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HALL EFFECT STUDY OF ELECTRON IRRADIATED Si (Li)*

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I. INTRODUCTION

Measurement of the Hall coefficient as a function of temperature between 15 and 300 K allows the separate determination of donor and acceptor concentrations in silicon. In this experiment these concentrations were monitored in samples which were irradiated at 240 K by 1-MeV electrons and then thermally annealed at 300 K. Presumably in both lithium- and phosphorus-doped silicon one would expect irradiation to increase the acceptor concentration and decrease the donor concentration due to the formation of vacancy donor pairs. Annealing should not change either concentration in phosphorus-doped silicon and should cause both concentrations to decrease in silicon doped with moderate amounts of lithium. In addition to this, in both lithium- and phosphorus-doped silicon the concentration and energy level of the A center can be measured at each point in the sample's history. This experiment was limited to float-zoned silicon doped with less than 6×10^{14} donors/cm^3.

II. THE A CENTER

Before going into the details of this experiment some evidence will be given concerning the anomalous activation energy previously reported for the A center. Measurements made on a variety of samples indicated a level at E_c -0.14 eV, instead of at E_c -19 eV as expected for the A center (Ref. 1). All of these samples were cut from one of two boules made by Dow Corning. A sample of Semi-element's pulled silicon was irradiated and the A center energy measured to be 0.19 eV. Another sample of 14 Ω-cm float-zoned Si(P) made by Dow Corning was then lightly irradiated and the production rate and energy of the A center measured. Then the same sample was irradiated much more heavily so that enough deep centers would be created to depopulate the level at 0.14 eV and indicate the presence of any deeper levels. The results of this experiment were as follows:

Dose, e/cm^2	Concentration, cm^{-3}	Energy, eV	Production rate, cm^{-1}
2×10^{14}	2.5×10^{13}	0.14	0.13
1.3×10^{15}	1.5×10^{13}	0.19	0.01

This data resolves the problem. In this boule centers at 0.14 eV and 0.19 eV are both being formed as a result of irradiation. However, the center at 0.14 eV is being formed with a much higher production rate than the usual A center at 0.19 eV. When the sample was heavily irradiated the Hall effect ceased to count the level at 0.14 eV and also began to indicate the presence of a level at E_c -0.19 eV. The level at E_c -0.14 eV may be related to the level at E_c -0.13 eV seen by Stein in pulled silicon (Ref. 2). If so, the only unusual property of this Dow Corning material is that the formation rates of these two levels are reversed

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in their normal order of importance. Since oxygen does form a number of different complexes in silicon, it is most likely that the 0.14 eV center is the usual A center but with perhaps an additional oxygen present in a nearby interstitial site. The possibility that another impurity such as carbon may be involved cannot be discounted, however.

III. LITHIUM AND THE A CENTER

The experiment to be described was designed to study the interaction of lithium with the A center. In order to determine what effects were due to the presence of lithium it was necessary to use a sample and a control cut from the same boule and having similar resistivities. The presence of both phosphorus and lithium in the sample reduced somewhat the variety of information obtainable, i.e., it was not possible to demonstrate that the LiV complex is formed during irradiation. A separate experiment would be necessary to investigate this question.

Two samples were prepared from the same boule of float-zoned 14 Ω-cm Dow Corning silicon containing 3.5×10^{14} donors/cm^3. Into one sample an additional 3.4×10^{14} lithium donors/cm^3 were introduced from a lithium in oil suspension using a tack-on and redistribution of 5/60/425°C. Measurements of the Hall effect versus temperature were made; (1) before irradiation, (2) after irradiation at 240 K by 1.7×10^{14} 1 MeV e/cm^2, (3) after 2 h, (4) and after 17 h at 300 K. The electrical contacts degraded due to thermal cycling after 17 h thereby terminating the experiment. Irradiation was performed at 240 K so that lithium could be considered immobile during irradiation. As a result the effects of irradiation could be separated from those due to lithium mobility. Donor and acceptor concentrations were obtained by least squares analysis of the data using Fermi statistics for silicon containing two kinds of donors and two kinds of acceptors. These calculations assumed the values of excited state splitting and ground state degeneracy obtained from optical experiments reported in the literature (Refs. 3-5).

Figure 1 shows the behavior of room temperature carrier concentration in the two samples as a function of annealing time and is the behavior expected. There was no measurable annealing in the phosphorus-doped sample and a decreasing carrier concentration in the sample containing lithium.

Figure 2 shows the change in donor concentration in these samples caused by annealing at 300 K. The most apparent difference between the two samples for annealing times longer than 2 h is that the donor concentration decreases in the lithium-doped sample and is constant in the phosphorus-doped sample. This change in the lithium-doped sample was clearly caused by radiation damage, since such samples do not show a change in resistivity with time prior to irradiation. From the data shown here it is not possible to show that the LiV complex forms during irradiation. From the pre-irradiation and post-irradiation points it is clear that there is more donor loss during irradiation in the sample containing both lithium and phosphorus than in the sample doped only with phosphorus. Unfortunately, several samples doped only with phosphorus showed a range of values for carrier removal rate. An experiment similar to this one, but using a sample doped only with lithium, would demonstrate the formation of LiV.

Comparison of the data before annealing and after 2 h of annealing indicates a decrease in donor concentration caused by bringing the sample up to room temperature from 250 K. This was not expected in the phosphorus-doped sample and represents a short-term thermal annealing in the direction of increased damage. Other samples containing phosphorus were irradiated at 250 K but were held at 250 K for 2 h before making any measurements. This was found to decrease the magnitude of the annealing stage, indicating that annealing occurs at 250 K as well as 300 K. In studies of unannealed Si(Li), data should be taken after substantial annealing at 250 K, which will remove this stage without allowing the lithium to be mobile. This short-term annealing is even more striking in Fig. 3, which shows the acceptor concentration.

The total measured acceptor concentration and A center concentration are represented by A_t and 0.14, respectively. For the phosphorus-doped sample the value indicated for the E-center concentration is the measured decrease in donor concentration caused by irradiation. Inspection of this data indicates that this annealing may be caused by thermal release of trapped vacancies which then form additional damage complexes. Such vacancies would have to be much more tightly bound than the vacancy-interstitial close-spaced pair, as the observed annealing temperatures are very high (Ref. 2). This behavior may also be a characteristic peculiar to these boules of silicon. As was expected, the behavior of acceptor concentration with continued annealing was very different in the two samples. Whereas annealing causes acceptor concentration to decrease in the lithium-doped sample, it has no effect in the phosphorus-doped sample. It is evident from this figure that A centers interact much more strongly with lithium than does the E center. Comparing the changes in total acceptor concentration with those in A center concentration it is apparent that almost 80% of those centers that are neutralized within 17 h were A centers. Since there were probably as many E centers in the lithium-doped sample as there were in the control sample, it is clear the A centers completely monopolized the neutralization process despite the fact there were more E centers than A centers.

By comparing the changes in donor and acceptor concentrations seen in Figs. 2 and 3 an idea can be obtained as to how many lithium ions are required to neutralize the A centers. The concentration changes between 2 and 17 h are:

$$\Delta Li^+ = -4.5 \times 10^{13} \text{ cm}^{-3}$$

$$\Delta A_t = -1.3 \times 10^{13}$$

$$\Delta 0.14 = -1.0 \times 10^{13}$$

Since the total acceptor concentration (A_t) includes the A center concentration (0.14) it is apparent that 80% of the annealed centers were A centers. Comparing this change to the much larger loss in lithium concentration it seems that as many as four lithium atoms may be required to neutralize this A center.

REFERENCES

1. Sonder, E., and Templeton, L., J. Appl. Phys., Vol. 31, p. 1279, 1970.
2. Stein, H., and Vook, F., Phys. Rev., Vol. 163, p. 790, 1967.
3. Aggarwal, R., et al., Phys. Rev., Vol. 138, p. A882, 1965.
4. Long, D., and Myers, J., Phys. Rev., Vol. 115, p. 1107, 1959.
5. Aggarwal, R., and Ramdas, A., Phys. Rev., Vol. 137, p. A602, 1965.

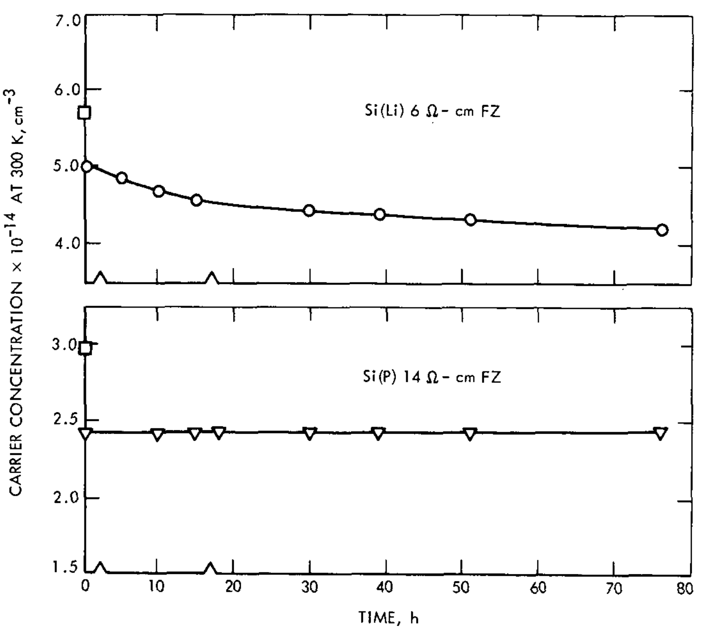

Fig. 1. Annealing of room-temperature carrier concentration, irradiated at 240 K by 1.7×10^{14} 1-MeV e/cm^2

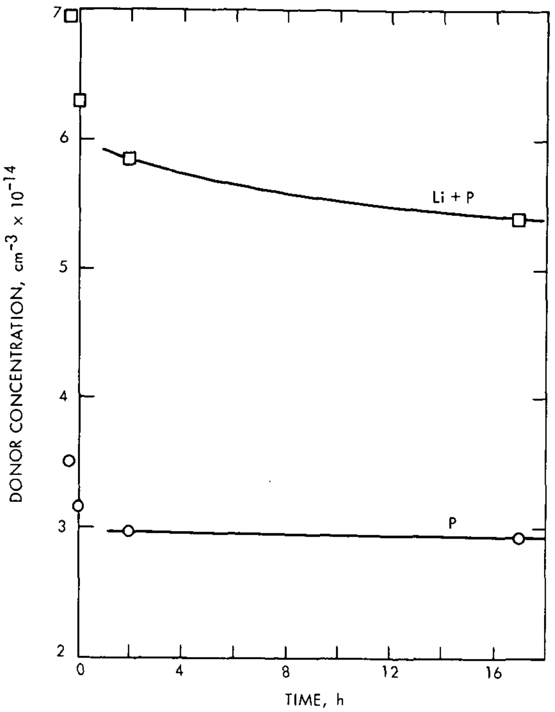

Fig. 2. Room temperature annealing of donor concentration in lithium and phosphorus-doped silicon

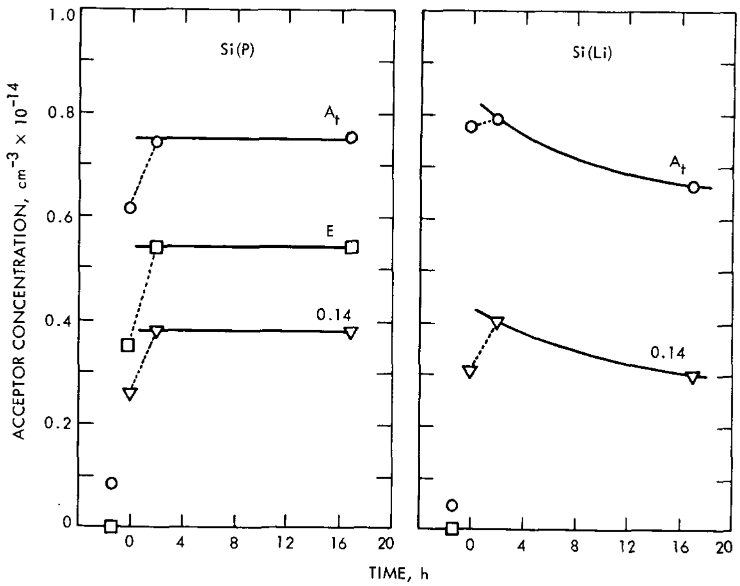

Fig. 3. Room temperature annealing of acceptor concentration in lithium and phosphorus-doped silicon