RADIATION DAMAGE AND ANNEALING OF LITHIUM-DOPED
SILICON SOLAR CELLS

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I. INTRODUCTION

The origination of the lithium-doped radiation-hardened silicon solar cell in 1966 (Ref. 1) has been followed by an intensive effort to study the specifics of the radiation damage and recovery processes. As one step in the direction toward optimizing the chemical and physical parameters of the cell for maximum radiation hardness, it is essential to determine the performance of this solar cell in various radiation environments. The amount and rate of this recovery process have been shown to depend on the oxygen impurity in the silicon, the type of irradiating particle, the fluence, and the temperature of the cell following the irradiation. In addition, low-flux rate irradiation as contrasted with Van de Graaff bombardment, have provided valuable information on the behavior of these cells in a simulated space environment. A part of this paper will discuss the recent results of a continuing real-time-rate irradiation (Ref. 2) which was begun in September 1969. Since that time, better lithium-doped cells have been made, and placed into the study. We shall also discuss the results of 1-MeV electron and 4-MeV proton Van de Graaff irradiation and annealing of a solar cell made from crucible-grown silicon which has been lithium-diffused for 8 h at 325°C.

II. EXPERIMENTAL

Three modes of radiation were used to study damage and recovery in the lithium solar cells. They comprised 1.2-MeV gamma photons from the Naval Research Laboratory (NRL) Cobalt 60 source, 1-MeV electrons from a Van de Graaff, and 4-MeV protons from a Van de Graaff. The damage caused by the 1.2-MeV gamma photon comes about from energized electrons which are produced in the chamber walls, in the solar cell holder, and within the solar cell by means of Compton interactions of the gamma ray with electrons in the material (Ref. 3). These electrons have a spectrum of energies ranging upward to 0.8 MeV. These energetic electrons create lattice vacancies in the silicon, followed by the formation of defects and recombination centers similar to those occurring in 1-MeV electron irradiated silicon. A first approximation for equivalency of damage in solar cells from Cobalt 60 gammas, as compared with electrons, can be made by determining the number of gamma photons that will produce the same number of lattice displacements as a 1-MeV electron. If values (Ref. 4) are used for the total number of displaced silicon atoms per unit of incident flux of 10^-2 for 1-MeV gamma photons and 4.6 for 1-MeV electrons, the equivalent electron dose corresponding to 1 rad (Si),
which is $2.22 \times 10^7$ photons/cm$^2$, is $4.35 \times 10^6$ e/cm$^2$. This equivalency factor is applicable only when the gamma environment is one of electronic equilibrium for the irradiated sample. In this case, this condition is essentially satisfied.

The flux values, in units of particles/cm$^2$-s, varied widely. In the case of gamma flux, the value was $5 \times 10^6$ e/cm$^2$-s, later increased to $2.7 \times 10^7$ e/cm$^2$-s. For the electron Van de Graaff irradiations the flux was $5 \times 10^{11}$ e/cm$^2$-s, and for the proton Van de Graaff, $3 \times 10^9$ particles/cm$^2$-s.

The solar cells discussed here are five types. There are four groups of Helliotek lithium-doped P/N cells, one of Centralab lithium-doped P/N cells, and a group of Centralab 10-Ω-cm N/P flight-quality solar cells. Table 1 shows the experimental matrix for the gamma ray portion of this study.

The experimental apparatus for the gamma irradiations consisted of three stainless-steel cylindrical cans about 7.6 cm in diameter, 24 cm long, with a 0.5 cm-thick wall. The solar cells were held in contact with temperature-controlled brass plates by means of spring clips. Each cell was loaded with a 10-Ω resistor, with pressure contact made through the spring clips and brass plate.

Illumination was provided during irradiation by means of five 12-V automobile lamps in each can. Replacement of lamps was required about every 3 mon because of radiation darkening of the glass bulbs. Then cans were evacuated after sealing, and back-filled with 0.7 N/cm$^2$ (1 psi) of argon to provide for thermal conduction of the heat from the lamps to the chamber walls. (Under vacuum, the bulbs failed in a few hours.)

The cell temperatures were controlled by means of a combination of electrical strip heaters and water-carrying copper tubing fastened to the rear of the solar cell mounting plates. One can was held at 30°C, and two cans at 60°C with a variation of ±1°C. For measurements of the I-V curves, the solar cells were removed from the cans and placed under a Spectrosun X-25L solar simulator calibrated for 140 mW/cm$^2$ air mass zero. Solar cell temperature was 25°C for all measurements at the simulator. During the times the cells were out of the irradiation chambers, they were held at dry-ice temperature to prevent annealing, except for the actual measurement time.

The irradiations at the NRL 2-MeV electron Van de Graaff were carried out on solar cells at room temperature, with forced-air cooling on the sample. The flux obtained was $5 \times 10^{14}$ 1-MeV e/cm$^2$. All of the solar simulator measurements were performed with cell temperatures of 25°C. The annealing of the solar cells after irradiation was done in forced-draft laboratory ovens at 60 and 30°C with solar simulator measurements being performed at intervals throughout the recovery period.

The 4-MeV proton bombardment was performed at the NRL 5-MeV proton Van de Graaff to a fluence of $2.2 \times 10^{11}$ p/m$^2$, with the two solar cells in a vacuum of $6.7 \times 10^3$ N/m$^2$ during the irradiation. As in the case of the electron-irradiated cells, these samples were measured at the solar simulator at 25°C at intervals throughout their 60°C annealing period.

### III. RESULTS

The results of Cobalt 60 gamma irradiations over a period of 18 mon will be discussed. During this time the solar cells were removed from the source 12 times for measurements. A total gamma exposure of $1.4 \times 10^8$ R was received by the cells, equivalent to a 1-MeV electron fluence of $6.1 \times 10^{14}$ e/cm$^2$. It should be mentioned that the dose rate was increased from $5 \times 10^6$ e/cm$^2$-s to $2.7 \times 10^7$ e/cm$^2$-s after a fluence of $2 \times 10^{14}$. The trend of the data show that the results were not affected by this increase. Figure 1 is a plot of the power output of the cells as they are irradiated at 60°C in a continuous gamma ray environment. The power is measured with a cell temperature of 25°C at one sun of illumination. It can be seen from Table 2 that the four types of lithium cells were much lower in initial efficiency than the N/P 10-Ω-cm cell which was used for comparison. The results of the 30°C irradiation showed slightly more damage than these at high fluences, although up to $1 \times 10^{14}$ e/cm$^2$ there was generally little difference between the 30 and 60°C data (Ref. 2). The groups H2 and H5 were designated generally to be low lithium content. In fact, junction capacity measurements on H5 indicated no lithium concentration near the junction. The poor radiation hardness attests to this finding. On the other hand, the more heavily doped H6 and H9 were also so low in efficiency that they were never competitive to the H2 and N/P cells in the course of the experiment.

A quite different picture of the performance of a lithium cell is given in Fig. 2. The maximum efficiency shown here for the C11A cell is 11.2% compared with 10.4% for the N/P cell. However, the rapid decrease in power brings the lithium cell performance exactly to the level of the N/P cell at 60°C irradiation temperature. The results of the 30°C irradiation show that the C11A cell output is definitely lower. One might assume that the increased mobility of lithium at the higher temperature causes a more rapid annealing rate for the damage centers which are being produced. The most important point of this figure is that the power level of the C11A cell ultimately stays above the N/P cell at fluences beyond $4 \times 10^{14}$ e/cm$^2$, with an improvement of about 5%. In terms of long exposures in an electron environment, it appears that the lithium cell will offer an advantage over the conventional N/P cell.

The next part of the study was to investigate the annealing rate of rapidly damaged solar cells as a function of temperature and cell type. The C11A lithium-doped cell was chosen because of its good characteristics, and was compared with the same type of N/P cell used throughout this work. Figure 3 depicts the post-irradiation annealing of the power lost through 1-MeV electron irradiation in C11A and N/P solar cells. The N/P cell shows a slight recovery immediately after the irradiation, then quickly saturating and even slightly declining. The C11A cell shows additional damage occurring within the first few hours following the...
irradiation. The 30°C annealing does not regain any of the power lost during the irradiation. However, annealing at 60°C produces a large recovery of the lost power. This result can be seen more quantitatively in Fig. 4 where the percentage of recovered power is shown. Percentage recovery is defined as

\[
\frac{P_a - P_r}{P_0 - P_r} \times 100
\]

where \(P_0\) is the original power, \(P_r\) is measured after the irradiation, and \(P_a\) after annealing. In Fig. 4 one observes that the lithium cell has recovered 42% of its power after 200 h at 60°C, while the N/P cell has recovered only 10%. In actual power level, the lithium is about 5% greater at 200 h (Fig. 3).

All of the previous results, for 60°C gamma radiation and 60°C annealing after electron radiation are summarized in Fig. 5. The maximum annealing time for this data is 100 days, whereas the time to gamma irradiate cells to this dose is about 200 days. With this fact in mind, we observe that more damage is produced during slow irradiation with simultaneous annealing than is left in the cells when they are rapidly damaged, then allowed to anneal for an equivalent length of time. Some of the Heliotek lithium cells used in the first part of the gamma experiment were removed after a fluence of \(2 \times 10^{14}\) e/cm\(^2\) and placed in a 60°C annealing temperature with and without illumination. No recovery of these cells was observed; indeed, many cells degraded somewhat further. Thus it is unlikely that the gamma-irradiated C11A cells would show recovery if the radiation were removed. It is interesting to note that in both experimental situations, the lithium-doped solar cells demonstrate a power margin of about 5% over the N/P cell.

The final portion of the experiment consisted of a 4-MeV proton bombardment of two C11A cells to a fluence of \(2.2 \times 10^{11}\) p/cm\(^2\). The cells were allowed to anneal in an oven at 60°C for 800 h, with L-V measurements made at intervals throughout. This data is summarized in Fig. 6, along with the electron-damage annealing data from Fig. 3. In both electron and proton Van de Graaff bombardment, the P/N lithium cells are degraded much more than the N/P cell. This difference between radiation hardness in P-type and N-type silicon solar cells has been established for many years (Refs. 5, 6). During the annealing, the lithium cell recovers to a higher power level than the N/P cell after 800 h at 60°C. Carter and Downing (Ref. 7) report a different behavior in similar solar cells irradiated to \(3 \times 10^{15}\) 1-MeV e/cm\(^2\) and annealed at 100°C. In their case, the lithium cell power recovered to a value for the N/P cell in 2 h. Since recovery rate depends on irradiation fluence and annealing temperature (Ref. 8), these two results are not necessarily conflicting. The recovery from proton damage follows a different behavior. There is no additional damage found during the first few hours after irradiation; recovery begins at once and proceeds more rapidly and to a higher degree than for electron damage. The percentage recovery at 800 h is 38% for electron damage and 68% for proton damage. The proton data shown for the N/P cell is a typical value extrapolated from a previous experiment (Ref. 6). No annealing data was available for the N/P cell.

IV. SUMMARY

Very conclusive evidence has been presented that a lithium-diffused crucible-grown silicon solar cell can be made with better efficiency than the flight-quality N/P 10 Ω-cm solar cell. When this lithium cell is exposed to a continuous radiation environment at 60°C (electron spectrum from gamma rays) it has a higher power output than the N/P cell after a fluence of \(4 \times 10^{14}\) e/cm\(^2\) (equivalent 1 MeV).

A comparison of annealing of proton- and electron-damage in this lithium cell reveals a decidedly faster rate of recovery and higher level of recoverable power from the proton effects. This fact strongly suggests that the lithium cell in a low-rate continuous proton flux would have even greater superiority over the N/P cell than it has in the case of electrons. Therefore, the lithium cell shows a good potential for many space missions where the proton flux is a significant fraction of the radiation field to be encountered. This is the case for many specified earth-orbit trajectories as well as interplanetary missions.

The need for additional proton radiation studies is obvious, in view of the superior performance of the lithium cells. Such work will be carried out utilizing various other proton energies of interest.

REFERENCES

Table 1. Co$^{60}$ Experiment sample matrix

<table>
<thead>
<tr>
<th>Cell group</th>
<th>Type</th>
<th>Li diffusion parameters</th>
<th>Quantity of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Illuminated 30°C</td>
</tr>
<tr>
<td>H-2</td>
<td>Li P/N crucible</td>
<td>90 min, 425°C-60 min, 425°C</td>
<td>5</td>
</tr>
<tr>
<td>H-6</td>
<td>Li P/N crucible</td>
<td>90 min, 450°C-60 min, 450°C</td>
<td>5</td>
</tr>
<tr>
<td>H-5</td>
<td>Li P/N FZ</td>
<td>90 min, 350°C-60 min, 350°C</td>
<td>5</td>
</tr>
<tr>
<td>H-9</td>
<td>Li P/N FZ</td>
<td>90 min, 425°C-60 min, 425°C</td>
<td>5</td>
</tr>
<tr>
<td>C11A</td>
<td>Li P/N crucible</td>
<td>480 min, 325°C</td>
<td>2</td>
</tr>
<tr>
<td>Centralab</td>
<td>N/P crucible 10 Ω-cm</td>
<td>NA</td>
<td>5</td>
</tr>
</tbody>
</table>

All cells are illuminated with tungsten light and are individually loaded with a 10-Ω resistor developing a load voltage of 0.21 to 0.24 V. The cells are removed from the chambers for measuring the electrical performance at 25°C under a solar simulator.

Table 2. Photovoltaic parameters of experimental cells

<table>
<thead>
<tr>
<th>Cell group</th>
<th>Type</th>
<th>$I_{sc}$ mA</th>
<th>$P_{max}$ mW</th>
<th>Efficiency, %</th>
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<tr>
<td>H-2</td>
<td>Li CG</td>
<td>64.5</td>
<td>27.8</td>
<td>9.9</td>
</tr>
<tr>
<td>H-6</td>
<td>Li CG</td>
<td>60.0</td>
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<tr>
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<td>Li FZ</td>
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<td>27.4</td>
<td>9.8</td>
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<tr>
<td>H-9</td>
<td>Li FZ</td>
<td>61.0</td>
<td>25.1</td>
<td>9.0</td>
</tr>
<tr>
<td>C11A</td>
<td>Li CG</td>
<td>71.6</td>
<td>31.0</td>
<td>11.1</td>
</tr>
<tr>
<td>N/P</td>
<td>10 Ω-cm</td>
<td>71.5</td>
<td>29.2</td>
<td>10.4</td>
</tr>
</tbody>
</table>
Fig. 1. Power loss in lithium-doped P-on-N solar cells compared to an N-on-P 10 Ω-cm solar cell irradiated by Co\textsuperscript{60} gamma flux at 60 °C.

Fig. 2. Power loss in lithium-doped P-on-N solar cells and 10 Ω-cm N-on-P solar cells irradiated at 30 and 60 °C by Co\textsuperscript{60} gamma flux.
Fig. 3. Post-radiation annealing of power lost through 1-MeV electron irradiation in lithium-doped P-on-N solar cells and N-on-P 10 Ω-cm solar cells.

Fig. 4. Percentage of power recovered through post-radiation annealing in solar cells irradiated by 1-MeV electrons.
Fig. 5. Comparison of power recovery by annealing following a 1-MeV electron radiation, and the power lost in a real-time Co$^{60}$ gamma radiation for lithium-doped P-on-N solar cells and N-on-P 10 Ω-cm solar cells. The annealing time extends to 2300 h, whereas the time to gamma irradiate to $5 \times 10^{14}$ is 200 days.
Fig. 6. Comparison of power recovery following a 1-MeV electron radiation and a 4-MeV proton radiation for lithium-doped P-on-N solar cells.