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by Joseph Mandelkorn, Lawrence Schwartz, Jacob Broder,
Harold Kautz, and Robert Ulman
Lewis Research Center
Cleveland, Ohio

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EFFECTS OF IMPURITIES ON RADIATION

DAMAGE OF SILICON SOLAR CELLS

by Joseph Mandelkorn, Lawrence Schwartz, Jacob Broder,
Harold Kautz, and Robert Ulman

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

Some effects of impurities in the base material of silicon solar cells on junction characteristics and radiation damage were determined in previous work comparing n-on-p and p-on-n solar cells.[1,2,3] This work had established the fact that the substitution of boron for phosphorus in the base material of solar cells increased the minority-carrier diffusion length preserved in the base material after bombardment. It was also determined in the same work that the optimum concentration of boron in the base material of cells for achievement of good junction characteristics and maximum power output after bombardment corresponds to that of 10-ohm-cm material.

Later experiments indicated that the diffusion-length degradation in the base region of the n-on-p cell, caused by high-energy-particle bombardment, was related to interaction of boron atoms with bombardment-produced lattice defects.

A theory was formulated to explain the effects of impurities on the basis of the following hypothesis: The probability of a donor or acceptor atom associating with a lattice defect in silicon to create a recombination center is determined by the properties and concentration of donor or acceptor atoms and the density of lattice defects.

The density of lattice defects in a single-crystal silicon ingot varies with position in the ingot and is a function of single-crystal growth conditions. The defect density in silicon is further increased by processing the material to make a device or by high-energy-particle bombardment. If the hypothesis holds true, then no matter what the density of lattice defects or their cause (growth, processing, bombardment), there should be an observable dependence of minority-carrier diffusion length on the specific acceptor or donor element as well as on its concentration in the material or device.

To test the hypothesis, solar cells were made from silicon ingots containing either boron, aluminum, indium, gallium, or gadolinium as acceptors. Gadolinium and other rare earth elements exhibit valence behavior similar to that of the elements in Group 3 of the periodic table, and gadolinium was found to act as an acceptor in silicon.

The concentrations of the various acceptor elements in the silicon ingots grown for the experiment were controlled to yield silicon in the 10- to 20-ohm-cm resistivity range, in accordance with previous findings.[2,3] Some difficulty was encountered in growing a large-diameter 20-ohm-cm silicon ingot doped with gadolinium. Apparently, only a small percentage of gadolinium atoms added to silicon undergo room-temperature ionization. At first, a good-quality 50-ohm-cm gadolinium-doped ingot was grown. Subsequently, by addition of large quantities of gadolinium to a silicon melt, a 20-ohm-cm ingot was grown; however, the strains produced by the high concentration of gadolinium in the ingot reduced minority-carrier diffusion lengths in most regions to values below 100 microns. The best sections of the ingot were selected, and cells were made from wafers cut from these sections. These cells had initial base-region diffusion lengths exceeding 120 microns.

Additional groups of cells were made from several boron-doped ingots having boron concentrations corresponding to a range of resistivities from 1 to 1000-ohm-cm.

Finally, since oxygen has been identified as an impurity affecting radiation damage in silicon,[4] groups of cells were also made from various grades of 10-ohm-cm float-zone silicon. Typical float-zone silicon differs from conventional Czochralski silicon in that it contains approximately one-hundredth the oxygen concentration that Czochralski silicon contains.[5]

All cells were made by a fabrication process previously described.[3] The cells had good junction characteristics and diffusion lengths exceeding 120 microns. Many of the cells made from aluminum-doped silicon had unusually good junction characteristics and diffusion lengths exceeding 150 microns.

Selected groups of cells were first subjected to a series of 1-Mev electron bombardments. The junction characteristic,[3] diffusion length, and power output under a solar simulator were measured for each cell after each bombardment.

Table 1 presents average characteristics of the selected groups of cells after bombardment. Because the cells within each group had uniform characteristics after bombardment, valid differentiation in terms of average diffusion length preserved was possible.

Comparison of the 1-, 10-, and 100-ohm-cm C-B cell group data clearly shows that decreasing the boron concentration in the base material increased the magnitude of diffusion length preserved after any specific bombardment dose.

Fig. 1 shows the diffusion length plotted as a function of the bombardment dose. The slopes of the plots do not conform with the half-power dependence predicted from simple recombination theory.[6] The magnitudes of the slopes for the various boron-doped groups increases with increasing boron concentration in the base region of the cells. The 50-ohm-cm Gd group plot has the smallest magnitude of slope despite the fact that the acceptor concentration in the base region of the cells in the Gd group is much higher than that of the 100-ohm-cm C-B group.

Equivalent results were obtained in a series of 10-Mev proton bombardments of the various boron-doped Czochralski cell groups. Several of the 10- to 20-ohm-cm groups containing acceptor elements other than boron were also subjected to the series of 10-Mev proton bombardments.[7] A relative-long wavelength collection efficiency method[7] was used to measure diffusion lengths of proton-bombarded cells. The aluminum-doped cells preserved considerably longer base-region diffusion lengths after each bombardment than cells doped with an equal concentration of boron.

The Table 1 data do not show any significant difference between the 10-ohm-cm FZ-B group and the 10-ohm-cm C-B group in degradation of diffusion length and thus indicate no large effects on radiation damage were produced by oxygen in this case. The 10-ohm-cm FZ-B-Cl_2 group does, however, undergo less diffusion-length degradation than the other 10-ohm-cm groups. The superior behavior of the FZ-B-Cl_2 group did not manifest itself in a series of 10-Mev proton bombardments.

Subsequently, sample wafers of the materials used to create the different groups were analyzed for impurity content by mass spectrography. The samples included wafers from completely processed solar cells that were treated to remove contacts and the diffused region. The FZ-B and the Czochralski materials were found to contain less than 0.2 part per million of chlorine, whereas the FZ-B-Cl_2 samples contained approximately 1 part per million of chlorine. Further evidence that chlorine affects radiation damage of float-zone material was obtained from an experiment in which cells were fabricated from wafers of a float-zone ingot by using two different diffusion processes to form the p-n junction. In one case the standard process was used,[3] and, in the second case, phosphorus trichloride was carried in a stream of reducing gas over the heated wafers. Under electron bombardment, the phosphorus trichloride cells had superior behavior comparable to that of the FZ-B-Cl_2 group, whereas they showed no superiority under proton bombardment.

Table 1 also presents data on curve-power-factor degradation of bombarded solar cells. The curve power factor (CPF) is defined as the ratio, expressed in percent, of the maximum power output of a cell to the product of its open-circuit voltage and short-circuit current. The decreases in curve power factor listed in the table occur because of increases in base-region series parasitic resistance as a result of majority-carrier removal under bombardment. The 100-ohm-cm C-B group is very adversely affected after the first bombardment, while the 10-ohm-cm cells are seriously affected only after the final dose. Of the 10-ohm-cm cell groups, the C-B group is most affected, while the FZ-B group is least affected. The latter result indicates that oxygen in silicon acts to increase carrier removal rate.

After final bombardment measurements were made, two of the FZ-B-Cl_2 cells were reduced to a thickness of 0.006 inch from the original thickness of approximately 0.015 inch. Measurement of the CPF of these cells showed that the cells regained the CPF values they had after the third bombardment. Cells 0.006-inch thick have been fabricated without difficulty and may find use in lightweight collapsible module solar cell arrays having small surface area when collapsed.

Degradation of the 10-ohm-cm cell due to carrier removal is not of practical concern because of the extremely heavy bombardment dose required to affect the CPF of 10-ohm-cm cells. Carrier removal, however, does affect the validity of diffusion-length measurements made on high-resistivity cells. The diffusion lengths listed in Table 1 were obtained by the method described by Rosenzweig,[8] which relates the short-circuit current measured under electron beam irradiation to diffusion length. The extremely high base series parasitic resistance that existed in the 100-ohm-cm cells after the fourth bombardment prevented the measurement of short-circuit current of the cells. The 10-micron diffusion length listed for the 100-ohm-cm C-B cells is, therefore, the apparent rather than the actual diffusion length. Similarly, data obtained on 1000-ohm-cm cells after small bombardment doses were not valid and therefore are not listed in Table 1.

In conclusion, a relation between the element used as an acceptor or donor in the base region of solar cells and the diffusion length preserved in the base region after bombardment has been shown to exist. Since simple recombination theory does not take into account the role of acceptors or donors as participants in the formation of recombination centers, it cannot be expected that the results of the experiments conform with the aforementioned theory.

The effects of impurities on the original characteristics of silicon material and devices is often obscured by uncontrolled variables in growth and processing. High-dose particle bombardment was used to inject sufficient lattice defects to make the effects of original defect density variation in the materials investigated negligible. Bombardment thus permitted the clear discernment of the effects of impurities. The aluminum-doped cells were found to be highly superior in terms of diffusion length retained after bombardment. This result correlates with the fact that many of the aluminum-doped cells had superior diffusion lengths prior to bombardment. A similar correlation occurred in that the high chlorine content float-zone material, from which cells with superior bombardment behavior were made, had a higher minority-carrier lifetime than other samples of float-zone material grown by identical processes. These correlations are in agreement with predictions based upon the hypothesis stated at the beginning of the paper.

Analysis of junction characteristics of the various groups of cells made in this study and in a previous study[3] revealed a dependence of the junction characteristic on the specific acceptor element and on its concentration in the base material of the cells. It was found that, the lower the concentration of various acceptors in the base material, the more "ideal" were the junction characteristics of cells.[3] Aluminum appears to be the most desirable acceptor element in silicon for the creation of fine quality junctions. Impurities in silicon affect junction characteristics by creating strains in the material due to misfit in the lattice, by associating with lattice defects to create recombination centers in the junction region, and by migrating to and precipitating in the junction region during high-temperature fabrication processing. The aluminum atom apparently creates minimum disturbance in the silicon lattice, and, as the bombardment results show, has the least tendency to combine with lattice defects to form recombination centers. Aluminum is, therefore, a most attractive acceptor for use in silicon.

The activity of acceptor or donor atoms in the creation of recombination centers in silicon is attributed to association of vacancies with these atoms to produce a recombination-center configuration. Spin resonance measurements have permitted determination of configurations of vacancies in silicon with oxygen or phosphorus that act as trapping centers.[9,10] It is, therefore, reasonable to assume that certain configurations of vacancies in silicon with impurities result in recombination centers.

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Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, February 10, 1964

TABLE 1. - EFFECTS OF 1-MEV ELECTRON BOMBARDMENT ON DIFFUSION LENGTH, L, AND CURVE POWER FACTOR, CPF, OF SOLAR CELLS

Cell group (a)	Number of samples	Dose, e/sq cm							
		1.2×10^{15}		4.8×10^{15}		1.5×10^{16}		4.1×10^{16}	
		L	CPF	L	CPF	L	CPF	L	CPF
1-ohm-cm C-B	5	17	70	9	70	4.5	68	2.5	68
10-ohm-cm C-B	8	30	70	18	70	11.5	66	8.5	60
10-ohm-cm FZ-B	5	32	70	19	70	12.5	68	8.5	66
10-ohm-cm FZ-B-Cl_2	4	43	70	26	70	16	68	10	63
50-ohm-cm C-Gd	4	37	60	26	54	----	--	15.5	--
100-ohm-cm C-B	6	65	30	44	--	31	--	10	--

[a]C, Czochralski; B, boron doped; FZ, float zone; Cl_2, high chlorine content; Gd, gadolinium doped.

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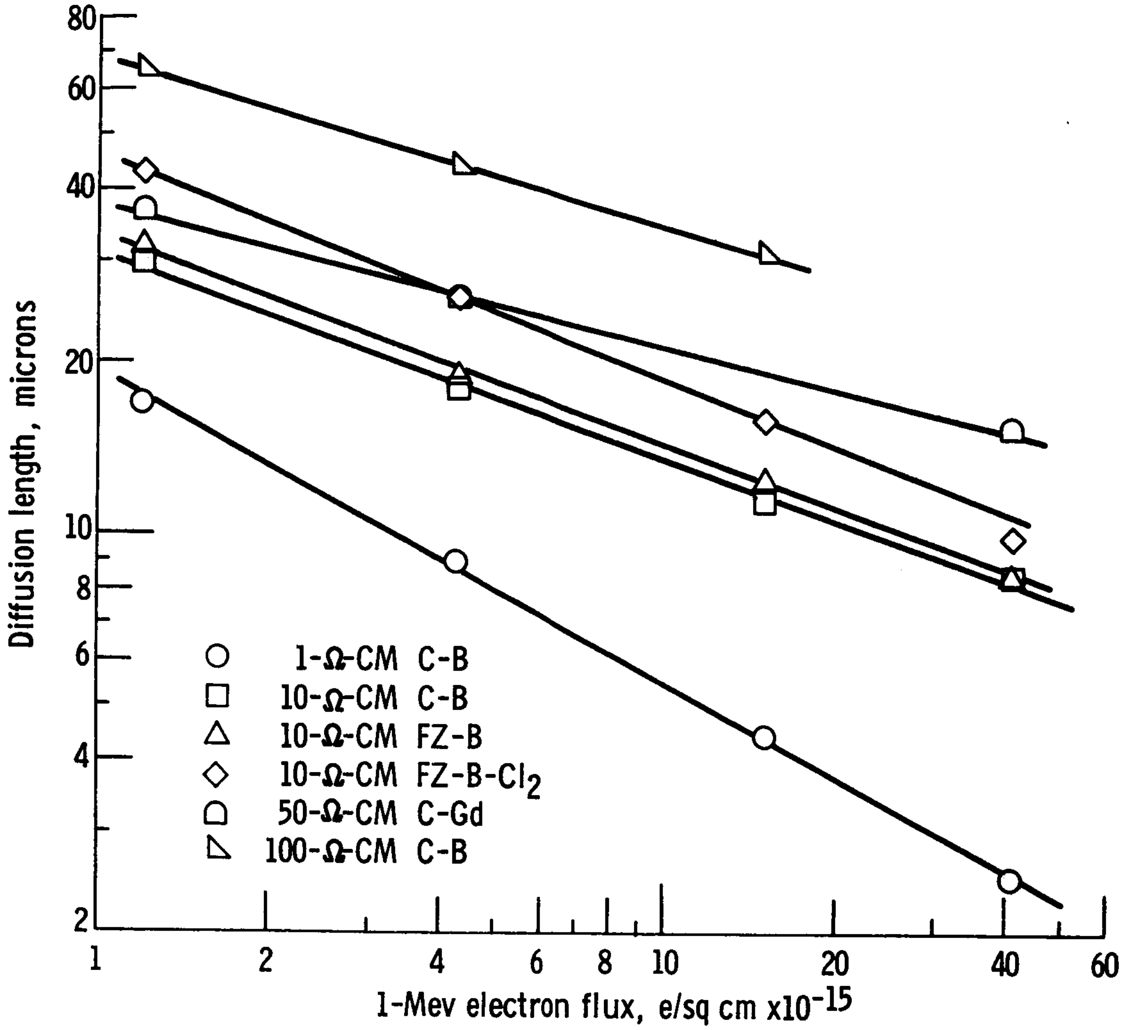

Figure 1. - Diffusion-length degradation versus 1-Mev electron flux.