scattering cross section. The quantity m^* represents an average effective mass of electrons at the top of the Fermi sea.

Equation (3) suggests that the discrepancy between the experimental data and Eq. (2) arises from the deviation of m^*/m from unity in bismuth. If so interpreted, the data indicate that the value of this ratio is of the order $m^*/m = 10^{-4}$.

In summary then, there is little doubt empirically that there is an emf associated with a current flow constriction. Those gross properties of this emf which have been investigated seem to correlate well with those derived from the hydrodynamic principles which motivated this research. Although this explanation of the configurational emf appears to be the most reasonable one at present, it has not been totally verified. Further investigation on a variety of materials has been initiated to resolve the matter. It is hoped that new experimental results will be available for presentation soon to supplement the extended theoretical analysis which is in preparation.

The author is indebted to Professor John R. Pellam for many helpful discussions and to Professor Richard P. Feynman for theoretical insights.

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SHALLOW IMPURITY TRAPS AND ELECTRON TRANSFER DYNAMICS IN n-TYPE SILICON AT LIQUID HELIUM TEMPERATURES*

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From combined electron spin resonance and photoconductivity experiments on samples of phosphorus-doped silicon with boron compensation, we have been able to determine some interesting properties of shallow impurities in silicon. These include (a) rate of electron transfer[1] from a neutral phosphorus impurity to a neutral boron impurity at various impurity concentrations and temperatures, and (b) ratio of positive phosphorus ion trapping cross section to neutral boron trapping cross section for conduction electrons. In addition, the technique we introduce allows an accurate determination of the ratio of donor concentration to compensating acceptor concentration without recourse to transport phenomena. The technique also permits controlling the number of ionized impurities in a given sample while at low temperatures (liquid helium); this makes it possible to investigate in a simple manner physical properties which may depend on ionized impurity concentration, such as low-temperature mobility. Information on the lifetimes of hot carriers as a function of their energy can also be obtained.

We now describe the experimental procedure and theory relevant to the above studies. Consider a sample of n-type silicon containing P phosphorus impurities/cm^3 and B boron impurities/cm^3. In equilibrium at liquid helium temperatures, the neutral phosphorus concentration P^0 equals $(P-B)$, the positive phosphorus ion concentration P^+ is equal to B, and the negative boron ion concentration B^- also equals B. The P^0 contain unpaired electrons, and thus the electron spin resonance signal[2] is proportional to P^0. We now produce electron-hole pairs uniformly throughout the sample by illuminating with intrinsic radiation (1.03 microns)[3] near the indirect transition threshold. The electrons and holes are rapidly captured; the electrons predominantly by the P^+ ions, and the holes predominantly by the B^- ions. If the rate of generation of electron-hole pairs is much greater than the rate of electron transfer from the P^0 to the B^0, then the P^0 concentration builds up very close to P. The new resonance signal is thus $(1-B/P)^{-1}$ times the original resonance signal, and the compensation B/P is directly determined. If the intrinsic radiation is now turned off and the resonance signal monitored, the rate of electron transfer from P^0 to B^0 can be determined. The electron transfer rate can be increased greatly by delocalizing the electrons with extrinsic radiation. A wavelength of about 2 microns insures a strong predominance of free electrons over holes because of the free-carrier absorption peak[4] in n-type silicon. If we consider a simple model in which P^+ and B^0 are the only electron traps, then the following kinetic equations characterize the decrease of P^0 as it approaches its equilibrium value of $(P-B)$:

$$dP^0/dt = -SP^0 + pP^+n_e,$$

$$dn_e/dt = SP^0 - pP^+n_e - bB^0n_e. \qquad (1)$$

S is the rate of extrinsic ionization of the P^0, p and b are, respectively, the capture probabilities for a conduction electron of P^+ and B^0, and n_e is the conduction electron concentration. The solution of Eq. (1) gives P^+ or P^0 $(=P-P^+)$ as a function of t, as well as n_e as a function of t. These solutions are

$$\frac{2bSt}{p} = \ln\left\{\left(\frac{PB-(P+B)P^+ + (P^+)^2}{PB-(P+B)P_i^+ + (P_i^+)^2}\right)\right.$$

$$\left.\times\left[\frac{(P^+-P)(P_i^+-B)}{(P_i^+-P)(P^+-B)}\right]^{(P+B)/(P-B)}\right\}, \qquad (2a)$$

$$n_e = S(P-P^+)/(pP^+ + bB^0). \qquad (2b)$$

P_i^+ is the value of P^+ at $t=0$. In Fig. 1(a), P^0 vs $2(b/p)St$ is plotted from Eq. (2a). Since S can be directly determined from the electron interchange spin relaxation time[5] associated with the two phosphorus hyperfine lines, we are able to determine b/p by fitting the theoretical curve to the experimental values of P^0 obtained by spin resonance. In Fig. 1(b), n_e vs $2(b/p)St$ is plotted from Eq. (2b), and the experimental photoconductive current also appears. If the mobility remained constant and the simple model we have chosen were correct, the two curves would coincide. The discrepancies will be discussed below.

The same model used above also predicts the time dependence of P^0 and n_e during the P^+ trap-filling process with the intrinsic radiation on. In Fig. 2(a), the experimental and theoretical curves of P^0 vs time are seen. P^0 increases essentially linearly with time at a rate corresponding to the rate of electron-hole pair production. In Fig. 2(b), n_e and the observed photocurrent are plotted against time during the trap filling process. Agreement between these last curves depends on the mobility constancy, the adequacy of the model, and the inclusion of hole current. Electron current dominates even under intrinsic excitation, as seen from photo-Hall measurements, but it is probable that the hole current must also be taken into consideration in this case.

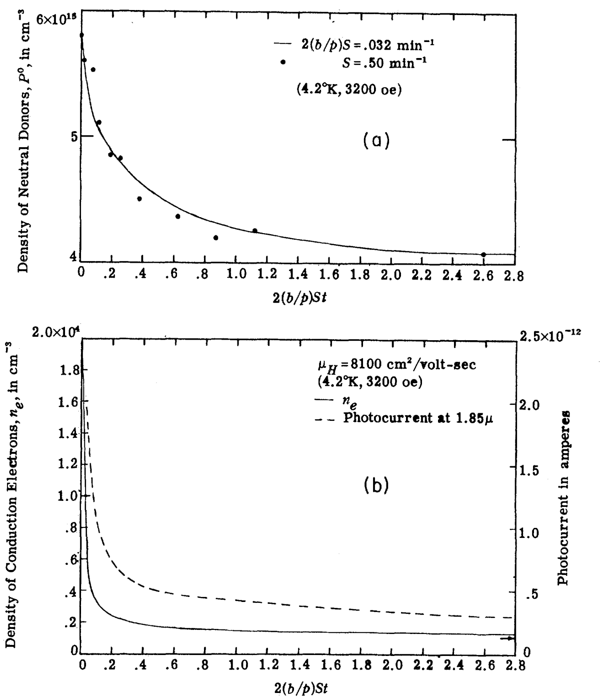

FIG. 1. (a) Decay of neutral phosphorus concentration P^0 under 1.85-μ extrinsic radiation, after the P^+ traps are filled with electrons. Experimental points are obtained from spin resonance measurements, and solid curve gives theoretical decay based on Eq. (1), with value of b/p chosen for best fit. (b) Decay under same conditions as (a) of conduction electron concentration n_e based on Eq. (1) and of observed photocurrent. Arrow denotes extrinsic photocurrent for equilibrium trap occupancy. μ_H remains fairly constant from photo-Hall measurements. The silicon sample contains 6.0×10^{15} P/cm^3 and 2.0×10^{15} B/cm^3.

The experiments were performed on a sample of silicon containing nominally 5×10^{15} P/cm^3 and 2.5×10^{15} B/cm^3. A combination of Hall effect measurements and experiments of the type discussed above which yield B/P [see Fig. 2(a)] indicate actual concentrations of 6.0×10^{15} P/cm^3 and 2.0×10^{15} B/cm^3. The electron transfer time from P^0 to B^0 in the absence of extrinsic radiation from the monochromator exceeds 15 minutes at both 4.2°K and 1.3°K. It may be considerably longer than 15 minutes, since a small amount of leakage radiation is probably present. The b/p ratio which is obtained from Fig. 1(a) is 0.032, to an accuracy of about 50%. It is temperature independent between 1.3°K and 4.2°K. The discrepancies between the n_e and photocurrent curves in Figs. 1(b) and 2(b) are believed to be

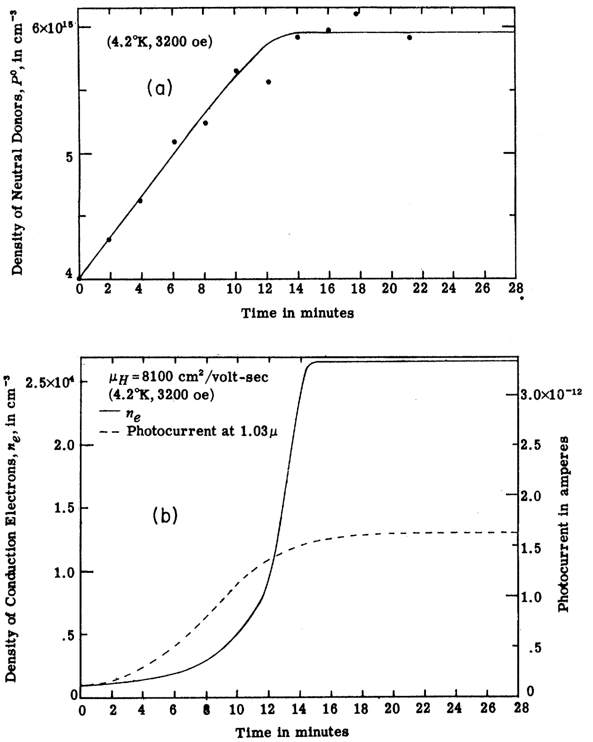

FIG. 2. (a) Growth of neutral phosphorus concentration under 1.03-μ intrinsic radiation, due to the process $P^+ + e \rightarrow P^0$. Experimental points are obtained from spin resonance measurements. Solid curve gives theoretical growth. (b) Growth of intrinsic photocurrent under same conditions as in (a). Theoretical growth of n_e is given by solid curve. The silicon sample contains 6.0×10^{15} P/cm^3 and 2.0×10^{15} B/cm^3.

due to the inadequacy of the model used. The low-temperature mobility as measured by photo-Hall effect appears to be fairly constant as the P^+ traps are filled, and yet a large photocurrent increase results from a relatively small decrease in impurity ion concentration. The data suggest that at high ion concentrations, the lifetime against trapping for 2-micron extrinsically excited electrons depends more nearly on $(1/P^+)^2$ rather than on $(1/P^+)$, which was assumed in our model. The total enhancement of the photocurrent, i.e., the ratio of the photocurrent when the maximum number of traps are filled to the photocurrent for the equilibrium trap electron occupancy, is smaller than predicted by our model, indicating the presence of other types of lifetime-limiting traps.[6] These may be deep traps, or possibly P^0 traps which can form stable P^- centers, the analog of the bound hydrogen negative ion. A photoconductivity experiment with highly spin-polarized electrons, which would not be expected to be trapped by similarly polarized P^0 centers, was inconclusive.

The extrinsically (2-micron) generated electron's lifetime against trapping, for the equilibrium trap situation where $P^+ = B$ (2×10^{15}/cm^3 for the sample under discussion), is determined from the expression $\tau = n_e/SP^0$, where n_e is measured by Hall effect and S is the rate of ionization of P^0, which is determined from the interchange spin relaxation time[5] as mentioned above. At 4.2°K and 1.3°K, we obtain $\tau \cong 5 \times 10^{-11}$ sec. If about 20-micron extrinsic radiation is used, τ is somewhat decreased by less than a factor of 2, and μ_H is decreased by a factor of about 4, compared with the 2-micron generated electrons. This suggests that an appreciable part of the lifetime of the 2-micron extrinsically generated electrons is spent in thermalization. The 20-micron excited electrons are not as "hot," and apparently thermalize and get trapped more quickly.

In an experiment performed with a sample of silicon nominally containing 5×10^{16} P/cm^3 and 2.5×10^{16} B/cm^3, kindly lent us by Dr. Ludwig of General Electric Research Laboratories, the dark conductivity at 4.2°K decreased by a factor of 5 upon irradiating with intrinsic light. We attribute this to the filling of the P^+ traps, and the attendant decrease in impurity band conduction which results from lowering the concentration of ions.

We would like to thank Dr. Bruce Rosenblum of R. C. A. Laboratories for having kindly provided the principal silicon sample used in these experiments and for an early discussion of some of the photoconductive aspects of this problem.

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[1] A. Honig, in Proceedings of the International Conference on Semiconductor Physics, Prague, 1960 (to be published).

[2] R. C. Fletcher, W. A. Yager, G. L. Pearson, A. N. Holden, W. T. Read, and F. R. Merritt, Phys. Rev. 94, 1392 (1954).

[3] With shorter wavelengths, where electron-hole pairs are produced mostly on the illuminated surface, the traps still get filled within the bulk, even though the free-electron diffusion length is very small. The nature of the diffusion process has not yet been ascertained. It may be due to hopping from large-orbit P^- traps to empty P^+ centers, or possibly to leakage of long-wavelength radiation.

[4] W. Spitzer and H. Y. Fan, Phys. Rev. 108, 268

(1957).

[5] A. Honig, Quantum Electronics-Resonance Phenomena Conference, September, 1959 (Columbia University Press, New York, 1959), p. 450.

[6] For a purer sample (about 10^{14} P/cm^3), larger photocurrent enhancements were obtained upon filling the P^+ traps with electrons. The question arises as to whether a superior photodetector can be made with the double-illumination technique. For background-limited photodetectors, an improvement in the signal-to-noise ratio is possible when the background and signal are in different spectral regions. We would like to thank Dr. Henry Levinstein for discussion of this point.

VACANCY INTERACTIONS IN SILICON

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The production and properties of vacancies in silicon are subjects upon which much empirical work has been done. For the most part the interpretation of the data in terms of detailed models has been inconclusive. Recently the interaction of radiation-induced defects (suggested to be vacancies) with chemical impurities has been demonstrated.[1] In this Letter, experiments of a new type are described which demonstrate that vacancies do indeed interact with certain chemical impurities. These experiments involve the trapping and annihilation of vacancies by interstitial impurities which thereby become substitutional. The effect has been detected by spin resonance techniques for the impurities manganese and chromium; vacancies were introduced into silicon by the precipitation of copper or silver, or by electron irradiation. The experiments involving Cu and Mn will be described first, followed by a brief description of those involving Cu and Cr, and of the irradiation experiments.

Manganese has been previously detected in Si in the forms Mn^- and Mn^{++}. Samples have now been prepared in a manner similar to that previously described[2] except that Cu as well as Mn is alloyed and diffused into the samples. When such samples are cooled relatively slowly, two new spectra are seen due to isolated Mn, one in *n*-type and the other in *p*-type material. It is proposed that if only Mn is introduced and if the sample is quenched sufficiently rapidly, the Mn is in interstitial sites. On the other hand, in samples which also contain copper, vacancies are created during the quenching. These vacancies are annihilated by the interstitial Mn with most of the Mn becoming substitutional. In *n*-type silicon containing an excess of phosphorus, the substitutional Mn is in the form $Mn^=$. In *p*-type silicon containing an excess of boron, the substitutional Mn is in the form Mn^+.[3] A summary of the spin resonance results for the four isolated forms of Mn is given in Table I.

The resonance measurements indicate that the Mn in each of these cases is in a tetrahedral crystalline environment as an isolated impurity. The two negatively charged species of Mn are both seen in the presence of uncompensated phosphorus, indicating that they are not different charge states of one impurity site, but represent different sites. There are only two different sites which show the tetrahedral symmetry of the host lattice, the substitutional site and the interstitial site. Thus one species must be substitutional and the other interstitial. Similar arguments apply to the two positively charged species, since each is seen in silicon containing an excess of boron.

A dramatic difference between Cu-doped and Cu-free samples is the stability of the resonance center. For example, the Mn^{++} spectrum dis-

Table I. Electron spin resonance parameters for four isolated species of Mn in Si. S is the electron spin, a, the cubic field interaction parameter, and A, the (isotropic) hyperfine interaction parameter of the Mn nucleus. Both a and A are expressed in units of 10^{-4} cm^{-1}.

	Interstitial		Substitutional	
Ion	Mn^+	Mn^-	Mn^+	$Mn^=$
S	5/2	1	1	5/2
g	2.0066	2.0104	2.0259	2.0058
a	+19.88	...	...	+26.1
A	-53.47	-71.28	-63.09	-40.5