RADIATION TOLERANCE OF ALUMINUM-DOPED SILICON*

O. L. Curtis, Jr., and J. R. Srour
Northrop Corporate Laboratories
Hawthorne, California

ABSTRACT

Data are presented that indicate that heat-treated Czochralski-grown aluminum-doped silicon that undergoes an appreciable resistivity increase ($\gtrsim$ a factor of two) during heating at $\sim$450°C is significantly more resistant to both neutron and gamma irradiation than boron-doped material (or aluminum-doped material that either has not been heat-treated or does not experience an appreciable resistivity change during such a treatment). Data interpretation is, however, quite difficult due to the occurrence of severe trapping effects in heat-treated material. Studies of radiation effects on aluminum-doped silicon solar cells are planned for the near future to resolve these uncertainties in the bulk material results.

I. INTRODUCTION

The development of methods for increasing the radiation tolerance of silicon could result in significant additions to the technology employed in fabricating semiconductor devices that are to be used in a radiation environment. Lithium-doped silicon, for example, exhibits radiation resistance (Refs. 1, 2) and is currently being studied in detail for possible solar-cell applications by various workers. The quite interesting properties exhibited by lithium-doped material lead one to speculate as to whether there might be other dopants which would create desirable radiation-tolerance characteristics. (As a recent example, it has been reported (Ref. 3) that copper-doped N/P silicon solar cells appear to be more radiation tolerant than conventional cells.)

During recent years, there have been occasional reports by different researchers within the technical community that aluminum-doped silicon is more resistant to radiation than is material doped with other acceptors. For example, Mandelkorn, et al., (Ref. 4) reported that aluminum-doped silicon solar cells were more radiation-tolerant than boron-doped units (1-MeV electron and 10-MeV proton bombardment). Additionally, we have reported (Ref. 5) that neutron-irradiated aluminum-doped bulk silicon exhibits a lifetime damage constant[1] significantly larger (i.e., more radiation-resistant) than that for boron- and gallium-doped material. Attempts by other workers to reproduce results obtained on aluminum-doped material apparently were not successful. Our previous finding for neutron-irradiated bulk material (Ref. 5) was reproduced (Ref. 6), but it was not entirely clear at that time what conditions were necessary in order to prepare radiation-tolerant aluminum-doped silicon. In this paper, we present results of a study of the radiation resistance of aluminum-doped silicon in which it

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[1] Defined as the amount of radiation required to reduce the lifetime of initially perfect material to 1 μs. That is, damage constant = $K = \phi[(1/\tau) - (1/\tau_0)]^{-1}$, where ϕ is the fluence, and τ_0 and τ are the pre- and post-irradiation lifetimes, respectively.

is shown that heat-treated aluminum-doped Czochralski-grown material can be prepared that appears to exhibit significantly improved tolerance to both neutron and gamma irradiation when compared to boron-doped silicon.

II. BACKGROUND

A chronological review of the results of our previous studies on aluminum-doped silicon is presented first for the purpose of placing our most recent results in the proper perspective. Figure 1 shows the results of a systematic study (Ref. 5) of damage constants for neutron-irradiated P-type silicon of various resistivities. The increase in damage constant with increasing resistivity is readily explained in terms of the Hall-Shockley-Read model, but the particular parameters shown should not be considered significant. The sample designation system used in Fig. 1 is as follows: first letter corresponds to manufacturer (K = Knapic, D = Dow, M = Merck, T = Texas Instruments); second letter corresponds to growth process (C = Czochralski, V = vacuum float zone, L = Lopex); third letter(s) corresponds to dopant (gallium, boron, and aluminum). Only one aluminum-doped specimen was examined, but it was found that the damage constant was significantly higher than for boron- and gallium-doped material of the same resistivity. However, since the pre-irradiation lifetime for this sample was very low, and since a significant amount of trapping was observed in the photoconductivity decay, this result was considered tentative at best.

Following our initial finding, a more detailed investigation of aluminum-doped material was conducted (Ref. 7). Samples prepared from a Czochralski-grown silicon ingot exhibited an extremely short pre-irradiation lifetime, so it was decided to anneal the specimens in an attempt to increase the lifetime. Anneals at 350 and 400°C apparently increased the lifetime but also changed the resistivity. The samples were neutron-irradiated along with boron-doped control samples, and damage constant results of this earlier study are shown in Fig. 2 (circles only). It was found that the aluminum-doped material was considerably more radiation-resistant that the boron-doped specimens. However, trapping was still present to such an extent that the data was not considered to be highly accurate.

In an attempt to remedy the trapping problem, which was presumably associated with the presence of a large oxygen concentration, we repeated the above experiment with aluminum-doped float-zone material. These samples had long lifetimes and trapping effects were small. However, the float zone specimens were found to be just as radiation-sensitive as boron-doped silicon. Subsequent experiments with better Czochralski-grown material were likewise unsuccessful. This led us to postulate that the radiation resistance observed earlier was associated with the heat-treatment given to the specimens. Additional work indicated that heat-treated samples were not radiation resistant unless the annealing resulted in appreciable carrier concentration changes, which is the topic of the present paper. Before presenting out most recent findings, a brief review of pertinent literature on the effects of heat-treating on silicon is presented.

Resistivity changes in undoped heat-treated pulled-crystal silicon were first reported 16 years ago (Ref. 7). Such changes were explained qualitatively on the basis of the formation of silicon-oxygen compounds, one of which (SiO_4) acts as a donor below ~500°C (Ref. 8). A detailed study of the effects of acceptors and oxygen on heat-treated silicon was performed by Fuller, Doleiden, and Wolfstirn (Ref. 9). In this study, results for gallium-doped material were found to be quite similar to those obtained for boron doping, but aluminum-doped material exhibited a somewhat different behavior. Before discussing the differences, some general features of the results of Fuller, Doleiden, and Wolfstirn are summarized. Heating oxygen-containing acceptor-doped silicon for long periods at the proper temperature (typically in the range of 400 to 500°C) results in the formation of donor sites with accompanying carrier concentration changes. The amount of change depends primarily on four parameters: (1) acceptor concentration; (2) oxygen concentration; (3) heat-treatment temperature; (4) amount of time the specimen is heat-treated at a particular temperature. The reactions that produce the observed carrier concentration changes were not definitely determined by Fuller, Doleiden, and Wolfstirn, but the data supported the postulation of the formation of primarily three distinct compounds: (1) SiO_4 donor sites; (2) neutral oxygen-acceptor sites; (3) acceptor-oxygen sites that act as donors. Considerably larger carrier concentration changes could be obtained in aluminum-doped material than in comparable boron-doped specimens. In fact, particular aluminum-doped samples were actually converted to N-type; this was not possible in the boron case. It is postulated that the reason for this difference may be that acceptor-oxygen donor sites are formed more readily in the aluminum case than for boron doping.

III. EXPERIMENTAL RESULTS

A considerable amount of research on aluminum-doped silicon was performed, the primary conclusion of which was the following: heat-treated Czochralski-grown aluminum-doped material that undergoes an appreciable resistivity increase (≳a factor of two) is apparently much more radiation tolerant than boron-doped material or aluminum-doped material that either has not been heat-treated or does not experience an appreciable resistivity change during such a treatment. It should be noted that float-zone aluminum-doped silicon is excluded as a radiation-tolerant material by this conclusion because the resistivity does not change appreciably during heat-treatment.

Much of the work leading up to the conclusion stated above involved studying the variation of resistivity during heat-treatments of ~450°C, employing the results of Fuller, Doleiden, and Wolfstirn as a guide. Resistivity was monitored at various times during anneals using four-point probe techniques. Figure 3 shows the resistivity variation with time at 450°C for a low-resistivity specimen. After 315 h, the resistivity had increased by a factor of ~1.7. In a number of ~1 Ω-cm specimens examined, the resistivity typically doubled after 24 h at 450°C.

Following heat treatment, pre-irradiation lifetime measurements were performed and then specimens were gamma-irradiated at a Co^{60} source (dose rate ~1.2×10^5 R/h). Other specimens were subjected to neutron irradiation in a TRIGA reactor. Following irradiation, damage constants were determined. Figure 4 shows typical results for gamma-irradiated specimens. It is seen that aluminum-doped material that experienced a 50 to 100% resistivity change upon heat treatment was significantly more radiation tolerant than both the boron-doped control samples and the aluminum-doped samples which did not undergo an appreciable resistivity change. Figure 2 shows results for neutron-irradiated aluminum- and boron-doped specimens (triangles only). It is seen that the earlier results (circles) were qualitatively reproduced, once again indicating tolerance to neutron irradiation.

A carrier removal experiment was performed on neutron-irradiated heat-treated aluminum-doped silicon. The study involved examination of both pre- and post-irradiation resistivity profiles for both boron- and aluminum-doped samples. The neutron dose employed was 1.65×10^{14} nvt (>10 keV). No significant differences between the two types of samples were observed; i.e., the percent resistivity increase in aluminum-doped material due to carrier removal was similar to that observed in boron-doped material. This result suggests that heat-treated aluminum-doped silicon may be advantageous from the standpoint of lifetime degradation but may offer no improvement of the carrier removal problem.

IV. DISCUSSION

The interesting question is raised as to whether heat-treated boron-doped material, which experiences an appreciable resistivity change, would also be more radiation tolerant. Fuller, et al., (Ref. 9) indicate that significant resistivity changes are possible for oxygen-rich boron-doped specimens. However, they also found that donors produced in heat-treated boron-doped material disappear above ~800°C, as compared to ~1100°C in aluminum-doped material. Hence, heat-treated boron-doped material would seem to be less suitable for applications requiring high-temperature diffusions (>800°C).

It is difficult to specify at present what mechanism is responsible for the observed decrease in radiation sensitivity for aluminum-doped material. The effect of the radiation-induced defects on carrier lifetime is presumably diminished by an interaction between these defects and one or more of the three types of compounds (mentioned above) thought to be formed during heat treatment. The SiO_4 donors can most likely be ruled out because they are presumably present in considerable quantity in heat-treated material which has not experienced a significant resistivity change. Because of the indicated correlation between resistivity change and decreased radiation sensitivity, it is tempting to speculate that the stable aluminum-oxygen donor sites are involved in reducing the effectiveness of the radiation-induced defects.

There is a problem regarding the interpretation of our data which should be emphasized. Damage constant measurements for bulk material have all been based on minority carrier lifetimes determined using photoconductivity decay techniques (Ref. 10). Because of severe trapping that occurs in the heat-treated aluminum-doped material, analysis of transient decays has been quite difficult at best. Our feeling is that the radiation-tolerance results are still qualitatively accurate. However, final proof will not come until diffusion length measurements are made on heat-treated aluminum-doped material before and after irradiation. We are currently working toward this goal. Solar cells are presently being fabricated from aluminum-doped material, and radiation testing will follow. If the cells are radiation hard, as our bulk studies have predicted, a considerable effort would undoubtedly have to be expended to optimize the fabrication technique in terms of maximizing both the pre-irradiation conversion efficiency and the radiation tolerance of aluminum-doped solar cells.

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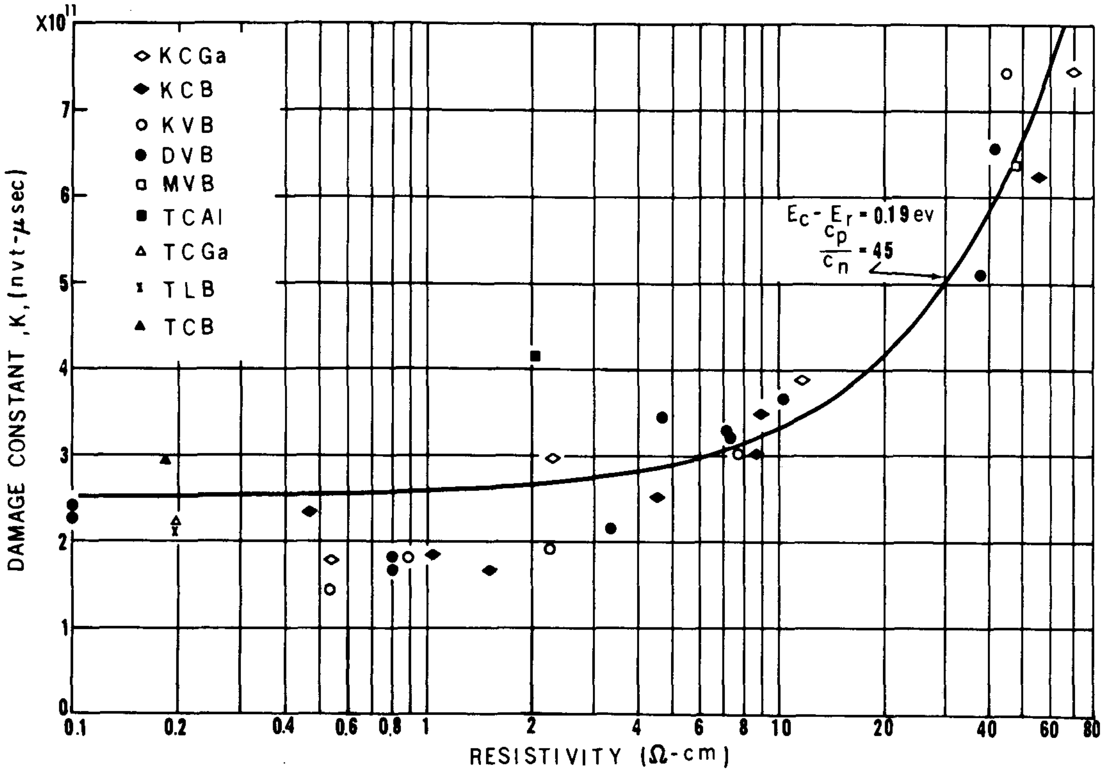

Fig. 1. Damage constant versus resistivity for neutron-irradiated P-type silicon. Damage constant is expressed in nvt (>10 keV) required to reduce the lifetime of an initially perfect sample to 1 μs. The theoretical curve corresponds to energy level parameters determined from temperature dependence measurements.

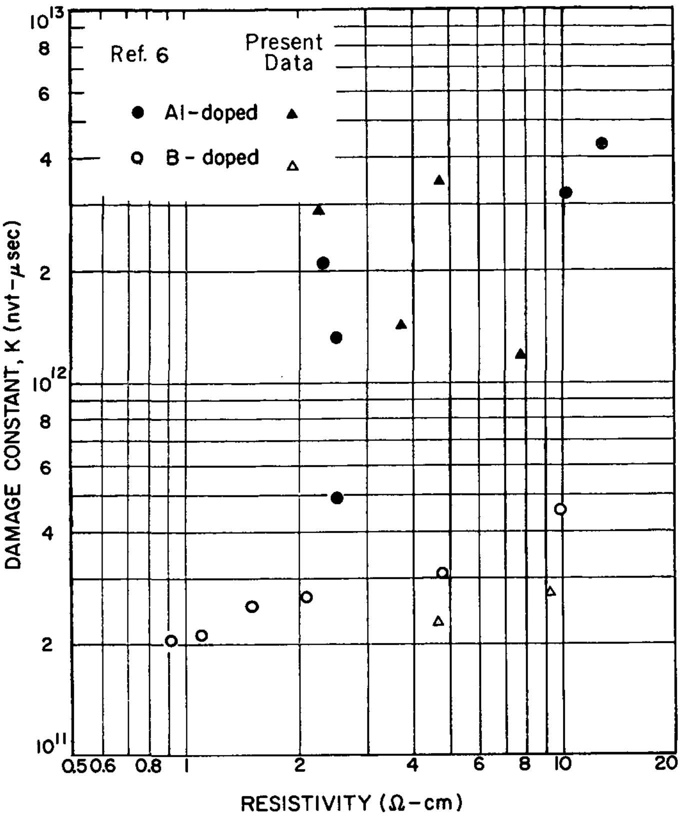

Fig. 2. Comparison of damage constants for neutron-irradiated Czochralski-grown aluminum- and boron-doped silicon. The aluminum-doped specimens were heat-treated.

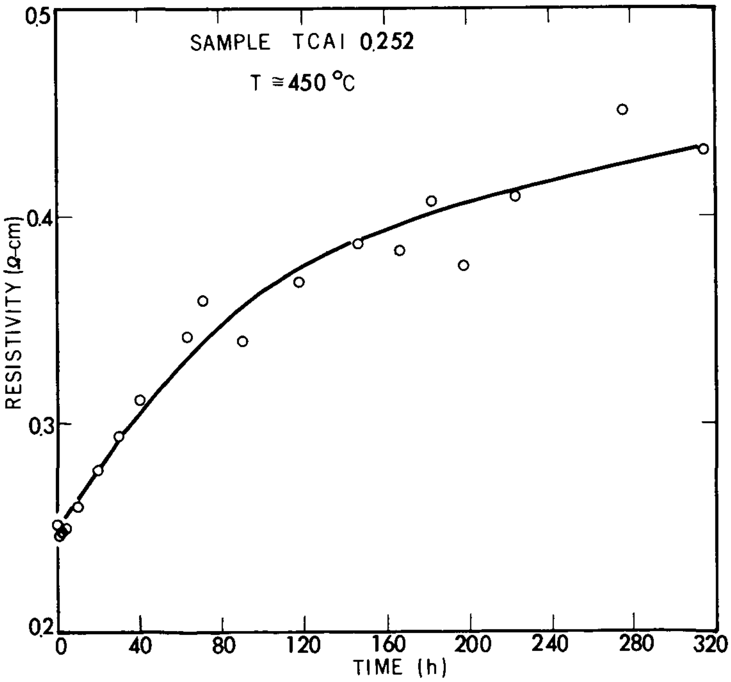

Fig. 3. Variation of resistivity with time at ~450 °C for a low-resistivity aluminum-doped silicon sample

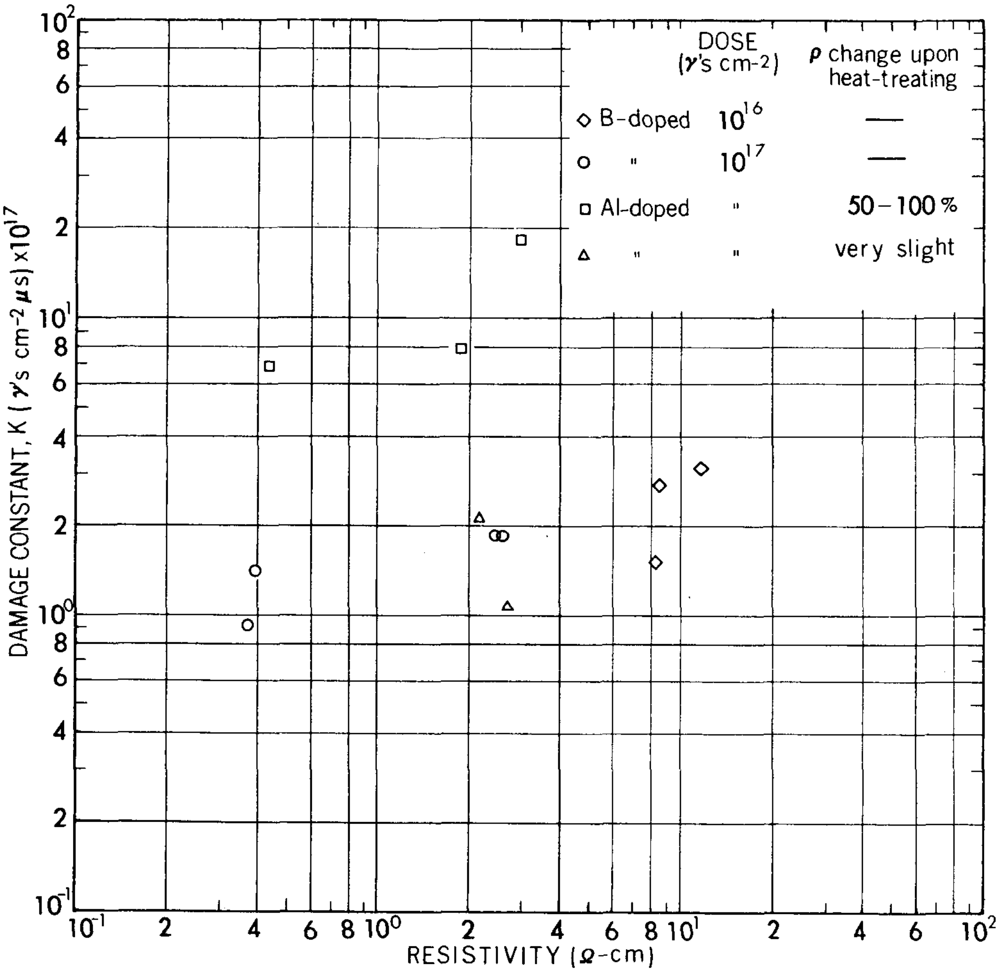

Fig. 4. Comparison of damage constants for gamma-irradiated Czochralski-grown aluminum- and boron-doped silicon. The aluminum-doped specimens were heat-treated.