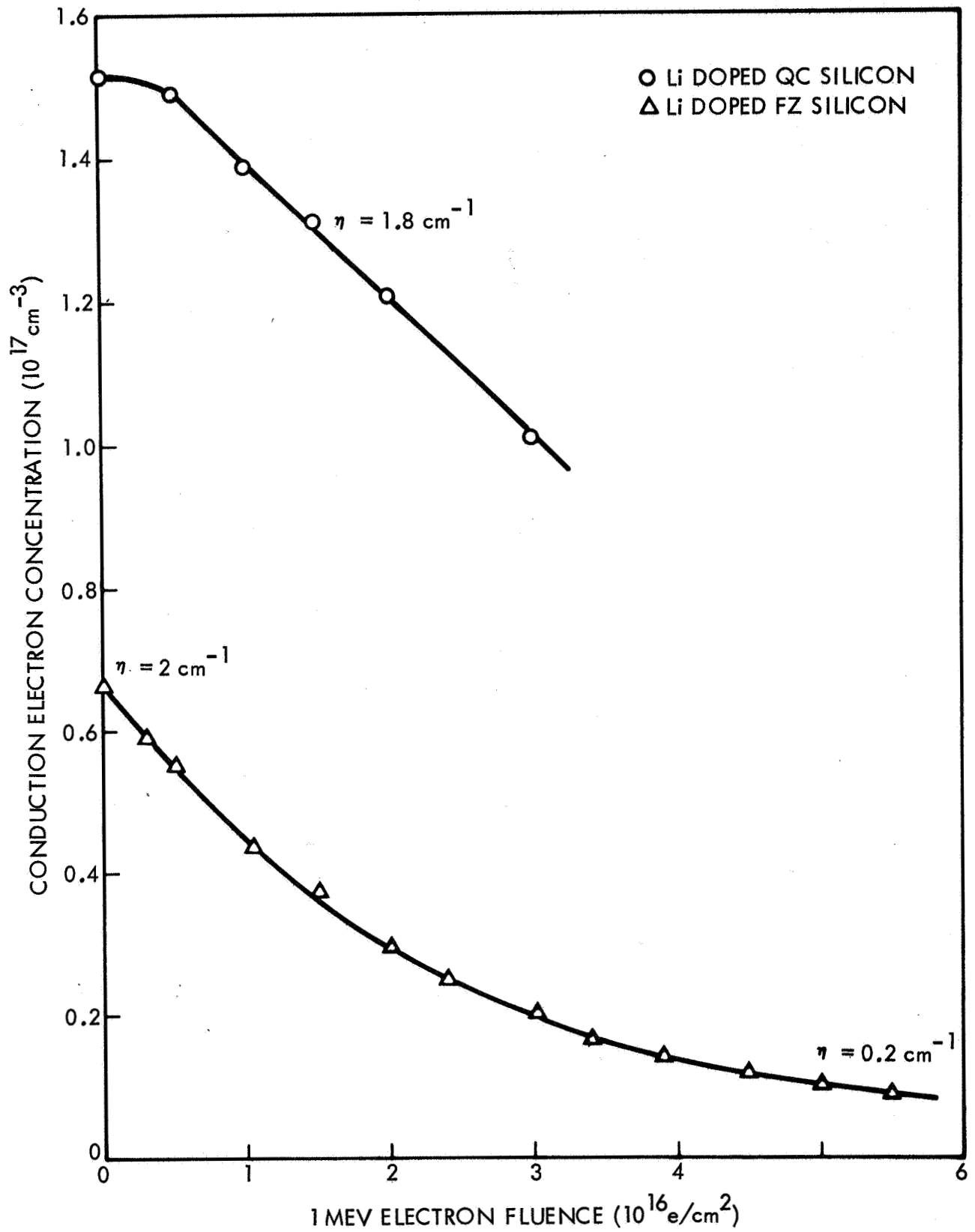


FIG. 3 MAJORITY CARRIER REMOVAL IN LITHIUM DOPED SILICON UNDER ELECTRON IRRADIATION

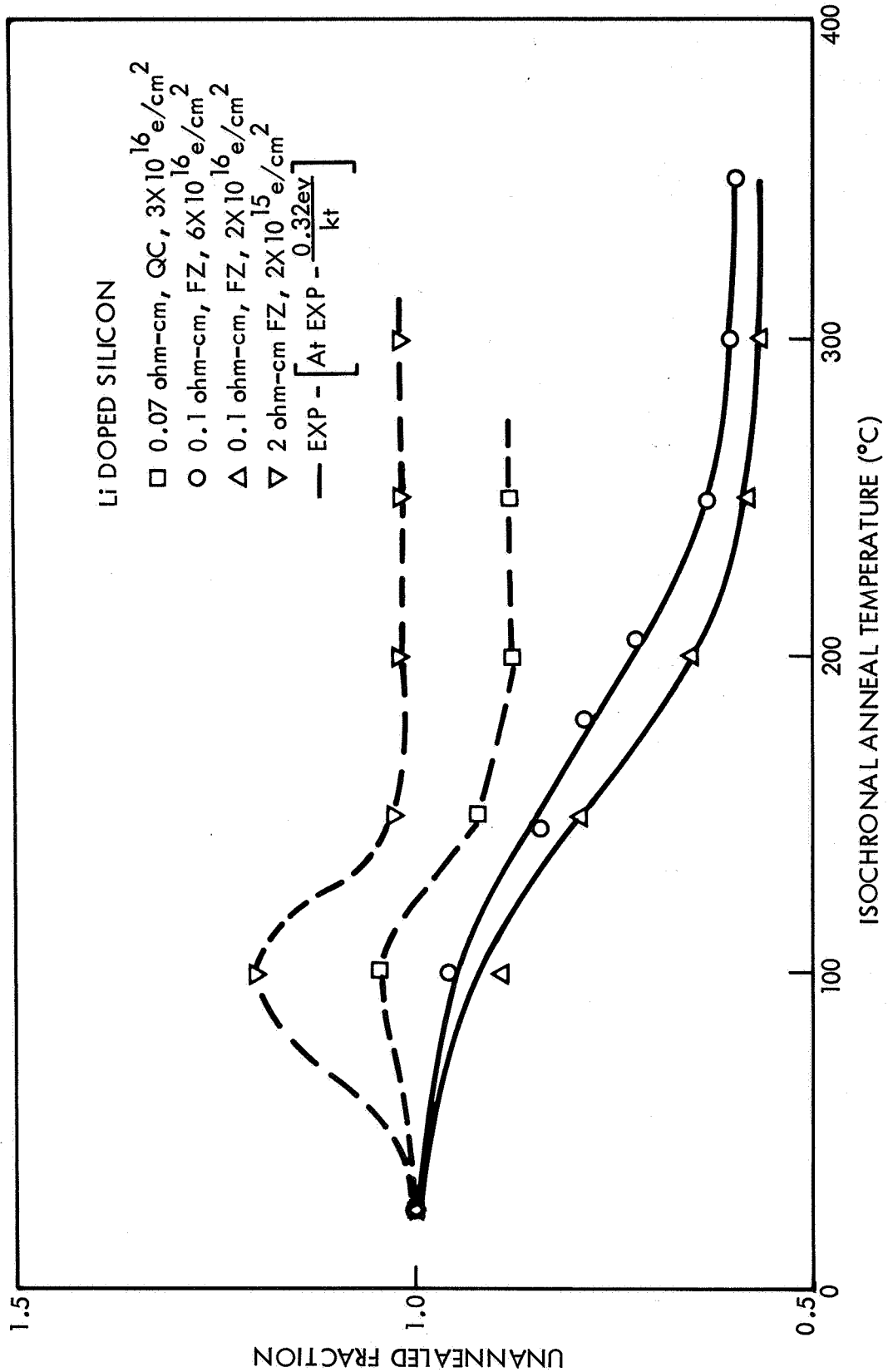


FIG. 4 ANNEALING OF CARRIER REMOVAL DAMAGE IN LITHIUM DOPED SILICON