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Effects of Lithium Doping on the Behavior of Silicon and Silicon Solar Cells

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Preface

The work described in this report was performed by the Guidance and Control Division of the Jet Propulsion Laboratory.

Contents

Contents (contd)

Abstract

The Jet Propulsion Laboratory is sponsoring investigations into the applicability of lithium doping for improvement of silicon solar cell radiation resistance. This report discusses the author's interpretation of the results of the industry programs, in particular the efforts to improve cell processing techniques and the experiments conducted to improve the theoretical understanding of the action of lithium in irradiated silicon and silicon solar cells. The major conclusions reached as a result of the investigations are presented, and suggestions for future work are made. It appears that lithium-doped solar cells can be fabricated which exhibit (recovered) efficiencies significantly in excess of efficiencies associated with state-of-the-art N/P solar cells after exposure to high fluences of 1-MeV electrons and neutrons.

Effects of Lithium Doping on the Behavior of Silicon and Silicon 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 anticipated 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 quite dependent upon the irradiation spectrum and fluence. This problem is circumvented 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 oftentimes 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. Effort has therefore been directed to develop an improved radiation-hardened solar cell, and there has been significant progress to date to suggest that the lithium-doped solar cell can be developed to the status of a practical device. Preliminary tests have shown that lithium-doped solar cells can be designed and fabricated to be significantly more radiation-resistant than conventional silicon solar cells. They also can be made repeatably and with initial conversion efficiencies equal to those of the state-of-the-art cells.

Before a solar cell can be considered for a space mission it must be state-of-the-art several years before the anticipated launch date. This means that the cell must be flight qualified and that intimate knowledge of cell characteristics as a function of the anticipated environments must exist. Lithium-doped silicon solar cells have

exhibited considerable annealing of radiation damage at temperatures between 25 and 100°C. Much remains to be done, however, to determine the characteristics of the lithium-doped cells as a function of actual space-type environments. At the present time JPL has the responsibility for the NASA-sponsored lithium-doped solar cell development program. It is believed that the possible advantages of the lithium-doped solar cell, coupled with the possibility of requirements for spacecraft with large-area solar arrays in the near future, warrant an intensive and broad-based investigation. Therefore, a very considerable effort, both economically and technically, is in progress; this report describes some of the results obtained by the industrial organizations performing as subcontractors to JPL.

A team of industry and university contractors has been assembled on the present JPL-directed solar cell radiation programs which includes many competent and experienced people working in this field. Through the

Table 1. Organization summary

Organization	Function
Heliotek Division of Textron, Inc. Centralab Division of Globe Union	Lithium-doped cell development, analysis, and fabrication.
Naval Research Laboratory Philco-Ford Corp. Lockheed Georgia Corp.	Investigation of behavior and operating characteristics of lithium-doped silicon cells in a simulated space environment.
RCA TRW Systems	Evaluation and analysis of lithium-doped silicon, silicon diodes, silicon solar cells. Investigation of radiation damage model and annealing kinetics.
Gulf General Atomic Naval Research Laboratory	Evaluation of lithium-doped silicon. Investigation of radiation damage model and annealing kinetics.
University of Illinois	Luminescent and tunneling phenomena in irradiated silicon.
University of Utah	Radiation kinetics in electronic material.
Rensselaer Polytechnic Institute	Investigation of structure of radiation damage in lithium-diffused silicon solar cells.
University of Denver	Effects of space particle bombardment on solar cell materials.
University of Kentucky	Structural damage in lithium-doped solar cells by neutrons.
Brown University	Effects of subthreshold electron irradiation on silicon.
Jet Propulsion Laboratory	Direction and coordination of all above programs. Performance of radiation experiments to expand knowledge in the field of radiation effects to photovoltaic devices.

efforts of this team, significant progress is being made in fabricating, measuring, and understanding the performance of lithium-doped solar cells for use in a space radiation environment.

A listing of the individual organizations involved is shown in Table 1. The interorganizational cooperation to develop the lithium-doped cell is being coordinated by JPL. The present data indicate that these lithium-doped solar cells, when properly optimized for a particular mission environment, will effectively be, with little increase in cost, three times more radiation-resistant to electrons and ten times more radiation-resistant to protons and neutrons than present-day conventional 10 Ω-cm N/P solar cells.

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 at least the general characteristics of lithium-doped cells as a function of cell design. Consequently, JPL is now in a better position to obtain quantitative evaluations.

One of the major objectives of the present program is to assure that the participating organizations are all studying the same kinds of cells; that is, cells so fabricated to be more or less identical. Also, emphasis is being placed on supplying enough cells of a specific design to permit the investigators to obtain reasonable statistics in their experiments. Another objective is 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 Ω-cm N/P type cells on the basis of irradiation by 1-MeV electrons. Another major effort is being made 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 is being carried out to obtain better techniques: (1) for diffusion of the P/N junction; (2) for introduction of lithium (primarily to obtain more uniform and controlled concentration profiles, both laterally and transversely); and (3) to improve reproducibility.

Still another extremely important objective of the present program is 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. While significant progress in the development of lithium-doped silicon solar cells is still entirely possible without detailed knowledge of the physics involved, a tremendous saving in time and expense can be obtained if the basic processes that underlie the empirical results can be determined.

III. Analytical Techniques

A number of analytical tools are being utilized at this time 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 being used are:

(1) Irradiation by 1-MeV electrons.

(2) Solar cell electrical characteristics (primarily current-voltage characteristics).

(3) Minority carrier diffusion length and lifetime measurements.

(4) Junction capacitance measurements to determine the concentration 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.

The analytical investigations are being carried out with lithium-doped silicon bulk samples, diodes, and solar cells. In the majority of the present investigations, 1-MeV electrons are used for radiation since many of the organizations have the capability of obtaining 1-MeV electrons, and most of the past work on lithium-doped cells has been done with 1-MeV electrons. Thus, continuity between previous and present investigations can be maintained. Moreover, a great deal of data is available on the behavior of state-of-the-art N/P and P/N non-lithium doped cells after exposure to 1-MeV electron irradiation.

Solar cell parameters, such as current-voltage, diffusion length, and junction-capacitance characteristics are being monitored before and after irradiation and as a function of environmental conditions such as time and temperature.

In order to more fully understand the effects of lithium doping and irradiation on the solar cell current-voltage characteristics, the minority carrier diffusion length is being determined as a function of irradiation as well as time and temperature. The minority carrier diffusion length is an extremely powerful parameter which can be used to determine energy levels created within the "forbidden gap," and one which is also related to the solar cell short-circuit current, reverse-saturation current, and open-circuit voltage. Diffusion length measurements are of great value since they are obtained by using highly penetrating 1-MeV electrons, thereby permitting determination of the diffusion length in the base (bulk) region independently of surface conditions. Also, measurements can be made on diodes as well as on solar cells.

Junction-capacitance measurements have proven to be quite valuable in determining the ionized lithium concentration near the P/N junction. The ionized lithium concentration near the junction is being determined for various conditions of lithium doping, irradiation, and various time and temperature treatments.

The use of electrical resistivity measurements in conjunction with Hall-effect measurements can determine changes in majority carrier concentration and mobility caused by exposure of lithium-doped silicon to irradiation. Electrical resistivity measurements are also used in conjunction with an etching technique to determine the lithium concentration profile throughout the cell. This can then be correlated with the specific lithium diffusion parameters to determine their effects on the lithium profile within the body of the cell. The Hall-effect measurements are also valuable in determining majority carrier removal rates and for determining changes in Hall mobility.

ESR measurements are a sophisticated tool for providing information not only on defect energy levels, but also on the symmetry, and hence the structure of the defect.

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. The behavior of lightly lithium-doped silicon can be significantly different than that of heavily lithium-doped silicon due, for example, to 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, 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. With respect to these latter measurements, it was decided to first emphasize higher lithium concentrations since the effects of the lithium-doping should be more readily identifiable.

B. Characteristics as a Function of Lithium-Dopant Concentration

Much of the past work performed by TRW has involved heavily lithium-doped silicon samples, which are not typical of solar cell doping levels. Presently, samples are being fabricated and evaluated with lower lithium concentrations ($10^{14} - 10^{16}$ lithium atoms/cm³). The Hall measurements performed on the more 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 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.

The lightly lithium-doped float-zone material irradiated by TRW 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 appears 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.

RCA has observed a minimum in the carrier removal rate versus reciprocal bombardment temperature curves for lightly lithium-doped (10^{14} lithium/cm³) float-zone silicon irradiated by 1-MeV electrons and measured at 78°K. This minimum was observed in all five samples studied, and occurred for a bombardment temperature of 95°K. Such a minimum has not been previously observed and is believed to be due to the location of the Fermi level near a defect energy level at this bombardment temperature. Carrier density versus reciprocal temperature curves for lightly lithium-doped silicon irradiated by 1-MeV electrons indicated a spread of energy level over a wide range, possibly due to the existence of more than one energy level. These observations in lightly lithium-doped silicon may have been masked or modified in previous investigations of more highly lithium-doped samples.

A distinct dependence of annealing properties of lithium-doped silicon on lithium concentration was observed by RCA in float-zone silicon with lithium densities between 2×10^{14} and 2×10^{16}/cm³. 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 highly lithium-doped silicon. The lightly lithium-doped float-zone silicon exhibited annealing characteristics which are very similar to highly 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 dissassociation 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 material can be made to behave in a manner similar to high oxygen content material if the ratio of lithium to oxygen remains relatively constant.

Lithium-diffused float-zone silicon has been irradiated by 30-MeV electrons and examined for changes in minority carrier lifetime τ by Gulf General Atomic. 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 4×10^{14} 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 the more lightly lithium-doped silicon by Gulf General Atomic indicated that the preirradiation τ was determined by two centers, one located approximately 0.17 eV below the conduction band ($E_c - 0.17$ 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 highly lithium-doped silicon annealed completely at room temperature.) The high temperature center was significantly annealed in 1 h at 380–400°K.

Two highly lithium-doped float-zone silicon samples were irradiated at Gulf General Atomic by neutrons with energy >10 KeV to fluences up to 6.75×10^{10} 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 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.

Hall measurements of lithium-doped float-zone silicon samples performed by NRL (Naval Research Lab-

oratory) indicated little E-center (phosphorous-vacancy defect) formation after irradiation by 1-MeV electrons but a very large acceptor concentration deeper than 0.2 eV below the conduction band. A level (of undetermined structure) at 0.12 eV below the conduction band was observed after electron irradiation. Annealing at 300°K initially caused a shift in this level deeper into the gap, after which a decrease in defect concentration was observed as the annealing continued. The shift in energy occurred rapidly and went to completion during a time in which only a small fraction of the centers were rendered electrically inactive. Thus, the annealing appears to occur in at least two stages, one stage corresponding to the shift in energy level and the second stage corresponding to the neutralization of the defect. The lithium-doped samples indicated greater damage than non-lithium doped (phosphorous background doping) control samples due to the greater number of deep acceptors produced in the former samples (although the E-center production is significantly reduced in the lithium-doped samples). This agrees with the results of Gulf General Atomic which showed that the K of electron-irradiated float-zone silicon increased with increasing lithium concentration for irradiation by electrons.

The NRL has irradiated moderately lithium-doped float-zone (oxygen-lean) silicon with 1-MeV electrons to a fluence of 1.7×10^{14} e/cm^2 at an irradiation temperature of 240°K and annealed the sample at room temperature. No high temperature structure with an activation energy near 0.17 eV was observed, indicating that the A-center (oxygen-vacancy) concentration was less than 5×10^{12} cm^{-3}. This agrees with results of Gulf General Atomic which indicated that A-center introduction rate was down by a factor of 10 for highly lithium-doped float-zone silicon according to ESR measurements.

C. ESR Investigation of Divacancy Production

ESR measurements were investigated by Gulf General Atomic as a tool for the determination of the mechanisms for production and annealing of the divacancy (a predominant defect in float-zone silicon) in lithium-diffused N-type float-zone silicon irradiated with 30 MeV electrons. The position of the Fermi level with respect to the divacancy levels determines whether or not the divacancy will be paramagnetic in the single negative charge state and therefore responsive to ESR measurements. Examination of lithium-doped samples, irradiated by 30 MeV electrons in small fluence steps at 77°K and measured at 20°K in the ESR spectrometer, indicated no paramagnetic resonances even after a significant number of attempts and variations in experimental techniques.

Either the introduction rate of the divacancies was too low, or they were nonparamagnetic. There is considerable difficulty in obtaining a fluence which is amenable to the observation of the divacancies, even if they do exist. If the fluence is too low, not enough divacancies are formed to be observed above the "noise," while if the fluence is too high, the Fermi level is too low to provide the right charge state for the divacancies to be observed through ESR. It is, therefore, quite easy to miss this relatively narrow "window."

In order to obtain further information on the divacancy and the reason for the absence of a resonance in the ESR measurement, some preliminary infrared absorption studies were made at Gulf General Atomic. Infrared absorption is less sensitive than ESR but has the advantage of not requiring the divacancy to be in a particular charge state for observation of the divacancy absorption band. The spectra obtained at a temperature of 77°K indicated absorption at or near the expected wavelength of 1.8 μm for both lithium-diffused and non-diffused silicon attributed to the divacancy. After a 15-min anneal at 300°K, the 1.8-μm band disappeared and two new bands appeared in the lithium-doped silicon, indicating a change in the nature of the defect.

D. ESR Investigation of Oxygen-Vacancy Center Production

Gulf General Atomic has utilized the ESR technique 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}/cc. After 300°K irradiation by 30 MeV electrons to fluences of the order of 10^{16}–10^{17} electrons/cm², 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. After 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.

E. 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 General Atomic, 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 highly 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 General Atomic 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 at various temperatures 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, 2, and 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 un-irradiated lithium-doped crucible silicon. Thus a very good agreement is obtained among results of annealing studies done independently by TRW, RCA, and Gulf General Atomic, 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.

V. Lithium-Doped Solar Cell Development

Lithium-doped solar cells have been produced by diffusing the lithium into N-type silicon. Prior to the introduction of the lithium, a P/N junction is formed in the silicon blank by diffusion of boron to a depth of approximately 3000 Å, thus giving a P/N cell configuration. When cells are fabricated in this manner, significant room temperature annealing of radiation damage induced by exposure to electrons having an energy of 1 MeV has been observed. Similar results have also been obtained after exposure to neutrons and protons.

One of the original problems encountered with lithium-doped solar cells was an initial cell efficiency so low that even after complete recovery, the cells had much less power after irradiation than state-of-the-art cells. Recently, lithium-doped cells have been fabricated which have initial efficiencies approaching state-of-the-art N/P cells; that is, greater than 11% at air mass 0, at a cell temperature of 28°C.

This work is being carried out by Globe Union, Centralab Semiconductor Division, and Heliotek Division of Textron, Inc. One of the primary areas of investigation is concerned with the diffusion of boron into the silicon blank to form the P/N junction. The state-of-the-art boron trichloride (BCl₃) source results in an undesirable etching action (which makes the fabrication of special structures such as a P⁺N⁺N configuration, discussed in Section VIII of this report, extremely difficult) and is also suspected of inducing strains and dislocations in the silicon material. Investigations are being carried out to develop an alternate boron junction diffusion technique, preferably one which would not etch the silicon blank surfaces and which would introduce fewer strains. Efforts have been concentrated on the utilization of boron tribromide (BBr₃) as a diffusion source. Progress has been made in utilizing a BBr₃ source, with some resultant cells exhibiting efficiencies equal to cells fabricated with the BCl₃ source. The yield distribution of cells fabricated using the BBr₃ diffusion source, however, has not been as high as that of the BCl₃ diffused cells, and work is continuing to further improve the BBr₃ process.

Etch pit measurements performed by Centralab showed excessive dislocation introduction after diffusion by the BCl₃ source, while the BBr₃ source did not appear to introduce any significant number of dislocations. Also, resistance probing after simultaneous lithium diffusion indicated that the lithium profiles of BCl₃ and BBr₃ junction diffused slices were similar to one another. Heliotek has found that large-area cells fabricated utilizing the BCl₃ source gave visible signs of warpage, indicating that the induced stresses are significant. In contrast, several large-area cells have been fabricated utilizing the BBr₃ technique and have not exhibited warpage. Perfection of the BBr₃ technique will allow the fabrication of large-area, lithium-doped, P/N cells.

One of the major reasons for investigating BBr₃ as a junction diffusion source was the fact that very significant increases in induced stress and dislocation density were observed after the BCl₃ diffusion operation. As an alternative approach to reducing the number of dislocations resulting from the junction diffusion, Centralab has investigated modified BCl₃ diffusion schedules. It was found that reduction of the boron tack-on cycle time greatly reduced the number of dislocations and eliminated cell warpage often associated with the standard technique. Cells fabricated from oxygen-lean (float-zone and Lopex) silicon appeared to show an improvement in resultant efficiency (primarily through an increase in open circuit voltage) with the modified diffusion schedules, while the cells fabricated from oxygen-rich (crucible-grown) material did not exhibit a significantly different efficiency yield distribution.

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 deposited 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 region 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 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 cause 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 possible stressing of the cell to develop. To a great extent, the use of a lithium aluminum hydride solution, developed by TRW, has alleviated most 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. The use of evaporated lithium as a lithium-diffusion source has yielded high efficiency, high recovery lithium-doped cells; however, the yield distribution is not as good as that obtained with the standard 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 which has been used in the past. Additional work is being carried out to obtain better yield distributions.

Cells with an oxygen-rich layer of approximately 1-mil thickness at the front surface were fabricated by Centralab by diffusion in an oxidizing atmosphere. Cells fabricated in this manner have been obtained from Lopex and float-zone silicon with outputs as high as 27 mW for a 1×2 cm² cell as measured in a solar simulator at 140 mW/cm², at 28°C. It has been found by TRW that the recovery characteristics are very similar to those of cells fabricated from crucible-grown material, and the recovery rate is several orders of magnitude lower than is normally observed in float-zone and Lopex cells. Furthermore, after an anneal of 1000 h at 100°C the stability of the oxygen layer cells fabricated from Lopex silicon is within 2% versus a 25% degradation for control cells without the oxygen layer. The original reason for investigating the oxygen layer was to obtain the fast recovery associated with oxygen-lean silicon with the stability associated with oxygen-rich silicon. It is of considerable interest that a relatively shallow oxygen layer was so extremely influential in reducing the recovery rate and increasing the cell stability. This might indicate that it is only the material characteristics near the junction which influence the lithium cell behavior.

Heliotek has performed contact pull tests on lithium-doped cells which indicate more silicon fracture than normally observed for N/P cells, but similar to that observed in non-lithium-doped P/N cells. The silicon fracture may be a result of the normal P/N fabrication process (such as the BCl_3 junction diffusion). Humidity tests performed on lithium-doped cells by Heliotek showed that the use of Ti-Pd-Ag and Al contacts in place of the standard Ti-Ag contact increases the tolerance of these cells to high humidity environments.

Lithium concentration profiles obtained by Centralab indicated that the lithium concentration is more uniform for high-oxygen-content material than for oxygen-lean material. The "drive-in," or redistribution cycle, tends to decrease the lithium concentration at the junction and the back surface and to decrease the total lithium concentration as the time is increased. These effects are more pronounced on oxygen-lean silicon. As the lithium-diffusion temperature is decreased, the short circuit current I_{sc} for all silicon forms is increased, but the open circuit voltage V_{oc} of high-oxygen silicon remains unaffected while the V_{oc} of oxygen-lean silicon appears to decrease.

Both Centralab and Heliotek have found that the resultant cell parameters have a wider variation for lithium-doped cells fabricated from oxygen-lean silicon than from oxygen-rich silicon, especially with respect to V_{oc}. Moreover, lithium-doped cells are found to be typically 2–3 mW higher in electrical output when they are fabricated from oxygen-rich rather than oxygen-lean silicon.

The use of low-temperature, long-time lithium diffusion schedules (e.g., 325°C for 8 h) has yielded very high efficiency cells (e.g., the median output of 1×2 cm² cells of Lot H3A was 30 mW at M = 0, 28°C conditions) that exhibit recovered powers which are more than 20% higher than state-of-the-art N/P cells as measured in a solar simulator after exposure to 3×10^{15} 1 MeV electrons/cm². This improvement in radiation resistance is in excess of that achieved when N/P solar cells replaced P/N cells as the standard cell for use in the NASA

space program. Furthermore, all indications are that there is an even greater advantage of lithium-doped cells when the irradiation is by protons and neutrons (whereas the advantage of N/P over P/N non-lithium cells becomes smaller for these heavier particles).

VI. Analysis of Lithium-Doped Solar Cells

A. General

Capacitance measurements performed by TRW indicate similar carrier removal characteristics for float-zone (oxygen-lean) and crucible-grown (oxygen-rich) moderately lithium-doped solar cells, in that a large decrease of lithium concentration occurs simultaneously with recovery of the degraded I_{sc}; however, during an irradiation of 3×10^{15} 1 MeV e/cm^2, an order of magnitude fewer lithium donors are removed in the crucible-grown samples. Since the number of lithium donors removed during recovery is comparable for both float-zone and crucible-grown samples, one might conclude that the number of damage centers created were similar in both cases, and it would, therefore, seem that different damage centers are created in float-zone and crucible cells. This seems especially likely when one considers that the quantity of lithium removed during irradiation of the crucible samples would not be adequate to provide a lithium atom in the structure of each damage center. Furthermore, for moderately lithium-doped cells fabricated from crucible silicon, TRW has found that the carrier removal rate during 1-MeV electron irradiation does not appear to be a function of the lithium-concentration, and it is therefore postulated that the initial radiation-induced defect in lithium-doped crucible silicon may not contain lithium. In contrast to the results obtained during irradiation, which indicated little dependence upon lithium concentration for crucible silicon, the carrier removal rate during annealing was found to be a very strong function of the lithium concentration, and it is therefore thought that the lithium donors associate with and neutralize the radiation-induced defect centers.

RCA has found that lithium-doped cells fabricated from crucible silicon have been stable at room temperature for periods of greater than 500 days and are competitive in power with state-of-the-art N/P cells; most lithium-doped cells fabricated from oxygen-lean silicon, however, exhibit lower recovered powers and greater instabilities. RCA has also found that, for lithium-doped cells fabricated from crucible silicon, the time to half-recovery appears to be linearly related to the lithium

density near the junction, as determined from capacitance versus voltage measurements, for density gradients between 10^{18} and 5×10^{19}/cm^4 and a given fluence. This correlation might prove to be a very powerful tool for quantitative prediction of cell annealing characteristics. A general trend of greater and faster recovery with greater lithium doping was observed by RCA. It was also observed that one group of cells (T2 series) developed high series resistance after exposure to 3×10^{15} 1 MeV e/cm^2, due to excessive majority carrier removal resulting from the combination of high fluence and relatively low-base doping.

B. Lithium-Doped Cell Instabilities

Several types of cell instabilities have been determined by RCA only in highly 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 high lithium-concentration gradients 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. Effects of Silicon Background Dopant

It was found that lithium-doped cells fabricated from silicon doped with antimony, rather than phosphorus (as is the standard background dopant for lithium-doped cells), exhibited extremely slow recovery. Further investigations by RCA indicated that significant minority carrier lifetime recovery did occur in lithium-doped cells with antimony base doping during a 6-h 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. This seemingly adverse effect might be useful in reducing lithium motion across the junction if a phosphorus-doped silicon blank is diffused with a thin layer of antimony to form a P+N+N structure. The antimony-doped N+ region could have the twofold benefit of not only reducing lithium diffusion across the junction, but also reducing the effects of majority carrier removal by maintaining a low resistivity region independent of lithium concentration.

D. Recovery Rate of Lithium-Doped Cells

TRW has exposed groups of lithium-doped float-zone silicon solar cells to fluences of 3×10^{14} and 3×10^{15} 1 MeV electrons/cm^2 and subsequently stored them at room temperature. Half-recovery times of 0.5 h and 2 to 3 h were observed for the lower fluences. Experiments on lithium-doped crucible cells indicated that although the annealing times were considerably longer, both the initial outputs and the maximum annealed outputs were higher than the float-zone cells investigated here. It has been found that storage of lithium-doped cells fabricated from crucible-grown silicon at temperatures between 60 and 100°C produces annealing times comparable to that of moderately lithium-doped float-zone cells stored at 28°C. Since solar panel equilibrium temperatures in near-Earth space are of the order of 60°C, the advantages of the higher initial efficiencies and greater stability of lithium-doped cells fabricated from crucible silicon are not mitigated by slow recovery.

E. Advancement in Cell Design

A major advancement in lithium-doped cell design has occurred during this period. It has been found that the use of a long-diffusion-time, low-temperature schedule for lithium introduction into crucible silicon, results in

cells having excellent preirradiation electrical characteristics, as well as excellent recovery after irradiation. TRW has irradiated these cells to a fluence of 3×10^{15} 1 MeV electrons / cm^2 and found the recovered power to be approximately 20% greater than state-of-the-art 10 Ω-cm N/P cells (irradiated to the same level) as measured in a Spectrosun, X-25L solar simulator at 140 mW/cm^2 as shown in Fig. 1.
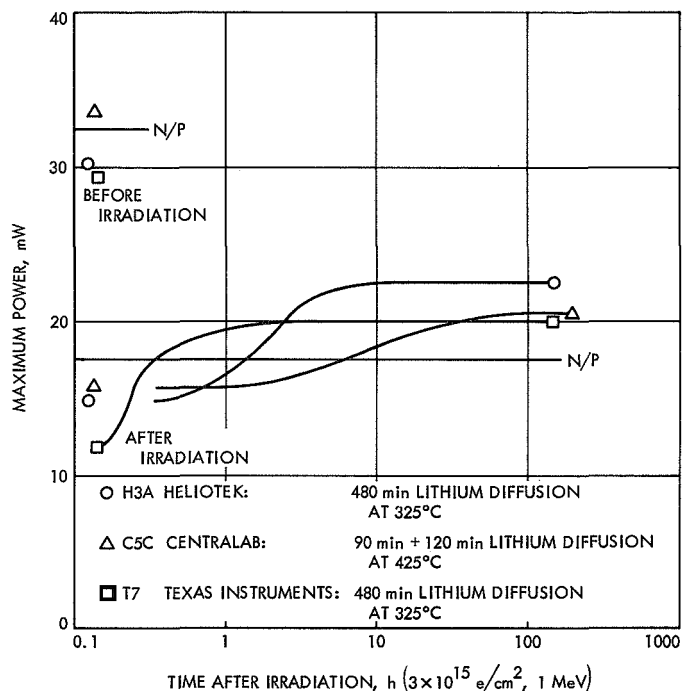

Fig. 1. Lithium-doped, crucible silicon, solar cell maximum power output, after recovery (the data used to produce this figure were extracted from Fig. 3 of Reference 4, courtesy of Mr. R. G. Downing)

F. Neutron Irradiation of Lithium-Doped Cells

Although the majority of the lithium-doped solar cell irradiations have involved 1 MeV electrons, RCA has observed very significant annealing effects after exposure to protons and neutrons. TRW has exposed lithium-doped solar cells to fast neutrons as 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. 2. 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/cm^2 than similarly irradiated 10 Ω-cm, state-of-the-art N/P cells.
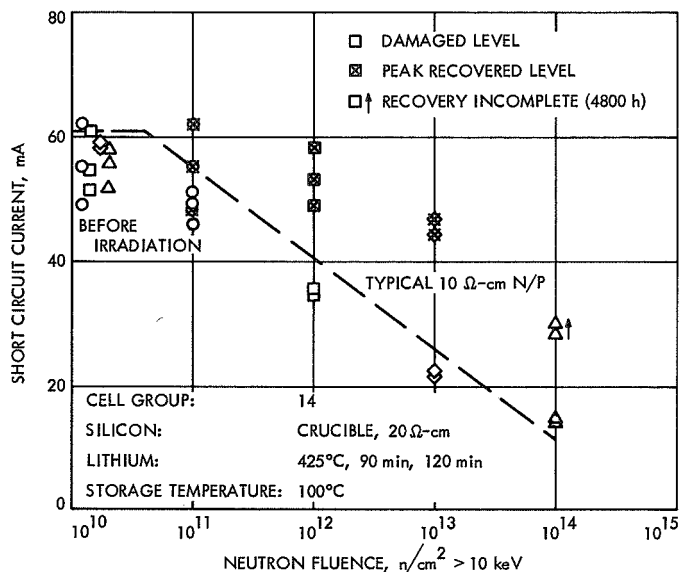
Fig. 2. Lithium-doped solar cells, fast neutron irradiation (the data used to produce this figure were extracted from Fig. 4 of Reference 4, courtesy of Mr. R. G. Downing)

VII. Environmental Testing of Lithium-Doped Cells

Much of the irradiation analysis conducted thus far has utilized particle accelerators to rapidly irradiate samples to fluences which are representative of those which would be encountered in space. This technique is convenient and economical, and provides immediate information on the relative radiation characteristics as a function of cell design. The fluxes (rate of irradiation) however, are orders of magnitude higher than would be encountered in near-Earth space, and hence may yield non-representative results. Therefore, in order to correlate the results of the high flux investigations with near-Earth space-type radiation fluxes, experiments are being conducted at NRL, Philco-Ford Corp., and Lockheed Georgia Corporation to determine the characteristics of lithium-doped cells and state-of-the-art cells under simulated near-Earth space-conditions. These experiments also have the advantage of providing information on the combined effects of other environmental factors such as temperature, illumination level, etc., on the cell characteristics over a period of time (of the order of months). The NRL experiment is less sophisticated than the Philco-Ford and Lockheed Georgia experiments, but was much more rapidly set up and preliminary results are already being obtained. The other experiments are just getting underway and should provide extremely valuable engineering data during the next year.

The NRL Cobalt-60 gamma pool source is utilized for the low flux experiments being carried out at NRL.

The intensity of the radiation at the point where the experiment is located was initially 4.8×10^3 R/h, which corresponds to a 1-MeV electron equivalent flux of 5×10^{11} e/cm²/day. Three stainless steel cylindrical cans about 3 in. in diameter and 9-1/2 in. long are used for the irradiation chambers for the cells. The cells being investigated in this experiment are Heliotek cells having four basic designs, namely: (1) high lithium concentration in float-zone silicon, (2) low lithium concentration in float-zone silicon, (3) high lithium concentration in crucible-grown silicon, and (4) low lithium concentration in crucible-grown silicon. A group of 10 Ω-cm state-of-the-art N/P cells are being utilized for comparative purposes. All cells were measured under a Spectrosun X-25L solar simulator calibrated at 140 mW/cm² air mass zero by a balloon flight standard cell prior to test. Each cell is loaded with a 10 Ω resistor and illuminated by automobile-type lamps during irradiation. The cell temperatures investigated are 30 and 60°C ± 1°C. From three to five solar cells of each group are exposed to each set of experimental parameters so that a satisfactory statistical evaluation of the results can be made. The cells are periodically removed from the irradiation source for measurement of their current–voltage curves under illumination from a Spectrosun X-25L solar simulator at 140-mW/cm² air mass zero conditions.

During 7 mo of testing, the solar cells have been removed from the source and measured five times. After an equivalent electron fluence of 1.03×10^{14} e/cm², none of the lithium-doped cells have an output power as great as the conventional N/P 10 Ω-cm solar cell in this environment. However, on a relative power basis P/P_o, the highly lithium-doped cells appear to be slightly better than the N/P cells. Since lithium-doped cells recently fabricated indicate higher initial efficiencies than the cells being tested, it is possible that these cells would exhibit higher absolute powers than the N/P cells. The data indicated that the temperature of the cells during irradiation influences the amount of observed damage, since all groups of cells irradiated at 60°C are slightly more damaged than those at 30°C. There is also a certain amount of power degradation among cells which are held at 60°C without irradiation, possibly due to contact degradation. The experiment will continue for approximately 6 mo.

VIII. Lithium-Doped Silicon Cell Design

The behavior of lithium-doped solar cells has been found to be highly dependent upon the lithium concentration in the base region of solar cells. It has been

determined that, in general, high lithium content results in cells characterized by:

(1) Low initial cell efficiency.

(2) Fast recovery.

(3) Instability.

On the other hand, low lithium content results in cells which have:

(1) High initial cell efficiency.

(2) Slow recovery.

(3) Incomplete recovery (especially for high fluences).

Superimposed on the effects of lithium doping concentration are the effects of the starting material, namely crucible-grown and float-zone material. The general characteristics of the crucible-grown material are:

(1) High oxygen content.

(2) Low dislocation count.

(3) Economy.

(4) Amenability to large-area cells.

(5) Slow recovery of lithium-doped cells.

(6) No apparent instability of lithium-doped cells.

Crucible-grown material is particularly adaptable to use in large-area cells because it can be grown with relatively large diameters. There is no apparent degradation of the lithium-doped crucible material after storage at room temperature for periods exceeding 500 days.

The general characteristics of float-zone material are as follows:

(1) Low oxygen content.

(2) High dislocation count.

(3) Less economical than crucible-grown material.

(4) Less amenable to use in large-area cells.

(5) Fast recovery rate of highly-doped lithium cells.

(6) Instability of highly-doped lithium cells, especially after recovery of radiation-induced damage.

Because of the effects of lithium-dopant concentration and starting material on the resultant cell characteristics, it is quite likely that the optimum cell for a particular mission will have to be custom-designed on the basis of the expected total fluence, flux, and composition of the radiation (particle types and energy spectra) and cell equilibrium temperature. Some of the gross lithium cell design tradeoffs are shown in Table 2 and were obtained primarily from the material characteristics noted above. The numbers in parentheses in Table 2 indicate the relative desirability of the particular characteristic: the smaller the number the more desirable the characteristic. It can be seen from Table 2 that no one combination of crystal type and lithium concentration is best when evaluated in terms of relative recovery rate, relative cell efficiency, and tendency towards instability.

Highly lithium-doped float-zone material has the fastest recovery rate (which is most desirable) but yields the lowest relative cell efficiency and has the highest tendency towards instability, both of which are undesirable characteristics. The medium-doped crucible-grown

Table 2. Lithium cell design tradeoffs

Cell design		Relative recovery rate	Relative cell efficiency	Tendency towards instability	Comments
Crystal type	Relative lithium concentration				
Float zone	High	Fastest (1)[a]	Lowest (5)	Highest (5)	
Float zone	Medium	Fast (2)	Moderate (4)	Moderate (4)	
Float zone	Light	Moderate (3)	Moderate-good (3)	Small (3)	Possibility of incomplete recovery
Crucible grown	High	Fairly slow (4)	Moderate-good (3)	Small (2)	Economical
Crucible grown	Medium	Slowest (5)	Highest (1)	Smallest (1)	Economical

[a]Numbers in parentheses indicate relative desirability; smallest number indicates greatest desirability.

cell design has the slowest recovery rate, but the highest relative cell efficiency and the smallest tendency towards instability. The lightly-doped float-zone cell design is moderate in all three of these categories.

Characteristics of a lightly-doped crucible-grown cell design are not shown since it is to be expected that the extremely slow recovery rate for this cell design, coupled with a high probability of incomplete recovery, would make this a very undesirable design. It should be mentioned here that Lopex material is basically float-zone material with a much lower dislocation density, and is quite similar in behavior to float-zone material.

Possible improvements in basic cell design are:

(1) Lithium-doped cell fabricated from oxygen-lean silicon with narrow high-oxygen region (less than 1 mil thick) near the electrical junction obtained through diffusion, ion implantation, or other suitable method for oxygen introduction. It was hoped that this structure would give the rapid recovery associated with lithium-doped oxygen-lean silicon with the electrical stability associated with oxygen-rich silicon.

(2) Lithium-doped cell fabricated from oxygen-lean silicon with narrow region near the electrical junction (of the order of several microns) heavily doped with antimony to form a P^+N^+N structure. It has been shown that antimony reduces the effectiveness of lithium in annealing radiation damage, possibly through reduction of the lithium diffusion coefficient. If this is true, the antimony layer could inhibit the flow of lithium out of the base region into the diffused region, resulting in greater stability and a larger amount of lithium in the base region available for interaction with radiation-induced defects.

(3) Lithium-doped cell fabricated from either oxygen-lean or oxygen-rich silicon with a P^+N^+N construction. In this case the narrow N^+ region, obtained by diffusion of a suitable dopant such as phosphorus, results in a reverse field (as would also be the case in the design described in (2) above) which inhibits lithium flow across the junction. The N^+ region also maintains a low resistance region independent of the lithium donor concentration. This can be advantageous if significant numbers of lithium donors are removed during annealing which could result in a decrease in open circuit voltage and an increase in series resistance. The N^+ region can also result in a higher initial open circuit voltage.

(4) Lithium-doped cell having N-type dopant diffused into P-type base configuration, with the P-base being counter-doped with (N-type) lithium to a resistivity of approximately 10 Ω-cm. This configuration could result in improved radiation resistance since the N/P cell configuration is inherently more radiation tolerant than the P/N configuration.

IX. Requirements for Theoretical Model

Phenomena which must be explained by a valid theoretical model are:

(1) Room temperature annealing effect.

(2) Reduction in annealing rate with increasing oxygen content of silicon.

(3) Increase in annealing rate with increase in lithium concentration.

(4) Exhausting of the annealing effect by high fluence.

(5) Incomplete annealing which sometimes occurs.

(6) Decrease in annealing rate with increase in fluence.

(7) Persistence of recombination centers after manufacture and before irradiation, which are not removed by lithium.

(8) Spontaneous redegradation of recovered power of heavily-doped lithium cells fabricated from float-zone material after room temperature storage.

(9) Tendency of initial degradation to be dependent on the lithium concentration for oxygen-lean silicon and independent of lithium concentration for oxygen-rich silicon.

(10) Difference in radiation damage constant between lithium doped oxygen-lean and oxygen-rich silicon (order of magnitude lower in latter).

(11) Increase in carrier concentration after annealing observed in heavily lithium-doped oxygen-lean silicon but not in lightly lithium-doped oxygen-lean silicon or in lithium doped oxygen-rich silicon.

(12) Continued carrier removal observed after annealing in lithium-doped oxygen-rich silicon.

(13) Activation energies involved in annealing of all types of radiation induced damage are very similar to those associated with diffusion of lithium in silicon.

(14) Ratio of carrier removal occurring during irradiation to carrier removal occurring during annealing is a function of lithium and oxygen concentration in silicon.

Relationships that should be determined to completely characterize lithium-doped silicon solar cells are the effects and interactions of:

(1) Species of irradiating particle.

    (a) Electrons.

    (b) Protons.

    (c) Neutrons.

(2) Particle energy.

(3) Particle flux.

(4) Particle fluence.

(5) Temperature-time relationships.

    (a) Pre-irradiation.

    (b) During irradiation.

    (c) Post-irradiation.

(6) Lithium concentration profile.

(7) Minority carrier diffusion length.

(8) Lithium ion diffusion constant.

(9) Density and nature of recombination centers.

(10) Majority carrier removal.

(11) Mobility changes.

(12) Cell fabrication characteristics.

(13) Engineering parameters.

Cell fabrication characteristics (item 12 above) are primarily:

(1) Crystal type.

    (a) Crucible-grown.

    (b) Float-zone.

    (c) Lopex.

(2) Crystal resistivity.

(3) Method of lithium introduction.

(4) Lithium diffusion time and temperature.

(5) Lithium redistribution time and temperature.

Engineering parameters (item 13 above) consist primarily of the following current-voltage characteristics:

(1) Initial.

(2) Pre-irradiation stability.

(3) Unannealed radiation degradation.

(4) Recovery rate after irradiation.

(5) Percentage recovery after irradiation.

(6) Maximum absolute recovery after irradiation.

(7) Post-irradiation stability.

X. Summary of Major Results

A. Lightly Lithium-Doped Silicon

(1) Carrier density and mobility of irradiated lightly lithium-doped float-zone silicon change very slowly with time at room temperature, in contrast to the very fast changes observed in heavily lithium-doped float-zone silicon.

(2) Lightly lithium-doped float-zone silicon exhibits annealing characteristics very similar to highly lithium-doped crucible silicon.

(3) Increases in carrier density during room temperature annealing, attributed to dissociation of lithium from the radiation-induced defect site, have been observed in heavily lithium-doped float-zone silicon, but were not observed in lightly lithium-doped float-zone silicon.

(4) From (1), (2), and (3), above, it appears that the ratio of lithium concentration to oxygen concentration in silicon has a major effect in determining the annealing properties. Thus, low-oxygen-content silicon can behave in a manner similar to high-oxygen-content material if the ratio of lithium to oxygen is appropriate.

B. Irradiation Characteristics of Lithium-Doped Float-Zone and Crucible Silicon

(1) Some studies indicate that during irradiation of lithium-doped crucible silicon with 1-MeV electrons, an order-of-magnitude fewer lithium donors

are removed than is the case for lithium-doped float-zone silicon, and that the lithium loss in crucible silicon is not adequate to provide a lithium atom in the structure of each radiation-induced defect site. Furthermore, in these studies the carrier removal rate of lithium-doped crucible silicon did not seem to be a function of lithium concentration and it is therefore possible that the initial radiation-induced defect in lithium-doped crucible silicon does not contain lithium.

(2) In contrast to (1) above the carrier removal rate of irradiated lithium-doped crucible silicon *was* found to be a very strong function of the lithium concentration during annealing, and it therefore seems apparent that the lithium donors associate with and anneal radiation-induced defects.

(3) The degradation constant of lithium-doped float-zone silicon after exposure to 30-MeV electrons was found to increase with increasing lithium concentration. The degradation constant associated with light lithium doping was similar to that associated with non-lithium doped float-zone silicon, while the degradation constant associated with heavy lithium doping was twice that of undoped material. Heavily lithium-doped float-zone silicon also exhibited greater damage after 1-MeV electron irradiation than phosphorous-doped control samples, through an apparent increased production of deep acceptors. This indicates that in float-zone silicon, the lithium is involved in the structure of initial defects induced by electron irradiation.

(4) The degradation constant of lithium-doped float-zone silicon after exposure to neutrons, in contrast to (3) above, appears to be independent of lithium concentration and is similar to non-lithium-doped float-zone silicon. Thus, for neutron-induced defects (probably cluster defects), lithium is probably not involved in the structure of the initial defect, or at least does not significantly affect the effectiveness of the defect in acting as a recombination center.

(5) The degradation constant appropriate to irradiation by 1-MeV electrons was found to be an order of magnitude lower in lithium-doped crucible silicon than in lithium-doped float-zone material.

C. Annealing of Lithium-Doped Silicon

(1) A very strong point of agreement among investigators is that the activation energy associated with neutralization of radiation-induced defects in lithium-doped silicon (whether the defects be caused by 1-MeV electrons, 30-MeV electrons, or neutrons) is very close to the activation energy associated with diffusion of lithium in silicon and gives strong support to the theory that neutralization of radiation-induced defects is a result of lithium diffusion to the defect sites.

(2) It appears that for each recombination center neutralized, two lithium donors are removed.

(3) Lithium appears to effectively neutralize most radiation-induced recombination centers in silicon during post irradiation storage at room temperature or above.

(4) The rate of annealing in lithium-doped silicon decreases with increasing oxygen content, probably due to the decreasing diffusion coefficient of lithium in silicon with increasing oxygen concentration.

(5) The rate of annealing in lithium-doped silicon decreases with increasing antimony concentration.

D. Effects of Fabrication Parameters on Lithium-Doped Cells

(1) State-of-the-art BCl_3 solar cell junction diffusions give rise to large numbers of dislocations and to cell warpage due to induced strain.

(2) In contrast to (1) above, the use of BBr_3 as a junction diffusion source, or the use of BCl_3 with a reduced "tack-on" cycle, greatly reduces the amount of induced strains and dislocations.

(3) Oxygen-lean silicon appears to be more sensitive to the BCl_3 "tack-on" time, as indicated by the resultant cell efficiency, than oxygen-rich (crucible-grown) silicon. The major effect is an increase in the V_{oc}, and hence the maximum power, with decreasing "tack-on" time.

(4) Oxygen-lean silicon (float-zone, Lopex) is less predictable as to the resultant cell electrical characteristics than oxygen-rich (crucible) silicon. In particular, the V_{oc} has been observed to vary from 540 to 580 mV for the same lot for cells fabricated with oxygen-lean silicon.

(5) It is typical for cells fabricated from lithium-doped crucible silicon to be 2–3 mW higher in power output than cells fabricated from lithium-doped oxygen-lean silicon.

E. Lithium-Doped Cell Stability

(1) Some V_{oc} degradation has been observed in un-irradiated or lightly irradiated heavily lithium-doped cells fabricated from float-zone silicon. This V_{oc} degradation appears to be directly related to the loss of lithium donors in the base region near the junction as determined by capacitance–voltage measurements. The degradation appears to be independent of irradiation and to be more severe for high lithium concentration gradients near the junction.

(2) Redegradation of recovered I_{sc} has been observed in heavily lithium-doped irradiated cells fabricated from float-zone silicon, the redegradation occurring more rapidly and severely with increasing lithium density gradient near the junction. The speed of redegradation appears to be proportional to the product of lithium diffusion coefficient and the lithium density gradient.

(3) Irradiated and unirradiated cells fabricated from lithium-doped crucible silicon exhibited no detrimental instabilities as a result of storage at room temperature for more than 500 days and are competitive in power to state-of-the-art N/P cells similarly irradiated.

F. Irradiation Characteristics of Lithium-Doped Cells

(1) In most cells fabricated from lithium-doped crucible silicon tested thus far, the time to half recovery appears to be linearly related to the lithium density gradient near the junction as determined by capacitance–voltage measurements. Determination of the lithium gradient by means of capacitance–voltage measurements might be a very powerful tool for prediction of the cell annealing characteristics.

(2) Cells fabricated from lithium-doped oxygen-rich and oxygen-lean silicon irradiated with 1-MeV electrons, exhibit a large decrease of lithium concentration near the junction along with a simultaneous recovery of I_{sc}.

(3) Most cells made from oxygen-lean lithium-doped silicon exhibit lower initial and recovered powers and greater instability than observed in similar cells fabricated from oxygen-rich (crucible) silicon.

(4) A special lot of lithium-doped cells fabricated from oxygen-lean silicon with a 1-mil oxygen-rich layer at the front surface (in the hopes of obtain-ing the rapid recovery associated with oxygen-lean silicon and the stability associated with oxygen-rich silicon) exhibited recovery times two orders of magnitude lower and stability far greater than control cells without the oxygen layer after irradiation by 1-MeV electrons.

(5) From the results of (4) above, namely the observation that the introduction of a relatively shallow layer of oxygen drastically altered the annealing behavior, it is possible to conclude that the annealing characteristics of the lithium-doped cell may be almost completely controlled by the region within a few mils of the junction.

(6) Cells fabricated from lithium-doped crucible silicon stored at elevated temperatures (60–100°C) recover as rapidly as cells fabricated from lithium-doped oxygen-lean silicon stored at 28°C. The degree of recovery is approximately the same at the 60°C as at the 100°C storage temperature, but the recovery rate is much higher at the higher temperature. Thus fast recovery of cells fabricated from lithium-doped crucible silicon can be expected at 1 AU conditions, where the cells would attain an equilibrium temperature of the order of 60°C.

(7) Low-temperature, long-time diffusion schedules for lithium introduction yield cells with excellent initial and recovered power outputs. After exposure to a 1-MeV electron fluence of 3×10^{15} e/cm^2, the recovered powers of such cells was approximately 20% higher than state-of-the-art 10 Ω cm N/P cells, irradiated to the same level, as measured in a solar simulator calibrated to an intensity of 140 mW/cm^2.

XI. Conclusions

It appears that a very fortuitous situation exists with respect to the action of lithium in radiation-damaged silicon, in that lithium has the capability of associating with almost all radiation-induced defects, whether they be point defects, cluster defects, or defects associated with various impurities in various configurations, and of reducing the effectiveness of the defect in acting as a recombination center for electron-hole pairs. Although the rate of lithium diffusion in silicon is greatly influenced by the presence of oxygen, as is the nature and stability of the annealed center, a significant agreement exists among investigators that the annealing of the recombination centers in all types of silicon occurs as a result of diffusion of lithium through the silicon to the defect site.

At present, it appears that solar cells fabricated from float-zone silicon with moderate lithium doping might be appropriate for missions involving low temperatures, high fluences, and fluxes and relatively short durations. This is because of the fast recovery of this type of cell with a possibility of instability of electrical characteristics for a lengthy mission. Lithium solar cells fabricated from crucible-grown silicon with moderate to high lithium doping seem to be appropriate for moderate fluxes, high fluences, and longer missions because of the slow, steady recovery with little or no tendency to redegrade. It is, of course, still possible that continued work might lead to a cell which is optimum in all parameters; that is, fast recovery rate, high initial cell efficiency and high stability. However, the results presented here reflect only the status of lithium cell development without extrapolation beyond experimental data.

While a great deal has been learned about the nature of the interaction between lithium and radiation-induced defects, from a pragmatic viewpoint, the most significant accomplishment has been the reproducible fabrication of lithium-doped solar cells which are significantly more radiation resistant to neutrons, protons and electrons than state-of-the-art N/P solar cells on the basis of absolute power as measured under a solar simulator.

There is still a considerable amount of work to be done to further understand the interaction among silicon, impurities, radiation induced defects, and lithium; to obtain information as to the characteristics of lithium-doped cells under space conditions, including temperature storage, temperature cycling, thermal shock, etc.; to translate the fabrication process to production scale; to determine yields and costs; and to obtain more information pertaining to proton and electron irradiation. In addition, experimental lithium-doped cell structures, such as the oxygen skin cell, the P$^+$N$^+$N cell, the antimony layer cell, and the N/P lithium cell remain to be investigated.

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15. Supplementary Notes

16. Abstract

The Jet Propulsion Laboratory is sponsoring investigations into the applicability of lithium doping for improvement of silicon solar cell radiation resistance. This report discusses the author's interpretation of the results of the industry programs, in particular the efforts to improve cell processing techniques and the experiments conducted to improve the theoretical understanding of the action of lithium in irradiated silicon and silicon solar cells. The major conclusions reached as a result of the investigations are presented, and suggestions for future work are made. It appears that lithium-doped solar cells can be fabricated which exhibit (recovered) efficiencies significantly in excess of efficiencies associated with state-of-the-art N/P solar cells after exposure to high fluences of 1-MeV electrons and neutrons.

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