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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report 32-1574

*Development of Lithium-Doped Radiation-Resistant
Solar Cells*

Paul A. Berman

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**JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA**

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Preface

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Abstract

In the middle 1960s it was discovered that the addition of lithium to *n*-base silicon solar cells resulted in what appeared to be annealing of radiation-induced defects. For the past five years JPL has been intimately involved in an effort to exploit this phenomenon in order to develop a highly radiation-resistant, high-efficiency silicon solar cell. This paper discusses the results of the investigations carried out which represent major achievements with respect to attaining this goal. Lithium-doped solar cells have now been fabricated with initial lot efficiencies averaging 11.9% in an air mass zero (AMO) solar simulator and a maximum observed efficiency of 12.8%. The best lithium-doped solar cells are approximately 15% higher in maximum power than state-of-the-art *n-p* cells after moderate to high fluences of 1-MeV electrons and after 6-7 months exposure to low flux (approx 10^{12} e/cm²/day) irradiation by a Sr⁹⁰ beta source, which approximates the electron spectrum and flux associated with near-Earth space. Furthermore, lithium-doped cells were found to degrade at a rate only one tenth that of state-of-the-art *n-p* cells under 28-MeV electron irradiation.

Excellent progress has been made in *quantitative* predictions of post-irradiation current-voltage characteristics as a function of cell design by means of capacitance-voltage measurements, and this information has been used to achieve further improvements in lithium-doped cell design. Major improvements in cell processing have also been achieved, resulting in higher cell efficiency and greater reproducibility.

Development of Lithium-Doped Radiation-Resistant Solar Cells

I. Introduction

Increasing the radiation tolerance of solar cells is important in any solar array system since it results in greater reliability, reduction in array size and weight, and, if cell costs do not increase significantly, greater economy. While these factors are important for all missions, they become extremely important for those missions which require large-area solar arrays (such as manned orbiters, electric propulsion missions, and Jupiter flyby missions) because a specific percentage reduction in the number of cells required represents a significant absolute cost reduction. Missions requiring such large-area solar arrays could take place in the middle 1970s or even earlier. The amount of radiation expected for a particular mission is, of course, dependent upon the mission trajectory, time of launch (with respect to the solar cycle), and mission duration. However, there is always a probability of exposure to a significant amount of radiation from such sources as the Van Allen belts and solar proton flares.

State-of-the-art solar cells used in spacecraft solar array power systems degrade with electron and proton irradiation which occurs in near-Earth space as a result of the Van Allen belts and in deep space as a result of solar proton flares. The amount of degradation is de-

pendent upon the irradiation spectrum and fluence. This problem is resolved by overdesigning the panels with respect to the initial power output so that the degraded output will meet or exceed mission requirements. This approach is often used in conjunction with thick coverglasses which attenuate some of the radiation. Thus tradeoffs must be made between the power and useful lifetime of a solar array and its allowable size, weight, and cost.

A major advancement was achieved in the last decade with the replacement of the p diffused into n -base solar cells by the more radiation tolerant n diffused into p -base solar cells. A second major advancement in achieving greater radiation tolerance occurred during mid-decade when it was discovered that the addition of lithium to n -base silicon resulted in what appeared to be annealing of radiation-induced defects. For the past five years JPL has been involved in an effort to exploit this phenomenon in order to develop an even more radiation-tolerant solar cell, which, ironically, has the previously discarded p diffused in n -base configuration. To this end, NASA/JPL has technically and financially supported a large number of organizations in the investigation of various aspects of the problem of achieving high-efficiency, radiation-resistant, lithium-doped solar cells.

The advancements made with respect to lithium-doped cells development have clearly shown the power of the interdisciplinary approach which was adopted throughout the life of the program. Problems such as cell instability, low efficiency, poor process control, unpredictability of recovery characteristics, variations in recovery rate, cell size limitations, etc., that at one time seemed to be all but insoluble, appear to be falling by the wayside. These problems could not have been solved without the involvement of the expert team represented by the organizations participating in this program as shown in Table 1. Each organization isolated the problems with respect to its own area of expertise, and the resultant body of information was coordinated and distributed to the other organizations by JPL. It is strongly felt that such an approach is applicable to many other programs (e.g., application of space technology to the economic generation of terrestrial power by means of solar energy conversion) and should prove to be of immense value in the majority of cases.

II. Objectives

In the past, the vast numbers of unknowns associated with lithium-doped solar cells and their relationship to the cell characteristics made it somewhat impractical to fabricate quantities of similar cells. The program was in a highly developmental phase. Work has now progressed, however, to the point where there is an understanding of the general characteristics of lithium-doped cells as a function of cell design, and quantitative evaluations are now possible.

One of the major objectives of the program was to assure that the participating organizations were all studying the same kinds of cells, that is, cells so fabricated to be more or less identical. Also emphasis was placed on supplying enough cells of a specific design to permit the investigators to obtain reasonable statistics in their experiments. Another objective was to directly compare the electrical characteristics of the best float-zone and crucible-grown lithium-doped cells with those of state-of-the-art $10\ \Omega\text{-cm}$ $n\text{-}p$ type cells on the basis of irradiation by 1-MeV electrons. Another major effort was to obtain better process control of the lithium-doped silicon solar cells. It is obviously important that variables not associated with the parameters being studied (mainly lithium concentration and starting material) be controlled as closely as possible. Therefore, work was carried out to obtain better techniques: (1) for diffusion of the $p\text{-}n$ junction, (2) for introduction of lithium (primarily to obtain more uniform and controlled concen-

tration profiles, both laterally and transversely), and (3) to improve reproducibility.

In order to achieve these major objectives, it was necessary to determine the effects of cell design and pro-

Table 1. Organization summary

Organization	Function
Heliotek Division of Textron, Inc., Sylmar, Calif.	Lithium-doped cell development, analysis, and fabrication
Centralab Division of Globe Union, El Monte, Calif.	
Naval Research Laboratory, Washington, D. C.	Investigation of behavior and operating characteristics of lithium-doped silicon cells in a simulated space environment
Philco-Ford Corp., Palo Alto, Calif.	
Lockheed Georgia Corp., Marietta, Ga.	
RCA, Princeton, N.J.	Evaluation and analysis of lithium-doped silicon, silicon diodes, silicon solar cells.
TRW Systems, Redondo Beach, Calif.	Investigation of radiation damage model and annealing kinetics
Gulf Radiation Technology, San Diego, Calif.	Evaluation of lithium-doped silicon. Investigation of radiation damage model and annealing kinetics
Naval Research Laboratory, Washington, D.C.	
University of Illinois, Urbana, Ill.	Study of luminescent and tunneling phenomena in irradiated silicon
MIT, Cambridge, Mass.	
University of Utah, Salt Lake City, Utah	Study of radiation kinetics in electronic material
Rensselaer Polytechnic Institute, Troy, N.Y.	Investigation of structure of radiation damage in lithium-diffused silicon solar cells
University of Denver, Denver, Colo.	Study of effects of space particle bombardment on solar cell materials
University of Kentucky, Lexington, Ky.	Study of structural damage in lithium-doped solar cells by neutrons
Brown University, Providence, R.I.	Study of effects of sub-threshold electron irradiation on silicon
Jet Propulsion Laboratory, Pasadena, Calif.	Direction and coordination of all above programs

cessing parameters on the preirradiation and postirradiation cell characteristics and to develop methods of reproducibly effecting the desired cell design. This involved yet another objective, namely, development of analytical techniques to correlate cell design and processing with the observed effects on the preirradiation and postirradiation cell characteristics.

Still another extremely important objective of the program was to develop a better understanding of the underlying basic physical phenomena and to develop a theoretical model for the action of lithium in silicon solar cells and the interaction of lithium with radiation-induced defects.

III. Analytical Techniques

A number of analytical tools were utilized in order to gain understanding of the effects of lithium doping on both the fundamental physical properties and the device characteristics of silicon solar cells. Some of the major analytical tools used were:

- (1) Irradiation primarily by 1-MeV electrons, but also Sr^{90} β -sources, neutrons, protons, and high-energy (28–30 MeV) electrons.
- (2) Solar cell electrical characteristics measurement (primarily current–voltage characteristics).
- (3) Minority carrier diffusion length and lifetime measurements.
- (4) Junction capacitance measurements to determine the concentration and concentration gradient of ionized lithium near the junction.
- (5) Electrical resistivity measurements.
- (6) Hall-effect measurements to determine carrier removal rates and mobility changes.
- (7) Electron spin resonance (ESR) to determine the energy level and structure of radiation-induced defects.
- (8) Infrared absorption spectroscopy to determine radiation-induced defect levels.

The measurements shown in (2) through (8) above were generally monitored before and after irradiation and as a function of environmental conditions such as time and temperature. Of the analytical techniques discussed above, the most valuable technique (aside from the solar cell electrical characteristics measurements)

was found to be the capacitance–voltage measurement, which provided quantitative correlations with the cell radiation recovery characteristics.

IV. Analysis of Lithium-Doped Silicon

A. General

The results of measurements of carrier removal, diffusion length, and other such physical properties are often very strongly affected by the amount of lithium doping in the silicon. For example, the behavior of lightly lithium-doped silicon can be significantly different from that of heavily lithium-doped silicon because of masking effects or competing mechanisms. Thus great care must be taken in extrapolating the results of one level of doping to those of a different level of doping.

In some types of measurements, such as ESR and absorption spectroscopy, there is an inherent requirement for a particular concentration of defects in order that the structure be observed. Other techniques such as Hall effect, minority carrier diffusion length, and minority carrier lifetime measurements allow a wider latitude of lithium concentrations and can therefore be used to correlate results between low and high lithium concentrations.

B. Characteristics of Lithium-Doped Silicon as a Function of Lithium-Dopant Concentration

The Hall-effect measurements performed on heavily doped float-zone silicon indicated that all carrier removal occurred nearly instantaneously during irradiation by 1-MeV electrons. In the lightly lithium-doped float-zone samples, however, it appears that some carrier removal occurred during irradiation, but carrier removal continued to occur for a long time after termination of the irradiations, the loss during irradiation being related to the initial lithium concentration and the electron fluence. Capacitance–voltage measurements indicated that more lithium was consumed during recovery than during irradiation, which is not consistent with a model which assumes formation of a lithium vacancy defect during irradiation with subsequent association with a second lithium donor during recovery. Hall mobility values increased in a manner that indicates loss of lithium donors and no acceptor formation in the final state.

Lightly lithium-doped float-zone material irradiated with 1-MeV electrons indicated the formation of radiation-induced defects with a level 0.17-eV below the

conduction band as well as a second defect with a level deeper in the energy gap. The removal of both defects was seen during annealing. The introduction of the deeper level appeared to increase with increasing lithium concentration, indicating that lithium is probably associated with the structure of this defect. In contrast to this, the 0.17-eV-level introduction rate appeared to be independent of the lithium concentration. The introduction rate of the 0.17-eV level in lightly lithium-doped float-zone silicon, moderately lithium-doped crucible silicon and non-lithium-doped crucible solar cells was of the order of 0.2-cm^{-1} for all cases.

A distinct dependence of annealing properties of lithium-doped silicon on lithium concentration was observed in float-zone silicon with lithium densities between 2×10^{14} and $2 \times 10^{16}/\text{cm}^3$. The carrier density and mobility of lightly lithium-doped silicon changed very slowly with time at room temperature, in contrast to the very fast changes observed in heavily lithium-doped silicon. The lightly lithium-doped float-zone silicon exhibited annealing characteristics which are very similar to heavily lithium-doped crucible-grown silicon. The mobility increased slowly at room temperature and more rapidly at 373 K while the carrier density decreased. Increases in carrier density during room temperature anneal, which possibly indicates disassociation of lithium from defects, have been observed previously in heavily lithium-doped float-zone silicon but were not observed for the lightly lithium-doped float-zone silicon or heavily lithium-doped crucible silicon. It thus appears that the ratio of lithium concentration to the oxygen concentration has a major effect in determining the annealing properties of lithium in silicon. From this point of view, low-oxygen-content silicon can be made to behave in a manner similar to high-oxygen-content silicon if the ratio of lithium to oxygen remains relatively constant.

Lithium-diffused float-zone silicon was irradiated with 30-MeV electrons and examined for changes in minority carrier lifetime τ . The degradation constant K , thus obtained for lightly lithium-doped silicon, was lower by about a factor of 2 than previously measured for more highly lithium-doped silicon and was similar to that obtained for silicon without lithium doping, indicating that lithium is involved in the configuration of the initial damage center. Annealing of highly lithium-doped silicon after a fluence of $4 \times 10^{14} \text{ e/cm}^2$ resulted in an increase in τ which indicated annealing of 80% of the irradiation-induced recombination centers. Annealing was inhibited as the fluence was increased; the higher the lithium concentration, the greater the fluence required to inhibit recovery. These observations strongly

indicate that lithium is depleted during production and annealing of radiation-produced recombination centers.

The analysis of more lightly lithium-doped silicon indicated that the preirradiation τ was determined by two centers, one located approximately 0.17 eV below the conduction band ($E_c - 0.17 \text{ eV}$) and the other deeper than 0.35 eV from either band edge. Furthermore, at least two kinds of recombination centers appeared to be introduced in this material by the irradiation, one at $E_c - 0.17$ being dominant at temperatures above 150–200 K and the other, deeper than 0.35 eV from either band edge, being dominant at temperatures below 150–200 K. The low temperature center was not significantly annealed in 1 h at 390 K, but at least partially annealed over long times at room temperature. (The heavily lithium-doped silicon annealed completely at room temperature.) The high-temperature center was significantly annealed in 1 h at 380–400 K.

Heavily lithium-doped float-zone silicon samples were irradiated by neutrons with energy $>10 \text{ KeV}$ to fluences up to $6.75 \times 10^{10} \text{ N/cm}^2$. Minority carrier lifetime was monitored for both isothermal and isochronal anneals. More than 90% of the recombination centers were annealed at temperatures of about 400 K. The damage coefficient K was found to be independent of the total fluence, in contrast to results of electron irradiation which indicated a fluence dependence of K . Moreover, the K was quite similar to that observed in non-lithium-diffused silicon, also in contrast to the results of electron irradiation which indicated a K dependence on lithium concentration. This would indicate that for neutron irradiation, which is expected to produce cluster defects, the initial radiation-induced defect is not affected by the presence of lithium, but that the lithium is extremely efficient in reducing the effectiveness of the defect in acting as a recombination center after annealing.

C. Electron Spin Resonance Investigation of Oxygen-Vacancy Center Production

Electron spin resonance (ESR) measurements were used to investigate the formation of radiation-induced oxygen-vacancy defect centers, commonly referred to as A-centers, in lithium-containing crucible-grown silicon (with phosphorus background doping). Prior to irradiation a resonance line attributed to the lithium-oxygen donor was observed, the density of which was proportional to the lithium concentration. No resonance due to the phosphorus donor was found, even though the phosphorus doping density was of the order of

$10^{16}/\text{cc}$. After 300 K irradiation by 30-MeV electrons to fluences of the order of 10^{16} – 10^{17} electrons/ cm^2 , the lithium–oxygen resonance line decreased while the oxygen–vacancy resonance line increased. The introduction rate of oxygen–vacancy centers for lightly lithium-doped samples was similar to that obtained for non-lithium-doped samples, while for heavily lithium-doped samples the introduction rate was lower by about an order of magnitude, indicating that lithium is acting in such a manner as to inhibit the stable formation of this type of defect. Upon annealing the heavily lithium-doped sample between 300–600 K, the annealing was found to be centered near 325 K as contrasted with results on non-lithium-doped silicon, which indicated an anneal of the oxygen–vacancy center near 550 K. This again indicates that the presence of lithium reduces the stability of this defect.

D. Activation Energy Associated With Annealing

The activation energy for annealing of lithium-doped float-zone silicon after irradiation by 1-MeV electrons was found to be of the order of 0.66 eV by RCA on the basis of the relationship between reciprocal temperature and unannealed fraction. Gulf Radiation Technology, on the basis of τ measurements as a function of isothermal annealing times after irradiation by 30-MeV electrons, has found a similar activation energy of the order of 0.75 eV for lightly, moderately, and heavily lithium-doped float-zone silicon. On the basis of isothermal and isochronal annealing studies on lithium-doped float-zone silicon after irradiation by neutrons, Gulf Radiation Technology has determined an activation energy of approximately 0.69 eV.

Annealing rate studies at various temperatures have been conducted by TRW on lithium-doped solar cells fabricated from crucible (oxygen-rich) silicon after irradiation by 1-MeV electrons by utilizing the I_{sc} parameter to determine reciprocal half-time for recovery as a function of reciprocal annealing temperature. The apparent activation energy was found to be of the order of 1.10 eV. Studies performed by RCA on the annealing characteristics of lithium-doped cells fabricated from crucible silicon indicated an activation energy of approximately 1.07 eV on the basis of the relationship of reciprocal fraction of damage remaining as a function of annealing time. RCA has also made measurements of the lithium diffusion constant near room temperature for an unirradiated lithium-doped cell fabricated from crucible silicon and has determined an activation energy of 1.03 eV utilizing measurements of lithium drift capacitance.

The accepted activation energy of lithium in oxygen-lean silicon as determined by Pell (Refs. 1–3) is of the order of 0.65 eV, and thus the activation energies determined from annealing studies of irradiated lithium-doped oxygen-lean silicon are in very good agreement with this value. It should be emphasized that the agreement is reasonable for all types of radiation investigated (i.e., 1-MeV electrons, 30-MeV electrons, and neutrons) and is surprisingly consistent in view of Pell's observation that the activation energy increases with increasing oxygen concentration and the fact that the amount of oxygen in oxygen-lean silicon is not a controlled or measured parameter. Pell determined the dissociation constant (activation energy) of lithium- O^+ to be approximately 0.42 eV, so that when this activation energy is added to the 0.65-eV activation energy for diffusion of lithium in silicon, an activation energy of 1.07 eV appears to be reasonable for high-oxygen-content lithium-doped silicon. The activation energy, indeed, is quite consistent with the activation energies determined through annealing studies on irradiated lithium-doped crucible-grown silicon and with the activation energy determined for unirradiated lithium-doped crucible silicon.

Thus a very good agreement is obtained among results of annealing studies done independently by TRW, RCA, and Gulf Radiation Technology, among results of annealing studies done after different types of irradiation, between results of annealing studies done on oxygen-lean and oxygen-rich lithium-doped silicon, and between the results of studies done on diffusion of lithium in unirradiated silicon and annealing characteristics of irradiated lithium-doped silicon. These studies show that the activation energy associated with neutralization of radiation-induced defects in lithium-doped silicon, whether they be point defects or cluster defects, is well in agreement with the activation energy associated with diffusion of lithium in silicon and lends very strong support to the theory that the neutralization of radiation-induced defects is dependent upon diffusion of lithium to the defect sites.

E. Lithium Surface Concentration

Measurement of the lithium surface concentration in silicon as a function of lithium diffusion time indicated the occurrence of a peak in surface concentration with a subsequent falloff as the time was increased. The occurrence of lower lithium concentrations for longer diffusion times is indicative of diffusion from a limited source. The peak occurred more rapidly and was of

greater magnitude as the diffusion temperature was increased. Furthermore, the lithium concentration measured near the junction by capacitance voltage techniques was found to be as high as 7 times that calculated from the surface concentration measurements. This might be due to the effect of the space charge region near the junction. As the diffusion times were increased, the surface concentration not only decreased but exhibited larger sample-to-sample variations in lithium density as measured at the junction. This again is probably due to the fact that there is a limited lithium source.

F. Carrier Removal

Lithium-doped cells fabricated from high-oxygen-content silicon exhibit very small carrier removal rates during high-flux 1-MeV electron irradiation with much larger carrier removal exhibited during the recovery phase. The carrier removal rate during recovery appears to be directly proportional to the lithium donor concentration at that point in the cell. At a distance of $5\text{ }\mu\text{m}$ from the junction, 5 times as many lithium donors are removed as there are oxygen-vacancy centers at that distance. Since the oxygen-vacancy centers are introduced relatively uniformly throughout the n region by 1-MeV electrons, the amount of lithium reacting is not proportional to the concentration of the oxygen-vacancy centers but to the concentration of the lithium itself. It is possible that the oxygen-vacancy centers act as nucleation sites for precipitation of lithium in the silicon. For lithium-doped oxygen-rich silicon, 5 times as many lithium donors react per induced defect center during recovery from exposure to 3×10^{14} 1 MeV e/cm^2 as from 3×10^{15} 1 MeV e/cm^2 . This again indicates that the number of lithium atoms interacting with the radiation-induced defects is a function of the number of lithium atoms which are available for interaction. (Although fewer lithium donors reacted per defect at the higher fluence, the fractional recovery, as measured by short-circuit current was the same for both fluences.)

A similar effect was observed with respect to the removal rates of lithium-doped cells fabricated from oxygen-lean silicon. The ratio of carriers removed during irradiation to carriers removed during recovery decreased from 4 to 2 when the fluence was increased by an order of magnitude. That is, at 3×10^{14} e/cm^2 , four carriers were removed during recovery for each carrier removed during irradiation. For irradiation to a fluence of 3×10^{15} e/cm^2 , only two carriers were removed during recovery for each carrier removed during irradiation.

Again, it appears that the number of lithium donors interacting during recovery is dependent upon the number which are available for interaction.

In lithium-doped oxygen-lean silicon it was observed that higher carrier removal rates during the recovery phase promote more complete recovery and that for good recovery the carrier removal during recovery should be at least 1.5 times the removal which occurred during the irradiation. The fact that during satisfactory recovery from similar fluences of 1-MeV electrons the removal rate during recovery has been observed to vary between 1.5 and 4 times that observed during irradiation indicates that no discrete quantity of lithium appears to react with the radiation products. This is further evidenced by the observation that lower concentrations of lithium in oxygen-lean silicon Hall bar samples produced lower carrier removal rates than did higher concentrations of lithium.

The carrier removal studies indicate that the model used in the past, which simply assumed that two lithium donors were removed for each annealed damage center, must be severely modified. It now appears that the irradiation-induced defects can act as nucleation sites for precipitation of lithium donors. In heavily lithium-doped oxygen-lean silicon, the carrier removal reached equilibrium shortly after irradiation. In lightly lithium-doped oxygen-lean silicon and highly lithium-doped oxygen-rich silicon, carrier removal reached equilibrium approximately 1 to 2 years after irradiation. Thus the precipitation process does not go on indefinitely but reaches a state of equilibrium, and if sufficient lithium is present, about 25% of the donors appear to remain active. It should be noted that the carrier removal has not resulted in degradation of cell electrical characteristics after recovery of highly lithium-doped cells exposed to 1-MeV electron fluences up to 3×10^{15} e/cm^2 .

V. Solar Cell Development

During the course of the program it became clear that understanding and/or improvements of four major aspects of lithium-doped cell design would be required if the p - n lithium-doped solar cell was ever to be competitive with the n - p state-of-the-art solar cell; these were (1) starting material, (2) p - n junction diffusion, (3) lithium source introduction, and (4) lithium diffusion schedule. The successful attainment of these goals is described below.

A. Starting Material

Three major forms of silicon were investigated for use in the lithium-doped cell fabrication, namely, crucible grown, float-zone refined, and Lopex silicon. The latter two types of silicon have lower oxygen content (oxygen-lean) than the crucible grown silicon (oxygen-rich) and are quite similar to one another except that the dislocation density of Lopex silicon is much lower than that of float-zone silicon. Because crucible grown silicon can be grown with very large diameters as compared with float-zone and Lopex silicon it is more economical than the latter two silicon types and is amenable to fabrication of large-area cells.

Extensive analysis has been performed on the effect of starting material on the action of lithium in irradiated silicon and has been discussed in detail in the preceding sections. In summary, lithium interacts with radiation-induced defects to form configurations which are dependent upon the oxygen content of the silicon. However, the major difference, as far as cell behavior is concerned, is a slower recovery rate in lithium-doped, oxygen-rich silicon due to a higher activation energy and correspondingly lower lithium diffusion constant. That is to say, it takes longer for the lithium to diffuse through the silicon and associate itself with the radiation-induced defect in oxygen-rich (crucible grown) silicon than it does for the lithium to diffuse through oxygen-lean (float-zone and Lopex) silicon. It has been found that lithium-doped cells fabricated from oxygen-rich silicon recover at room temperature at a rate 2 to 3 orders of magnitude below that obtained from oxygen-lean cells with moderate lithium doping. When lithium-doped cells fabricated from oxygen-rich silicon are stored at a temperature of 80°C after irradiation, they recover at a rate equal to that of cells similarly irradiated which were fabricated from oxygen-lean silicon and stored at room temperature. The extent of recovery of lithium-doped cells fabricated from oxygen-rich silicon is at least as good as and more often better than that of cells fabricated from oxygen-lean silicon.

There are two major advantages to the use of oxygen-rich silicon for lithium-doped solar cells: (1) lithium-doped cells fabricated from oxygen-rich silicon are far more stable than those fabricated from oxygen-lean silicon, and (2) lithium-doped cells fabricated from oxygen-rich silicon appear to be more uniform in their electrical characteristics. The stability of the oxygen-rich cells is maintained even for cells stored at 80°C, after irradiation, for periods greater than one year, where the short-circuit current was found to decrease less

than 2%. Conversely, a significant number of lithium-doped cells fabricated from oxygen-lean silicon have experienced postrecovery losses in power as large as 10% when stored at room temperature for the same period of time. The speed and extent of the regeneration experienced in lithium-doped cells fabricated from oxygen-lean silicon appear to be directly related to the lithium density gradient near the junction and inversely related to the fluence. With respect to the uniformity of electrical characteristics, RCA reports that of 17 lots of lithium-doped cells fabricated from oxygen-rich silicon received since January 1970, all but three lots averaged higher initial power than n - p control cells, whereas only two of the nine lots of cells fabricated from oxygen-lean silicon were higher than the n - p control cells. Because of the greater economy, amenability to large-area cells, greater stability, and more uniform cell characteristics, it appears that at the present time oxygen-rich silicon presents decided advantages over oxygen-lean silicon for the fabrication of lithium-doped solar cells. Only in the case where the cells are to be operated at relatively low temperatures (of the order of room temperature) and fast recovery is required should the oxygen-lean silicon be considered for such cells at this time.

B. Effects of Silicon Background Dopant

It was found that lithium-doped cells fabricated from silicon doped with antimony, rather than phosphorus or arsenic (the standard background dopants for lithium-doped cells), exhibited extremely slow recovery. Further investigations indicated that significant minority carrier lifetime recovery did occur in lithium-doped cells with antimony base doping during a 6-hour anneal at 373 K; however, the more heavily antimony-doped cell recovered less than the more lightly doped cell, indicating that the antimony was inhibiting the recovery, or at least the recovery rate. Therefore, antimony should be avoided as a background dopant in the fabrication of lithium-doped solar cells.

C. P - N Junction Diffusion

One of the primary areas of investigation was concerned with the diffusion of boron into the silicon blank to form the p - n junction. It was found that the effects of the junction diffusion could entirely mask the effects of the subsequent lithium diffusion with respect to the solar cell electrical characteristics. Investigations showed that the boron diffusion technique previously used by both Heliotek and Centralab for the fabrication of p - n cells gave rise to undesirable etching action and induced

significant strains and dislocations in the cell blank. Consequently, investigations were carried out to develop an alternate boron diffusion technique, preferably one which would not etch the silicon blank surfaces and which would introduce fewer strains and dislocations.

Investigations of three boron diffusion techniques were undertaken: (1) investigation of boron tribromide as a diffusion source, (2) investigation of the modification of the boron trichloride source deposition time schedule, and (3) investigation of the boron trichloride source with oxygen as a carrier gas.

The results of the boron tribromide source investigation indicated that while the number of dislocation etch pits and the amount of induced strains in the silicon blank were greatly reduced, the resultant cell outputs were lower than those obtained with the standard diffusion. The results of the boron trichloride investigations also showed that there was a very great reduction in dislocation density and induced stresses in the silicon blank, but in this case significant improvements in cell efficiencies were also obtained. This was especially true for cells fabricated from oxygen-lean silicon, which until this time exhibited efficiencies considerably below those of lithium-doped cells fabricated from oxygen-rich silicon. Consequently, work on the boron tribromide diffusion was terminated, and emphasis was placed on optimizing the boron deposition time in the boron trichloride diffusions with and without oxygen as a carrier gas.

A large increase was observed in the short-circuit current measured in tungsten (long wavelength) light for cells fabricated using the shorter (2 min vs 8 min) boron deposition time. Cells fabricated using a 2-min and an 8-min boron trichloride deposition time were fabricated from oxygen-lean silicon and lithium-diffused at the same time. In tungsten light, calibrated to correspond approximately to 100 mW/cm² equivalent solar intensity, the shorter deposition time cells were 11 mA greater in short-circuit current than the longer deposition cells. When measured in a solar simulator corresponding to AMO sunlight, the shorter deposition time cells were 6 mA higher in short-circuit current than the longer deposition time cells. Since the tungsten light has a larger percentage of photons with longer wavelengths than the AMO light, this indicates that there is a preservation of minority carrier lifetime when the shorter boron trichloride deposition time is used. Furthermore, the highest open circuit voltage for the short deposition time cells was 0.615 V vs 0.595 V for the

longer deposition time cells. The maximum power as measured in the simulator ranged from 27.6 to 31.7 mW for the short deposition time cells as opposed to 23.6 to 28.8 mW for the long deposition time cells.

The third technique to be investigated was the use of the boron trichloride source with oxygen as a carrier gas. In this case the boron and oxygen interact to form a B₂O₃ glass layer, which then acts as a diffusion source. Two groups of 100 cells were fabricated, one group utilizing the short boron deposition time and the other using the standard time but with oxygen as a carrier gas. These cells were not lithium-diffused so as to minimize extraneous variables which might be introduced. The cells were etched rather than lapped before diffusion because neither diffusion process etches a sufficient amount of silicon to remove the surface damage. Measurement of the cell characteristics in the simulator indicated that the short deposition boron diffusion yielded cells which averaged 3 to 4 mW higher power than the cells fabricated with the oxygen carrier gas. This was primarily due to a lower open-circuit voltage and a higher series resistance in the latter cells. Under a newly initiated pilot line program, work has continued on the boron trichloride diffusion with oxygen carrier gas with significant improvement in cell efficiencies, which now approach those of the short boron deposition diffusions. The major advantage of the oxygen carrier gas technique is the indication that larger quantities of cells can be diffused at the same time. This is a requisite for large-scale production of lithium-doped cells, since at present only about 10 to 20 cells can be diffused at the same time with relative uniformity in resultant output powers.

As a result of the *p-n* junction diffusion investigation, lithium-doped solar cells having dimensions as large as 12 cm² are now possible, owing to the improved boron diffusion techniques, which stress the cells far less than techniques used previously. Lithium-doped solar cells fabricated from oxygen-rich silicon have been fabricated in sizes of 2 × 2 cm and 2 × 6 cm and have exhibited efficiencies of between 10.3 and 11.3% as measured in a solar simulator.

D. Lithium Source Introduction

One method of introducing lithium into silicon is to utilize a paint-on source which consists of lithium powder suspended in an oil. After the lithium is painted on the back surface of the cell, the cell is heated in a furnace to alloy the lithium and drive it into the silicon.

In many cases the cell is then removed from the furnace, the lithium alloy removed by etching, and the cell returned to the furnace for additional heat treatment. This is termed "redistribution," since it redistributes the lithium within the base region of the cell and changes the lithium concentration profile. Painting the lithium oil suspension onto the back surface of the cell is a critical operation, since thick layers can form spheres of lithium which cause the formation of large alloy pits when the lithium-coated cells are heated in the diffusion furnace. These alloy pits can result in large stresses, which in extreme cases are of sufficient magnitude to break the cell. Even when the painted layer is kept thin, it is still possible for conglomerations of lithium, small pits, and stressing of the cell to develop. To a great extent the use of a lithium aluminum hydride solution alleviated many of the problems associated with the oil suspension method, except for the cumbersome task of individually painting the solution on the back face of each cell.

While the paint-on technique is quite adequate for fabrication of small cell lots, it presented a bottleneck for larger cell lots and was highly operator-dependent. Consequently, a major effort was expended to develop a technique for evaporating the lithium on to the back surface of cell batches. While high-efficiency cells were attainable using this technique, initially the yield of such cells was lower than obtained from the paint-on technique. Through additional effort, however, the yields were increased so that they now are equal to or better than those obtained from the paint-on technique. The evaporation technique is more amenable to high volume production and should, if properly controlled, give greater reproducibility than the paint-on technique used in the past. Moreover, as will be discussed in subsequent sections, there is evidence to indicate that, in many cases, especially for long-time lithium diffusions, the lithium source is not infinite and can, in fact, become starved at these longer diffusion times. This can have very serious effects on the recovery characteristics of the lithium-doped cells, which are highly dependent upon the lithium concentration. Proper control of the lithium evaporation parameters should insure that the lithium source remain essentially infinite over the time period of the lithium diffusion.

E. Lithium Diffusion Schedule

As discussed in the preceding section, one technique for lithium diffusion involves a two-cycle lithium alloy redistribution schedule. A major investigation during

the course of this program was centered around optimizing the lithium diffusion to achieve highest initial and postirradiation-recovered cell efficiency. The time and temperature of both cycles were systematically varied, and it appears that the best result was achieved from an alloy cycle of 90 min and a redistribution cycle of 60 min, both carried out at a temperature of 425°C.

Subsequently, efforts were directed towards investigation of single-cycle lithium diffusion schedules. Again, the times and temperatures were systematically varied and the resultant cells were analyzed with respect to initial and to postirradiation recovery characteristics. The cells were lithium-diffused according to a JPL-designed experimental bi-variable matrix in which the temperatures ranged between 330 and 370°C and the diffusion times ranged between 3 and 7 hours. It was found that lowering the diffusion temperatures to between 340 and 370°C and increasing the diffusion time to between 180 and 480 min yielded lithium-doped cells with higher initial and post irradiation recovered power than those obtained from the best two-cycle schedules carried out at a temperature of 425°C. The single-cycle lithium diffusion technique not only reduces the complexity of the lithium diffusion over the two-cycle technique (which requires removal of the cells from the diffusion furnace, removal of the lithium alloy region, and reintroduction into the diffusion furnace), but also results in a greater degree of uniformity in the resultant cell characteristics.

Investigation of lithium-doped cell contact sintering, which acts upon the lithium as an additional diffusion step at a temperature of about 600°C for time periods of between 2 and 6 min, indicated large increases in cell maximum power obtained under solar simulator illumination (between 1 and 4 mW), mostly due to an open-circuit voltage improvement over nonsintered cells. Efficiencies as high as 12.8% were observed under solar simulator illumination, with the average efficiency being about 11.9%. This is significantly higher than the average efficiency of 10 ohm-cm *n-p* cells (state-of-the-art), which is about 11.3%. It is not clear at this time whether this improvement is due to a redistribution of the lithium, or to an improvement in the contact resistance at the back surface, or both. It is also not clear what effect this will have on the radiation recovery properties of the cell, but preliminary capacitance voltage measurements do not indicate drastic changes in lithium concentration gradient at the junction, and it is hoped that this increase in power will be maintained after radiation recovery.

VI. Lithium Density Gradient

The time-temperature schedule of lithium diffusion determines the distribution of the lithium within the body of the cell. A very convenient method for determining the lithium concentration near the junction is measurement of capacitance vs voltage as the cell is reversed biased. This technique is applicable to a distance of up to 10 μm from the junction, depending upon the silicon resistivity, after which the cell goes into "reverse breakdown." As a result of very thorough and extensive analysis, it now appears that nature has been *extremely* kind in that it is possible to quantitatively predict the lithium-doped cell radiation recovery characteristics by measurement of the lithium concentration gradient within this narrow region adjacent to the p - n junction by means of the nondestructive and relatively convenient capacitance-voltage measurement. (It should be noted that the modifying "relatively convenient" is used because the measurement does take some time to make, and while it is possible to measure small quantities of cells on a 100% basis, it would be prohibitive for large production lots except on a sampling basis.)

Once the power of the capacitance-voltage relationship was fully realized and utilized, many of the results which previously appeared to be anomalous became readily explainable. The most important of these was the different recovery behavior among cells from the same lot (which were supposedly identical). It was found that, in fact, the cells were not identical, but that the lithium density gradient could vary by a factor of more than 70. This was not at all obvious from the resultant cell electrical characteristics. For example, 10 cells from each of 10 experimental groups with diffusion times ranging between 3 and 7 hours and temperatures ranging between 330 and 370°C were measured in a solar simulator and were also measured with respect to lithium concentration. While the total spread of all cells was about 5% in open-circuit voltage, the spread in lithium concentration was of the order of 400%. The open-circuit voltage has been found in almost all cases to vary directly with the lithium density; however, this experiment showed that rather large changes are required in lithium concentration to effect small changes in open-circuit voltage. The short-circuit current of these cells also varied about 5%, but in this case the higher the lithium density the smaller the short-circuit current. This resulted in a smaller spread in the maximum power among all cells than in either the short-circuit current or open-circuit voltage, since cells having high short-circuit current generally would have lower open-circuit voltage and vice versa. Thus the spread in power

is even less affected by a spread in lithium concentration than either short-circuit current or open-circuit voltage.

When cells were reordered to correspond to their lithium density gradient rather than the lithium diffusion schedule, the results were found to be entirely predictable. This led to the selection of lithium diffusion schedules which not only gave cells with high initial efficiencies but also with similarly high radiation recovery capabilities, because for optimal lithium diffusion schedules, the lithium density gradient was found to vary by only a factor of 2 rather than 70 as for the worst case diffusions. The best uniformity in lithium density gradient was found for shorter diffusion times. The lithium concentration at the junction appears to decrease with increasing lithium diffusion time, which indicates diffusion from a starved source. This correlates well with lithium surface concentration measurements discussed in a previous section, which also indicated decreases with longer lithium diffusion times. Further evidence for the starved source theory was the observation that in one small lot of cells which compared evaporated lithium source vs paint-on lithium source for a lithium diffusion schedule of 8 hours at 325°C, the spread in cell maximum power and lithium density gradient at the junction was lower for the evaporated lithium cells than for the paint-on lithium cells. Thus it appears that the nonuniformity in lithium density gradient generally observed for long time diffusions is not inherent in the long time diffusions but rather is technique-dependent. This indicates that by properly controlling the method of lithium source introduction and lithium diffusion schedule, very good uniformity in lithium density gradient can be achieved, and with it very good uniformity of cell radiation recovery characteristics.

For a given fluence, the lithium-doped solar cell short-circuit current appears to be a linear function of the logarithm of the lithium density gradient as measured with the capacitance-voltage technique and a linear function of a logarithm of the minority carrier diffusion length.

The damage coefficient of lithium-containing cells immediately after irradiation appears to be a function of the fluence and exhibits a square root dependence on the lithium density gradient. Time to half recovery is linearly dependent upon the logarithm of the lithium density gradient as is the dependence of the recovered open-circuit voltage. While the damage coefficient immediately after irradiation is proportional to the square root of the lithium density gradient, after recovery, cells

irradiated to 3×10^{13} 1 MeV e/cm² maintain this dependence, recovered cells after an irradiation of 3×10^{14} 1 MeV e/cm² exhibit a smaller dependence of lithium density gradient, and cells recovered from exposure to 3×10^{15} 1 MeV e/cm² exhibit almost no discernible dependence of damage coefficient on lithium density gradient. Furthermore, the scatter in results increases as the fluence increases.

Short-circuit current values after recovery from exposure to 3×10^{15} 1 MeV e/cm² also show very little dependence on lithium density gradient, while cells recovered from lower fluences exhibit higher short-circuit currents with lower lithium density gradients. For lithium-doped cells having lithium density gradient of 10^{18} cm⁻⁴ exposed to 3×10^{14} 1 MeV e/cm², the ratio between the damage coefficient after recovery to the damage coefficient before recovery is less than 0.1. That is to say, nine-tenths of the effective damage centers were annealed out during recovery. When cells were exposed to a fluence of 1 MeV electrons of 3×10^{15} e/cm², the same nine-tenths recovery was found to occur only for high lithium gradient cells, that is, of the order of 10^{19} cm⁻⁴, while in cells having a lithium density gradient of 10^{18} cm⁻⁴, only seven-tenths recovery was found to occur.

As the fluence of 1-MeV electrons is increased, the dependence of recovered open-circuit voltage on lithium density gradient becomes increasingly more pronounced. This is to be contrasted with the results of the short-circuit current parameter, which showed a decreasing dependence on lithium density gradient as the fluence was increased. After recovery from 1-MeV electron irradiations to 3×10^{13} and 3×10^{14} e/cm², the open-circuit voltage of lithium-doped cells fabricated according to the previously discussed JPL-designed lithium diffusion schedule matrix averaged about 40 mV above that of 10 ohm-cm *n-p* cells. After exposure to a 1-MeV electron fluence of 3×10^{15} e/cm², however, only the lithium cells having a lithium density gradient greater than 10^{19} cm⁻⁴ maintained this 40-mV open-circuit voltage advantage. For each order of magnitude increase in the lithium density gradient, there appears to be an increase of 20 and 25 mV in open-circuit voltage after recovery from exposure to 1-MeV electron fluences of 3×10^{13} and 3×10^{14} e/cm², respectively. After recovery from a 1-MeV fluence of 3×10^{15} e/cm², however, there appears to be an increase of 50-mV open-circuit voltage for each order-of-magnitude increase in the lithium density gradient.

After exposure to 1-MeV electron fluences of 3×10^{13} and 3×10^{14} e/cm², there was no strong trend in recov-

ered power with respect to the lithium density gradient; however, cells with a lithium density gradient above 5×10^{18} cm⁻⁴ appeared to exhibit slightly lower recovered powers. This is believed to be at least in part a result of the higher damage coefficients after recovery associated with the higher gradient cells. In contrast to this, after exposure to 1-MeV electrons at a fluence of 3×10^{15} e/cm², a very decided trend towards higher recovered power with higher lithium density gradients is observed up to a lithium density gradient of about 4×10^{18} cm⁻⁴. For lithium density gradients greater than this, there is not much improvement in recovered power, probably because of the lower initial power associated with the high lithium density gradient cells. At the high fluence, cells with gradients less than 4×10^{18} cm⁻⁴ exhibit significantly lower power outputs. Thus it appears that cells having a lithium density gradient between 4×10^{18} and 2×10^{19} cm⁻⁴ are optimal for a moderate to heavy radiation environment.

VII. Cell Recovery Characteristics

A. General

Improvements in the open-circuit voltage of lithium-doped cells, in comparison with the open-circuit voltage associated with *n-p* cells, give significantly higher starting efficiencies for the lithium-doped cell types. This advantage gives rise to superior efficiency in lithium-doped cells at the intermediate 1-MeV electron fluence of 3×10^{14} e/cm², whereas previously, lithium-doped cells did not begin to show an advantage over *n-p* cells until higher fluences. The major advantage that lithium-doped cells hold over the 10 ohm-cm *n-p* cells is in a higher open-circuit voltage both before and after irradiation.

The recovery speed of lithium-doped cells at 80°C fabricated from oxygen-rich silicon is equal to the recovery speed of lithium-doped cells fabricated from oxygen-lean silicon maintained at a temperature of 26°C, while the recovery speed of the lithium-doped oxygen-rich cells is 3 orders of magnitude below that of the oxygen-lean lithium-doped cells with equal lithium gradients when both cells are maintained at temperatures of 26°C. RCA has found that, after recovery from exposure to 1-MeV electrons at a fluence of 3×10^{13} e/cm², all but five of the 22 cells tested from the JPL lithium diffusion schedule design matrix exhibit higher power under tungsten illumination than the highest *n-p* cells similarly irradiated, representing an average of 8% higher power. After recovery from a fluence of 1-MeV electrons of 3×10^{14} e/cm², all 29 lithium cells tested

exhibited higher power than the highest *n-p* cells similarly irradiated, for an average of 14% higher power. After exposure to the 1-MeV electron fluence of 3×10^{15} e/cm², all 16 lithium cells tested having lithium density gradients greater than 4×10^{18} cm⁻⁴ exhibit higher recovered power than the highest *n-p* cells similarly irradiated, for an average of 10% higher power. At the highest fluence of 3×10^{15} 1 MeV e/cm², however, of the nine cells which have lithium density gradients below 4×10^{18} cm⁻⁴ only three exhibit higher power than the highest *n-p* cells. This clearly indicates the need for higher lithium density gradients at fluences representing heavy irradiation environments. RCA reports that 14 out of the 17 lots of lithium-doped cells received since January 1970, averaged preirradiation and post-irradiation recovery performance above those of similarly irradiated 10 ohm-cm *n-p* cells.

For environments which result in lithium-doped cell equilibrium temperatures less than 50°C, lithium-doped cells fabricated from oxygen-rich silicon do not present a decided advantage over *n-p* cells for radiation equivalent to a 3×10^{15} 1-MeV e/cm²/year environment. For light to moderate radiation environments of the order of 3×10^{14} 1 MeV e/cm equivalent fluence per year, lithium-doped cells with lithium density gradients of the order of 1×10^{19} cm⁻⁴ would probably have adequate recovery speed at temperatures down to approximately 40°C. For moderate to heavy radiation environments at cell equilibrium temperatures in excess of 50°C, lithium-doped cells fabricated from oxygen-rich silicon should present significant advantage over *n-p* cells. The stability of lithium-doped cells fabricated from oxygen-rich silicon, even with very high lithium density gradients, has been excellent, exhibiting less than 2% short-circuit current change for 70 lithium-doped oxygen-rich silicon cells after one year's storage at a temperature of 80°C.

B. Lithium-Doped Cell Instabilities

Several types of cell instabilities have been determined in heavily lithium-doped cells fabricated from oxygen-lean silicon. One type of instability is associated with degradation of the V_{oc} parameter and has been found to occur in both irradiated cells and in unirradiated control cells. Thus this type of degradation appears to be radiation-independent and unrelated to changes in minority carrier diffusion length. The degradation appears to be more severe for cells having a high lithium-density gradient near the junction and to be related to the loss of lithium donors near the junction as determined by capacitance-voltage measurements. A second

major type of instability, again occurring only in cells fabricated from oxygen-lean silicon, is a degradation in minority carrier diffusion length (and hence I_{sc}) which occurs after the cells have been irradiated by 1-MeV electrons and have subsequently recovered. The minority carrier diffusion length degradation occurs only in irradiated cells and occurs more rapidly and severely for cells having a high lithium concentration gradient near the junction, as determined by capacitance-voltage measurement. It therefore seems that higher lithium-concentration gradients in oxygen-lean silicon tend to promote lithium-doped cell instability and that the capacitance-voltage measurements are extremely useful in determining the gradients and therefore the propensity for cell instability.

It had been postulated that a reason for some of the lithium-doped cell instabilities, observed in cells fabricated from low-oxygen-content silicon, might be associated with effects of deeper or nonuniform lithium diffusion at the cell edges. Consequently, cells were fabricated through all high-temperature operations as whole slices and subsequently cut to size to eliminate possible edge effects. These cells were compared with cells having the same design and processed in the normal manner (i.e., cut to size prior to high-temperature operations). Both RCA and TRW found no significant differences in cell behavior and radiation recovery between the cells fabricated by the two processes.

C. Incremental Irradiations

The irradiations described thus far in this paper have been concerned with very high fluxes. In subsequent sections a discussion will be given of a JPL low-flux irradiation program to determine the lithium cell characteristics at rates of irradiation which may be found in near-Earth space. As an intermediate approach, an experiment was carried out by TRW using incremental irradiations to determine if this would have an effect on the cell recovery characteristics. Lithium-doped cells fabricated from oxygen-rich silicon were irradiated in 10 increments of 3×10^{13} 1 MeV e/cm² and allowed to recover at a temperature of 60°C for 2 to 4 days between each increment. (From past results it was determined that 7 days would probably be adequate for maximum recovery to occur, but due to scheduling problems the recovery time was reduced to the 2 to 4 days mentioned.) As a basis of comparison, similar cells were irradiated in one step to the total fluence of 3×10^{14} 1 MeV e/cm². After final recovery, the two cells irradiated incrementally had tungsten-illuminated short-circuit currents of 51.5 and 52.6 mA. The single-step irradiated

cells had 53.0- and 54.0-mA tungsten-illuminated short-circuit current after their recovery. The recovered currents of both the incremental and single-step irradiated cells are well within the normal spread associated with cells from the same lot. Furthermore, the single-step irradiated cells had been stored several thousand hours at 60°C and had reached their maximum recovery. It is possible that with longer recovery times the incrementally irradiated cells would exhibit slightly higher short-circuit currents than they did; however, as mentioned, the differences, even as they exist, are not significant. It is concluded, to the degree possible based on such a small sampling, that there was no significant difference in the degree of recovery between the incrementally irradiated cells and the single-step irradiated cells with adequate recovery times.

D. 28-MeV Electron Irradiation

Lithium-doped solar cells fabricated from oxygen-rich silicon were irradiated with 28-MeV electrons to fluences of 3×10^{14} and 3×10^{15} e/cm². The short-circuit currents measured under tungsten illumination before recovery exhibited a dependence of fluence smaller than the 6.5 mA/cm² per decade of fluence generally observed in all other cell types, possibly because of annealing which occurred during irradiation. The fact that after annealing for times greater than 50 hours at a temperature of 60°C, the lithium-doped cells did exhibit the 6.5 mA/cm² per decade fluence dependence indicates that this conclusion is correct. The result of primary interest is the observation that the recovered short-circuit currents degraded with fluence of 28-MeV electrons at a rate only one tenth that of similarly irradiated *n-p* 10-ohm-cm cells, indicating a very great superiority in radiation resistance to 28-MeV electrons. Similarly, a great superiority of lithium-doped cells has been observed (Ref. 4) for irradiation by neutrons. It thus appears that the lithium is highly efficient in neutralizing the detrimental effects of defect clusters, and it is perhaps in this area that the lithium-doped cell presents the greatest advantage.

E. 4-MeV Proton Irradiation

Several lithium-doped cells fabricated from oxygen-rich silicon were irradiated with 4-MeV protons to a fluence of 2.2×10^{11} protons/cm² and stored for 800 hours at a temperature of 60°C. The annealing characteristics were compared with similar cells irradiated by 1-MeV electrons to a fluence of 5×10^{14} e/cm². The initial degradation in maximum power was greater for the proton-exposed cells by about 20% than for the electron-irradiated cells.

After about 25 hours recovery at 60°C, the power of the proton-irradiated cells was equal to that of the electron-irradiated cells, and for longer recovery times, the power of the proton-irradiated cells was higher than the electron-irradiated cells. The ratios of power after 800 hours at 60°C to power immediately after irradiation were 1.42 and 1.22 for the proton- and electron-irradiated cells, respectively. This indicates that the recovery process in lithium-doped solar cells is more efficient for 4-MeV proton irradiation than for 1-MeV electron irradiation.

F. Neutron Irradiation

Electron microscopy of neutron-irradiated lithium and non-lithium-containing solar cells was performed using a surface replication technique. The densities and diameters of the radiation-induced disordered regions were obtained as a function of lithium doping and neutron fluence. It was found that the number of disordered regions, observed by this technique, increased with increasing fluence and increasing lithium density. The diameters of the disordered regions, however, were found to decrease with increasing fluence and with increasing lithium concentration. At a specific fluence, the total volume of the disordered regions appears to be relatively constant with respect to lithium density, increasing lithium densities resulting in more numerous but smaller-diameter disordered regions. The defect density of the lithium-containing cells did not appear to change with annealing temperatures up to 1200°C, while the defect density of the non-lithium-containing samples did change. Electron transmission microscopy of the lithium- and non-lithium-containing cells indicated evidence of precipitate formation in both cell types.

Lithium-doped solar cells were exposed to fast neutrons at the Northrop Triga reactor. The behavior of short-circuit current of a group of lithium-doped cells fabricated from crucible silicon is shown as a function of the fluence of neutrons with energies greater than 10 keV in Fig. 1. The cells were allowed to recover at a temperature of 100°C and are 100% higher in recovered short-circuit current after a fluence of 10^{14} N/cm² than similarly irradiated 10 Ω -cm, state-of-the-art *n-p* cells.

G. Low Flux Radiation Testing

Most of the radiation testing on lithium-doped solar cells has involved exposure of the cells to high fluences of 1-MeV electrons because of the speed, economy, and convenience associated with such tests. Two low flux tests have now been carried out, however, to determine

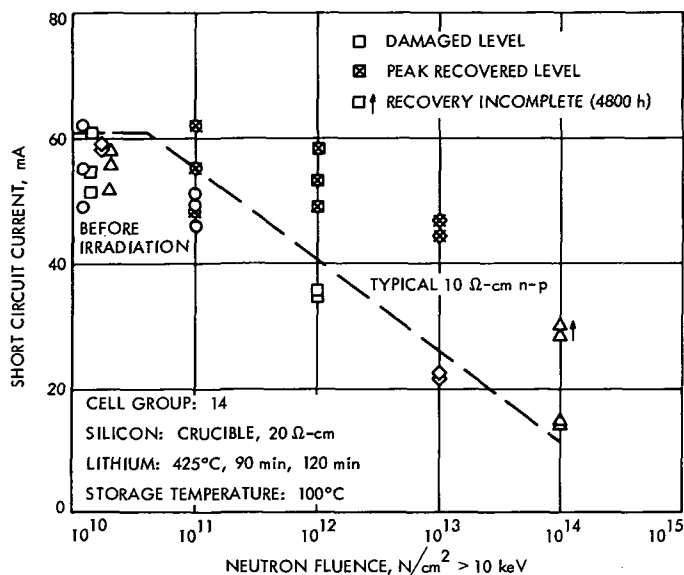


Fig. 1. Lithium-doped solar cells, fast neutron irradiation (the data used to produce this figure were extracted from Fig. 4 of Ref. 4, courtesy of Mr. R. G. Downing)

the effects of fluxes similar to those found in near-Earth space and of extended exposure to illumination and temperature during irradiation. Since the cells tested were fabricated more than a year ago, they do not represent the best state-of-the-art lithium-doped cells presently attainable. The results were similar to those obtained with the high-flux 1-MeV tests on similar cells and indicated no anomalous effects.

The tests used a strontium-90 beta source, which closely approximates the spectrum of electrons in near-Earth space up to 2 MeV, and *in situ* measurements of the cell electrical characteristics under light having a spectral distribution similar to AMO sunlight. The tests maintained the cells in an illuminated and loaded condition except for certain select cell groups which were intentionally shielded from the illumination to determine if there were differences between illuminated and non-illuminated cell radiation characteristics. (One test indicated there was a difference and one test indicated there was not.)

The cells were maintained in vacuum (vac-ion pumps being used to minimize contamination normally associated with diffusion pumps) at various temperatures between -50 and $+80^{\circ}\text{C}$. The cells were irradiated at fluxes of the order of 10^{12} e/cm²/day to a total fluence of about 10^{14} equivalent 1-MeV electrons/cm² after a total exposure time of 6–7 months. In both tests the *n-p* cells

were significantly more radiation-resistant at the lowest temperature (-50°C), where the lithium is almost immobile, with the lithium-doped cells exhibiting characteristics similar to non-lithium-doped *p-n* cells.

At the intermediate temperatures of 20 – 30°C , the lithium-doped cells fabricated from oxygen-lean silicon were slightly inferior to slightly better than the *n-p* cells with respect to maximum power, but appear to be degrading at a slower rate, so that at higher fluences they might present an advantage. The earlier vintage oxygen-lean cells used in this test had lower starting efficiencies than the *n-p* and the lithium-doped oxygen-rich silicon cells. More recent oxygen-lean lithium-doped cells have exhibited much higher (10–20%) initial powers than these earlier cells and, if they exhibit the same percentage degradation as the tested cells, the oxygen-lean cells would present a decided advantage over *n-p* and lithium-doped oxygen-rich cells in this temperature range. The lithium-doped oxygen-rich cells were inferior to the other cell types at 20 – 30°C .

At higher temperatures of 50 – 60°C , there was no clearly superior cell type; however, the higher initial efficiencies of more recent lithium-doped cells would make these superior if the same degradation rate is maintained. At the highest temperature, 80°C , the best lithium-doped oxygen-rich cells have about 15% more power at the end of the test than the *n-p* cell groups. Furthermore, the trend seems to be for greater superiority of the lithium-doped cells as the fluence increases. This is in agreement with 1-MeV high-flux electron irradiation of similar cell types, which indicated greater superiority of lithium-doped cells at 3×10^{15} e/cm² fluence than at 3×10^{14} e/cm².

It is of interest to consider the curve power factor (CPF), defined as the ratio of the maximum power to the product of the short-circuit current and the open-circuit voltage. The model for association of lithium with radiation-induced defects in oxygen-rich silicon indicates that the defects can act as nucleation sites for precipitation of lithium donors. This could be of concern if the quantity of lithium donors removed results in collapse of the current-voltage characteristic curve, as indicated by the CPF. It was found, however, that rather than collapsing, all lithium-doped cells fabricated from oxygen-rich silicon maintained or increased the CPF after seven months exposure to the radiation at all temperatures tested, while the *n-p* cells exhibited CPF degradations as high as 6%. The only lithium-doped cell type to exhibit significant CPF degradation was

a lot of cells fabricated from oxygen-lean silicon with a two-cycle lithium diffusion schedule of 90-min diffusion, 60-min redistribution at 350°C. Separate measurements made on similar cells of this type indicated virtually no lithium at the junction, and hence the CPF degradation is a result of too little lithium.

VIII. Suggestions for Future Work

Because of the greater stability, starting efficiency, and economy of lithium-doped cells fabricated from oxygen-rich silicon, the major effort during the past year was expended on this (crucible-grown) form of silicon. However, recent results on lithium-doped cells fabricated from oxygen-lean silicon have shown that very-high-efficiency cells (as high as 12.8% as measured in an AMO simulator) can be achieved with oxygen-lean silicon by making use of the improved fabrication processes discussed in the preceding sections. If such cells could be made with reproducibly high recovery and stability characteristics, it is possible that lithium-doped cells fabricated from oxygen-lean silicon could be advantageous for missions involving equilibrium cell temperatures down to 25°C. There is, at present, no JPL-sponsored program to investigate this possibility.

During this program, most of the silicon used to fabricate lithium-doped solar cells had a starting resistivity greater than 20 ohm-cm. Toward the end of the program, some lithium-doped cells were fabricated from oxygen-lean silicon having a starting resistivity of 10 to 20 ohm-cm, and although no extensive analysis was done, the cells appear to exhibit behavior similar to cells fabricated from higher-resistivity oxygen-lean silicon; that is, similar starting efficiencies and similar dependence of short-circuit current and damage coefficient immediately after irradiation on lithium density gradient. It would be of interest to know whether the ultimate recovery of optimized lithium-doped cells fabricated from oxygen-lean and oxygen-rich low-resistivity silicon would be superior or inferior to optimized lithium-doped cells fabricated from high-resistivity silicon, especially since there can be significant removal of lithium donors during radiation recovery. There are presently no plans to conduct such an investigation.

It has been found that sintering of the lithium-doped solar cell contacts for 3 to 6 minutes at a temperature of the order of 600°C results in a 1-4 mW improvement in cell power. At the present time, JPL has initiated a program for the pilot line production of lithium-doped solar cells and will evaluate the radiation resistance of

the sintered cell; however, additional optimization experiments are beyond the scope of the pilot line program.

Furthermore, the cell optimization program described in this paper did not result in a clearly defined optimum lithium diffusion schedule but rather indicated a region where one might expect to find an optimum. For example, the pilot line program is somewhat arbitrarily using a lithium diffusion schedule of 3 hours at 360°C. During the optimization program this schedule was found to yield lithium density gradients between 9 and $16 \times 10^{18} \text{ cm}^{-4}$, which is in the range needed to obtain good recovery from high radiation environments (3×10^{15} 1-MeV electrons/cm²) and which yields a cell-to-cell spread of less than a factor of 2. It was observed, however, that a lithium diffusion schedule of 3 hours at 340°C gave a lithium density gradient range of 6.2 – $9.0 \times 10^{18} \text{ cm}^{-4}$, which is also in the proper range for very good recovery for high radiation environments and yields an even smaller cell-to-cell spread. The indications are that the 3-hour, 340°C schedule might give better recovery at lower fluences than the schedule chosen.

Since the three major efforts in the pilot line program involve scale-up and control of the lithium introduction and diffusion and the boron *p-n* junction diffusion, it is impossible to introduce yet another variable, namely, lithium diffusion schedule. Hence there are no plans to further optimize the lithium diffusion schedule. This is particularly unfortunate since it is believed that some lithium diffusion schedules gave poor results (primarily large cell-to-cell variations in lithium density gradient) because of the finite nature of the lithium source so that at longer diffusion times the source became "starved." One of the major objectives of the pilot line, as previously mentioned, is to obtain better control of the lithium source introduction, and if this is achieved, a second look at the longer-time lithium diffusion schedules would be warranted, but is beyond the scope of the contract.

The restrictions imposed on the pilot line program, i.e., no further optimizations in cell design, do not present an irreversible situation. The optimizations discussed are simply ones of time and temperature studies with respect to the lithium diffusions. Once production-type processes have been developed, with appropriate control points and scale-up of processes, this can always be accomplished. In many respects, in fact, it makes more sense to establish the process limitations before proceeding with further optimization studies. If the

limitations are too severe, and this does not at present seem to be the case, perhaps there would be no point in expending further effort in improving the cell design.

An important investigation is the determination of the behavior of lithium-doped solar cells as a function of proton energy and fluence. There are indications that the lithium-doped solar cells might present significant advantages in proton environments. This must be verified and a functional relationship established between proton energy and fluence and recovered power of lithium-doped solar cells.

IX. Conclusions

The results of the investigations carried out during the past two years represent significant achievements with respect to the lithium-doped solar cell. Lithium-doped solar cells fabricated from oxygen-lean and oxygen-rich silicon have been obtained with average initial efficiencies of 11.9% and as high as 12.8% of air mass zero and 28°C, as compared to state-of-the-art *n-p* cells fabricated from 10 ohm-cm silicon with average efficiencies of 11.3% under similar conditions. Improvements in cell-processing techniques have made possible the fabrication of large-area lithium-doped cells. Excellent progress has been made in quantitative predictions of postirradiation lithium-doped cell characteristics as a function of cell design by means of capacitance-voltage measurements, and this information has been used to achieve further improvements in cell design. Specifically, analysis of irradiated lithium-doped cells has shown that the recovery characteristics can be very well predicted by the lithium density gradient near the junction and that very good cell-to-cell reproducibility of lithium density gradient can be obtained with single-cycle, 2-3 hour lithium diffusion schedules.

Since the radiation damage annealing rate for lithium-doped cells is a function of cell operating temperature and oxygen concentration in the silicon, the design of the lithium-doped cell must accommodate the desired annealing rate with respect to the cell operating temperature. Lithium-doped cells fabricated from oxygen-rich

silicon would probably not be appropriate for missions involving extended equilibrium temperatures below 50°C unless some means of auxiliary cell heating is provided.

The lithium-doped solar cell appears very promising. Lithium-doped cells fabricated from oxygen-rich silicon with lithium density gradients near the junction greater than $4 \times 10^{18} \text{ cm}^{-4}$ can be advantageously used in moderate to heavy radiation environments of up to 3×10^{15} 1-MeV equivalent electrons per cm^2 per year if the cells are maintained at a temperature of 50°C or greater. The advantage of lithium-doped cells is even greater for radiation environments consisting of high-energy protons, neutrons, and electrons, that is, for environments which result in damage clusters rather than simple point (vacancy-interstitial) defects.

The results of the beta-source low flux testing are extremely encouraging. The results are similar to those obtained from 1-MeV high-flux tests on similar cell types; the best lithium-doped cells are about 15% higher in maximum power at temperatures greater than 60°C than *n-p* cells after fluences of the order of 10^{14} e/cm^2 , and the trend indicates greater superiority would be achieved at higher fluences or for more recent cells with higher starting efficiencies (if the same degradation rate is maintained). Furthermore, there was no collapse of the characteristic current-voltage curve as a result of the irradiation for cells with even moderate amounts of lithium doping. The low fluxes used in these tests still represent about 6 times that expected in synchronous orbit, so that lithium-doped cells should have no problem keeping pace with the radiation damage at temperatures greater than 60°C for oxygen-rich silicon and greater than 20°C for oxygen-lean silicon. Even greater advantage to the use of lithium-doped solar cells should be obtained if the radiation environment contains a significant amount of moderate to high energy protons (i.e., 4 MeV or above).

The lithium-doped solar cell represents the most significant improvement in solar cell radiation resistance since the advent of the *n* diffused into *p* base solar cell developed in the early 1960s.

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