N72-10053

SOME MAJOR RESULTS OF THE FOURTH ANNUAL CONFERENCE ON EFFECTS OF LITHIUM DOPING ON SILICON SOLAR CELLS

P. A. Berman
Conference Chairman

I. INTRODUCTION

The conference was held at the Jet Propulsion Laboratory in Pasadena, Calif., on April 29, 1971. Attendees were members of the photovoltaic community interested in the radiation hardening of solar cells and personnel involved in research on lithium-doped silicon cells sponsored by NASA/JPL. A large body of information was presented, and a summary of all the significant points is not feasible. Some of the points that will be of interest to the majority of readers are summarized.

II. SUMMARY OF RESULTS

Lithium-doped silicon solar cells having dimensions as large as 12 cm^2 are now possible, due to significantly improved boron-diffusion techniques, which stress the cells far less than techniques used previously. A large increase was observed in the short-circuit current measured in tungsten (long wavelength) light for cells that were fabricated using the improved diffusion techniques as compared with previous cells, indicating a preservation of minority carrier diffusion length in the base region of the former cells. Sintering (at about 600°C) of the contacts of lithium-doped cells fabricated from Lopex silicon resulted in large increases in maximum power (of between 1 and 4 mW), mostly due to an open-circuit voltage improvement, over non-sintered cells. Efficiencies as high as 12.8% were observed, with the average efficiency being about 11.9%. The sample is small, but the efficiency is significantly higher than the average efficiency of 10 Ω-cm N/P cells (state-of-the-art) which is about 11.3 to 11.5%.

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

The uniformity of solar cells fabricated with the addition of a redistribution cycle was more difficult to control than that of cells fabricated using a single-cycle lithium distribution. Also, longer lithium distribution cycles gave rise to larger cell-to-cell variations in lithium concentration gradient and open-circuit voltage.

The use of ion implantation has provided additional flexibility in lithium solar cell design. Ion implantation was used to implant an N^+ region at the back face of the cell and to implant lithium through the N^+ layer. In this way, the amount of lithium introduced prior to lithium distribution (which is still accomplished by diffusion at 300 to 400°C) can be precisely controlled, and the ratio of electrically active lithium after distribution to the amount of lithium initially present in the cell can be determined. The presence of the N^+ region at the back surface was found to inhibit loss of lithium after lithium distribution by a factor of ten over the loss observed in samples without the N^+ region. Very good post-irradiation recovery has been obtained on ion-implanted cells fabricated in this manner, with recovered powers being greater than that of state-of-the-art N/P cells.

In highly lithium-doped float zone (low oxygen content) silicon the carrier removal reached equilibrium shortly after irradiation. In lightly lithium-doped float-zone silicon and highly lithium-doped crucible silicon, carrier removal reached equilibrium approximately one to two years after irradiation. A close pair vacancy-interstitial model applies quite well to lithium-doped crucible-grown silicon, but not as well for lithium-doped float-zone silicon.

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

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

Long lithium-diffusion times resulted in large variations in lithium density gradients (differences as large as a factor of 24) while shorter diffusion times yielded very small variations of lithium

density gradients (within a factor of 2). This indicates that one can tightly control post-irradiation recovery rates by proper control of the lithium distribution schedules.

Investigation of cells with various amounts of lithium coverage on the back prior to distribution (50, 80, and 100% coverage) indicated that the recovery of the 80 and 100% coverage cells were similar to one another while the 50%-coverage cells recovered more slowly and less completely. The rate and extent of recovery was directly related to the lithium concentration near the junction. These results indicate that careful control of the area coverage of the lithium prior to lithium introduction is not critical to the cell recovery characteristics.

It was postulated that the fact that the time to half-recovery appears to increase with increasing irradiation fluence might actually be a result of annealing that occurs during the irradiation (higher fluences generally require longer irradiation times), so that the damage measured after bombardment does not represent the actual total damage, and the apparent half-recovery time is longer than the actual half-recovery time. If the time to half-recovery does not increase with increasing fluence, this would simplify the description of the annealing kinetics.

It was observed that carrier removal rates increase with increasing lithium concentration and hence with distance from the P-N junction. That is, the amount of lithium which reacts with a radiation-induced defect during the recovery stage is proportional to the amount of lithium available for interaction with the defect, indicating that the defect can nucleate precipitation of large numbers of lithium atoms if they are present in the vicinity of the defect. For example, the change in lithium concentration at 5 μm from the junction was observed to be five times as great as the A-center (oxygen-vacancy defect) concentration at that depth. Furthermore, in lithium-containing cells fabricated from float-zone silicon, the carrier removal rate was found to decrease with increasing fluence, again indicating a defect-lithium interaction dependent upon the number of available lithium atoms per defect. This indicates that the model used in the past, which simply assumed that two lithium donors were removed for each annealed damage center, must be modified.

Annealing of 90% of the radiation damage was observed in lithium-doped silicon after isothermal and isochronal anneals of samples irradiated with fission neutrons and with high energy (30 MeV) electrons. Samples with high lithium concentration exhibited degradation coefficients immediately after electron irradiation which were greater than those of samples that did not contain lithium. The post-irradiation characteristics lend themselves to interpretation by a two-defect model, one defect controlling the minority carrier lifetime τ at low temperatures and the other controlling τ at higher temperatures. The annealing appears to be a first-order process, characterized by an activation energy and an atomic frequency factor.

From electron spin resonance measurements it was inferred that lithium inhibited the production of oxygen-vacancy radiation defect centers and that the centers annealed at 350 K rather than in the 600 K range observed for non-lithium-treated samples. In contrast, the production of phosphorus-vacancy radiation defects did not appear to be influenced by the presence of lithium. The radiation-induced divacancy, as observed by means of infrared spectroscopy, appeared to have an introduction rate in lithium-doped silicon similar to that observed in non-lithium-doped silicon, but in the lithium-doped silicon annealing of the divacancy proceeded much more rapidly. As the absorption band associated with the divacancy decreased through annealing, two new absorption bands appeared, indicating the formation of a new defect which is probably influenced by the association with lithium.

Hall measurements performed at 4 K allowed separate determination of donor and acceptor concentration in silicon. Electron-irradiated lithium-doped silicon exhibited a defect level located 0.14 eV below the conduction band. It is postulated that this defect may be a vacancy-oxygen defect (A-center) associated with another impurity such as an additional oxygen or carbon atom. It was inferred that lithium interacted much more strongly with the oxygen-vacancy defect than with the phosphorus-vacancy defect and that as many as four lithium atoms may be involved in the annealing of radiation-induced defect centers. Annealing was observed to result in the disappearance of acceptor levels in irradiated lithium-containing samples but not in irradiated samples containing phosphorus but no lithium. Also, the carrier concentration of irradiated lithium-containing samples was observed to decrease at room temperature while the carrier concentration of irradiated non-lithium-containing samples remained constant.

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

Low flux irradiations obtained using a Co^{60} source indicated a 4% superiority in maximum power of lithium-doped cells fabricated from crucible-grown silicon over N/P (non-lithium containing) 10 Ω-cm silicon cells after a cumulative dose of approximately 5×10^{14} equivalent 1-MeV electrons/cm^2 (100 days exposure) at a temperature of 60°C. Similar lithium-containing

cells irradiated at a temperature of 30°C were inferior to N/P cells at this fluence level. Similar groups of cells were also irradiated by means of a Van de Graaf generator to a fluence of 5×10^{14} 1-MeV electrons/cm^2 and allowed to anneal at 30 and 60°C. The same percentage superiority of the lithium-containing cells over the N/P cells was observed for the 60°C anneal as was observed for the cells exposed to the Co^{60} irradiation at this temperature. This indicates that the use of accelerated irradiation tests are valid for determining the relative radiation resistance of lithium-doped cells with respect to N/P cells.

Two low flux experiments have also been carried out using a Sr^{90} source for a time period of about six months (total fluence equivalent to about three years in synchronous orbit). The lithium-containing cells in these experiments represented the best cells obtainable about one year ago, but not the best cells presently being fabricated. For the cells maintained at temperatures of 50°C and above, lithium-doped cells fabricated from crucible-grown silicon exhibited maximum powers which were relatively constant over the life of the test and about 8% higher than non-lithium-containing N/P cells. In one of the experiments the cells were post-irradiation annealed at the test temperature with no significant changes in power output being observed. This indicated that the cells were annealed as well as they could be during the test; that is, maximum annealing of radiation-induced damage was occurring during the test.

There appeared to be no additional radiation protection afforded by 1-mil integral shields for the low flux environment studied. One of the experiments indicated that the maximum power of unilluminated cells was consistently about 4% higher than that of illuminated cells, while the other experiment was inconclusive with respect to this phenomenon. If the results of the former experiment are accurate, this would indicate that the results of most solar cell irradiation tests (i.e., not only lithium-doped cell tests), which are performed with the cells in an unloaded unilluminated condition, may significantly underestimate the amount of damage to the solar cell maximum power.

Lithium-doped solar cells fabricated from low oxygen content silicon appear to have optimum annealing characteristics at a temperature of about 20°C, while lithium-doped solar cells fabricated from crucible-grown (oxygen-rich) silicon appear to be superior for temperatures of 50°C and above, for the conditions studied in these low flux experiments.

Irradiation of lithium-doped cells fabricated from crucible-grown silicon by 28-MeV electrons to fluences of 5×10^{14} and 5×10^{15} e/cm^2 exhibited recovered short-circuit currents 100% higher than similarly irradiated state-of-the-art N/P cells. This is consistent with previous investigations using neutron irradiation, since in both cases considerable cluster damage occurs. All results obtained thus far strongly indicate that lithium is extremely efficient in reducing the detrimental effects of radiation-induced defect clusters on the cell electrical characteristics. This means that for environments consisting of high energy electrons, protons, or neutrons, lithium-doped solar cells should be vastly superior to state-of-the-art N/P solar cells.