

ported by the electrical conductivity which increases in this temperature region exponentially with an activation energy of 0.29 eV.

A second interesting feature of Fig. 2 is a bump in E_F vs T near the Curie temperature. An anomalous increase of E_F at a given temperature could only arise from an increase of the effective mass m^* due to band narrowing in approaching T_C . Although such behavior is conceivable,⁶ the E_F vs T curve should not show in this case two points of inflection near T_C , since this would mean that m^* after an initial increase decreases again. We are, therefore, inclined to assume that around T_C the curve of E_F vs T is not a true reflection of the behavior of the Fermi level. Instead, we propose that the charge carriers acquire in this temperature region an additional kinetic energy, ΔE_K , due to a magnon-hole interaction. If we calculate the difference between the original curve of Fig. 2 and a smooth curve drawn along the broken line shown in the figure, we obtain this additional kinetic energy as a function of temperature. The result of this calculation is plotted in the lower part of Fig. 2. At the Curie temperature ΔE_K reaches a maximum and falls off rapidly towards

higher and lower temperatures. This behavior is qualitatively consistent with the magnon-drag model since the magnon-carrier relaxation time becomes extremely short when approaching T_C from lower temperatures.¹ That ΔE_K does not disappear abruptly at T_C is an indication of magnetic short-range order up to approximately 230°K.

Although the above analysis shows a qualitative agreement of our data with the magnon-drag model, a final proof can only come through a quantitative comparison. For this we need to know the magnon-magnon and magnon-hole relaxation times, which we cannot derive from the present measurements. Further detailed electrical transport measurements are in progress.

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DIRECT OBSERVATION OF LITHIUM-DEFECT INTERACTION IN SILICON BY ELECTRON PARAMAGNETIC RESONANCE MEASUREMENTS*

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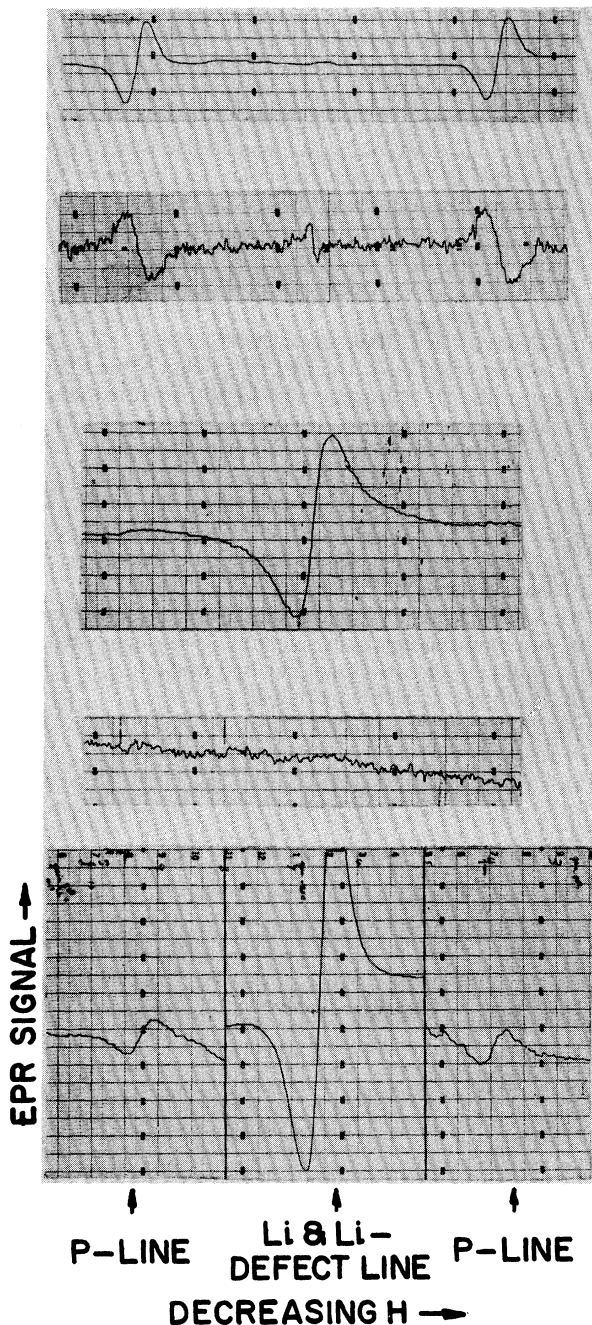
Electron paramagnetic resonance measurements have been used to observe directly the interaction of lithium with damage centers produced by electron irradiation in n -type, float-zone silicon. The silicon is characterized by low oxygen concentrations, with lithium as the predominant n -type dopant. Low oxygen concentrations might be expected to foster the interaction of lithium with radiation-induced defects on two counts: (1) Since in silicon containing $\sim 10^{18}/\text{cm}^3$ oxygen the shallow lithium donor is really a (Li-O) complex, the absence of oxygen might make the isolated lithium¹ more mobile and/or susceptible to trapping by other imperfections and defects; (2) the absence of oxygen removes the possibility of forming oxygen-vacancy complexes (A centers),² thus in-

creasing further the likelihood of lithium interacting with vacancies.

Float-zone silicon with quoted oxygen concentrations of $(1-2) \times 10^{15}/\text{cm}^3$ and a resistivity of 12 Ω cm (n type) was diffused with lithium from a Li-Sn alloy at 400°C to a resistivity of 0.3-0.4 Ω cm and a lithium concentration of about $2 \times 10^{18}/\text{cm}^3$. The material was then bombarded by a 1-MeV electron flux of $1 \times 10^{18}/\text{cm}^2$ at room temperature. The epr properties of the material were measured at 27°K using a Varian spectrometer operating at 9.1 kMc/sec. The major result of our preliminary work is the finding of a new lithium damage-center complex with a relatively high introduction rate which has not heretofore been reported.

The epr spectra of Fig. 1 illustrate our ba-

sic findings. The first spectrum is of a calibrated standard showing the positions and magnitudes of the phosphorus doublet lines. This silicon sample has a known phosphorus concentration which is in very good agreement with the sample's spin density as independently measured using the conduction-electron paramagnetic resonance of degenerate silicon as a standard. The second spectrum is of the starting material itself and shows only the phosphorus



doublet resonance lines for which a spin density of $6 \times 10^{14}/\text{cm}^3$ is calculated and is to be compared to the phosphorus concentration of $4 \times 10^{14}/\text{cm}^3$ as obtained from resistivity measurements. (The very small signal between the phosphorus lines is most likely due to some very small concentration of contaminants, surface states, etc.) The third spectrum is of lithium-diffused material. A single resonance line with no discernible angular dependence and a g value of 1.9985 ± 0.0005 is observed having a spin density of $1.3 \times 10^{15}/\text{cm}^3$. Since this spin density is essentially the same as the quoted oxygen concentration, $(1-2) \times 10^{15}/\text{cm}^3$, and since an epr absorption is not seen in oxygen-free silicon,³ this resonance line is almost certainly due to the (Li-O) donor.⁴ The fourth spectrum is of silicon which has not had any impurity added to it (besides the original phosphorus), but has been bombarded by a 1-MeV electron flux of $1 \times 10^{16}/\text{cm}^2$. No epr absorption is detected and, in fact, the phosphorus resonance has disappeared—the latter being consistent with reported behavior when deep-lying damage centers are produced.² The last spectrum is of lithium-doped material which has been electron irradiated. Here, a new resonance line appears which is about five times larger than that due to lithium alone. In addition, the phosphorus lines are now present. This new resonance line has no discernible angular dependence and has a g value of 1.9996 ± 0.0005 .

The spectra of Fig. 1 illustrate several important features of the new paramagnetic cen-

FIG. 1. Electron paramagnetic resonance spectra showing the formation of the L center. The first spectrum is of a silicon "standard" in which $N_d(\text{P})$, the phosphorus doping, $= 2 \times 10^{16}/\text{cm}^3$ and $N_s(\text{P})$, the phosphorus spin density, $= 1.8 \times 10^{16}/\text{cm}^3$; gain = 40. The remaining spectra are all of float-zone silicon containing $N_d(\text{P})$ of $4 \times 10^{14}/\text{cm}^3$, and oxygen concentrations of $(1-2) \times 10^{15}/\text{cm}^3$ and for which the 1-MeV electron bombardment fluxes are given by ϕ . The second spectrum has $N_d(\text{Li}) = 0$, $\phi = 0$, and $N_s(\text{P}) = 6 \times 10^{14}/\text{cm}^3$; gain = 800. The third spectrum has $N_d(\text{Li}) = 2 \times 10^{16}/\text{cm}^3$, $\phi = 0$, and $N_s(\text{Li}) = 1.3 \times 10^{15}/\text{cm}^3$, the same as the oxygen concentration; gain = 250. The fourth spectrum has $N_d(\text{Li}) = 0$ and $\phi = 1 \times 10^{16}/\text{cm}^2$; gain = 800. The last spectrum, $N_d(\text{Li}) = 2 \times 10^{16}/\text{cm}^3$, $\phi = 1 \times 10^{16}/\text{cm}^2$, $N_s(\text{Li}) = 6 \times 10^{15}/\text{cm}^3$, and $N_s(\text{P}) = 5 \times 10^{14}/\text{cm}^3$; gains = 500, 200, 500, respectively. All spectra are aligned so that their magnetic field values H are the same. H at the lithium line is about 3200 G.

ter, called the L center. It appears only in material which both contains lithium and has been electron irradiated. It has an apparent introduction rate $\sim 0.3-0.5/cm$. It does not involve phosphorus, since the doublet resonance lines seen in spectrum 5, Fig. 1, represent isolated phosphorus atoms in concentrations of $5 \times 10^{14}/cm^3$. It does not involve oxygen, since the oxygen concentration is $(1-2) \times 10^{15}/cm^3$ and the new center's concentration is greater than $6 \times 10^{15}/cm^3$.⁵ It is most likely a shallow level, for if it were deep it would probably affect the phosphorus resonance, as the A , C , and E centers do in n -type silicon. It has a low binding energy because in addition to a spontaneous room-temperature diminution, a 10-min anneal at $75^\circ C$ reduces the epr signal by about 60%. At irradiation fluxes of $(3 \text{ and } 5) \times 10^{16}/cm^2$, the resonance of the L center disappears, as does the phosphorus doublet resonance, and the epr spectrum shows only a broad, low-level resonance absorption.

It is considered premature at this time for any detailed speculation on a model for this new center and the mechanism for its formation; however, our present thoughts center on its being a lithium-vacancy complex which prevents the formation of A and E centers (both of which involve vacancies).² This is consistent with electrical measurements, reported elsewhere,⁶ which show that this new damage center does not produce the drastic reduction of minority carrier lifetime customarily observed when A centers (and possibly E centers) are formed.^{2,7} That the L center produces a

shallow level would account for its being an ineffective recombination center for holes.

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¹While (Li-O) acts as a shallow donor with an energy level about 0.039 eV below the conduction band, isolated lithium is reported to be a shallow donor with an energy level about 0.033 eV below the conduction band [T. E. Gilmer *et al.*, *J. Phys. Chem. Solids* **26**, 1195 (1965)].

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⁴It is suggested here, incidentally, that measuring the epr of the (Li-O) donor may be the most unambiguous quantitative method for measuring oxygen concentrations in silicon, as opposed to $9\text{-}\mu$ absorption [W. Kaiser, P. Keck, and C. Lange, *Phys. Rev.* **101**, 1265 (1965)] or donor formation by low-temperature anneals [H. Reiss and W. Kaiser, *Properties of Elemental and Compound Semiconductors* (Interscience Publishers, Inc., New York, 1959), p. 103.]

⁵Greater because a spontaneous room-temperature diminution of the center by about 30% has been observed during the course of several weeks.

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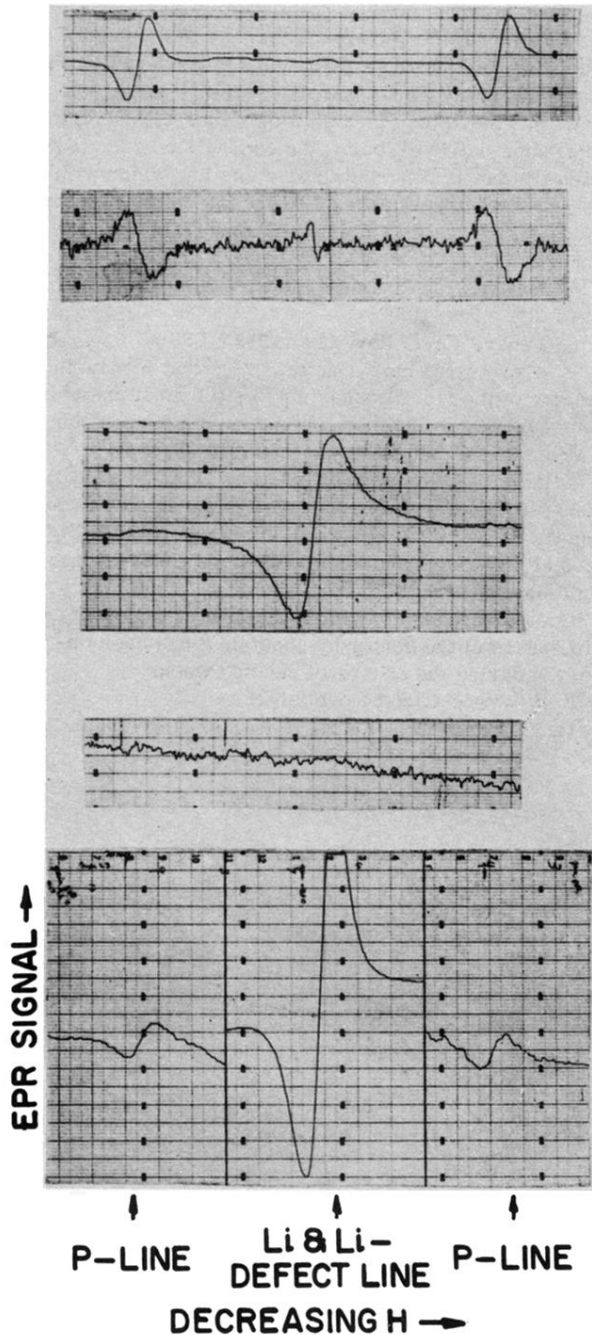


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