theoretical values for gadolinium obtained on the assumption of contributions by spin only. These are, respectively, $\mu_A = g[J(J+1)]^{\frac{1}{2}} = 7.94$ and $M_A = gJ = 7.00$ in Bohr magnetons, where for gadolinium the Lande factor g is 2 and the total angular momentum quantum number J has the value $\frac{7}{2}$. It appears that the presence of the diluent either brings into play contributions to magnetism by orbital moments, or alters the probability of transfers from the conduction-band electrons in a manner favoring an increased magnetic moment.

It is noteworthy that, except for the marked departures in the neighborhood of 60% Gd concentration, the Néel points θ_N and ferromagnetic Curie points θ_f of the alloys with yttrium tend to be close to the corresponding paramagnetic Curie points θ_p. Dilution with yttrium appears to change the magnetic properties of gadolinium for the most part continuously.

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Lifetime in p-Type Silicon

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By using the photoconductive decay method, lifetime is measured as a function of excess electron density in p-type silicon over the temperature range 200–400°K. The linear dependence of τ_n on Δn expected from the Shockley-Read theory of recombination is not obeyed; instead a much stronger dependence is found with minority carrier densities less than 10^{12} cm^{-3} than at larger densities. The data are discussed in terms of two separate recombinative levels of the Shockley-Read type of of more complex behavior for a single kind of center.

I. INTRODUCTION

OF the parameters which characterize the bulk behavior of a semiconductor, minority carrier lifetime is one of the most important, and many methods have been devised for its measurement. Unfortunately, various measurements on a single sample do not always agree, since there are two ways in which ambiguity can arise.

Firstly, the extent to which surface recombination adds to that of the bulk depends on the details of the experimental arrangement, and due attention must be paid to minimizing this perturbation. Secondly, we must note that in some materials, of which p-type silicon is a good example, bulk lifetime varies with the density of excess minority carriers and is meaningful only when expressed together with the corresponding carrier concentration.

Thus in p-type silicon it is desirable to measure the lifetime τ_n as a function of electron density Δn. Such measurements have been reported for one specimen by Bemski[1] who found a linear dependence of τ_n on Δn as expected from the Shockley-Read theory of recombination centers.[2] In brief reports on the work described in this paper,[3] it was noted that the dependence can depart from linearity, suggesting the influence of more than one recombinative level.

[1] G. Bemski, Phys. Rev. **100**, 523 (1955).
[2] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).
[3] J. S. Blakemore, Bull. Am. Phys. Soc. Ser. II, **2**, 153 (1957); **3**, 101 (1958).

II. EXPERIMENTAL ARRANGEMENT

Lifetime was measured from the time constant of photoconductive decay following 0.7-μsec pulses of light from a spark gap. Specimens were operated under constant-current conditions so that a transient voltage was developed on illumination. This was amplified and displayed on a Tektronix 514AD oscilloscope. In operation, the preamplifier gain and oscilloscope sweep rate were varied to match the photoconductive decay against an exponential curve drawn on the cathode ray tube face (Fig. 1). Since the decay is not a pure exponential, the time base speed was found for which a coincidence occurred between the drawn exponential and one section of the decay. From the sweep speed (which can be read directly on this

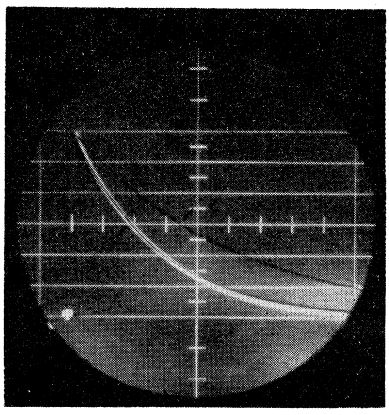

FIG. 1. Oscilloscope trace of photoconductive decay in p-type silicon. The time base is adjusted for coincidence between a portion of the trace and one of the two black exponential marker curves.

oscilloscope) and the signal amplitude, the time constant could be recorded corresponding to a certain excess conductance. This procedure was repeated for a wide range of light intensities to determine the dependence of τ_n on excess carrier density. Since in p-type silicon τ_n is smaller for lower electron densities, the decay drops below a simple exponential at later times, as Fig. 1 shows.

The specimens used were cut from single crystals of boron-doped DuPont silicon. This material was essentially free from traps[4] since long tails to the photoconductive decay were seen only at temperatures below 225°K. All specimens were checked for uniformity of resistivity and absence of bulk photovoltaic effects.

Illumination was confined to an area on the front face of a specimen comprising perhaps 25% of the length and 50% of the width, in order to avoid end contact effects and surface recombination on the side faces, respectively. Recombination at the front and rear faces is unavoidable, but conditions were arranged so that this was small compared with bulk recombination, and could be allowed for with a simple correction.[5] The higher order modes of surface recombination[6] which can seriously affect the initial period of a decay were obviated by using very penetrating light so that carrier generation was essentially uniform through the thickness of each specimen.

The nonpenetrating spectral components of the incident light may be removed with a filter made from the same semiconductor as the sample. This widely used practice was followed here, but our filters were of much greater thickness than commonly used, for a reason which merits a few words of explanation.

Consider the distribution of optical carrier generation rate g through the thickness d of a sample exposed to light through a filter of thickness a. If the light has $I(\lambda)d\lambda$ photons/cm² sec in a wavelength range $d\lambda$, for which the absorption coefficient is $\alpha(\lambda)$, then at depth x in the specimen the generation rate is

$$g(x)=\int_0^\infty I(1-r)^3\alpha \exp[-\alpha(a+x)]d\lambda, \qquad (1)$$

where r is the optical reflection coefficient. The terms involving multiple reflections are omitted since they do not materially affect the conclusions. Now I and r will be slowly varying functions of λ, and the integral is determined by the behavior of α for wavelengths around the intrinsic absorption edge. The optical data of MacFarlane, and Roberts[7] indicate that $\alpha \simeq \exp[K(\lambda_0-\lambda)]$ for wavelengths corresponding to penetration depths of a few millimeters, and when this is applied to (1) the result is

$$g(x)=I(1-r)^3/K(a+x). \qquad (2)$$

Thus the generation rate varies inversely as the total thickness of semiconductor penetrated, a conclusion which we have indirectly checked experimentally.[8]

This result demonstrates that it is desirable to use a filter at least as thick as the sample under test, and preferably even twice as thick. When only a thin filter is used, generation near the front face is much faster than the volume average and high-order modes of surface recombination come into play. At the same time, bulk recombination is reduced in a material such as p-type silicon where τ_n increases with Δn, since now most of the extra electrons are clustered in a small volume and enjoy the long lifetime appropriate to such a large local density. Unless bulk lifetime is an exceedingly sensitive function of carrier density, the additional surface recombination will generally be the more powerful of the two opposing tendencies. This is illustrated in Fig. 2 for a p-type silicon filament 2.5 mm thick, when illuminated through thick or thin filters. For various light intensities, the apparent lifetime

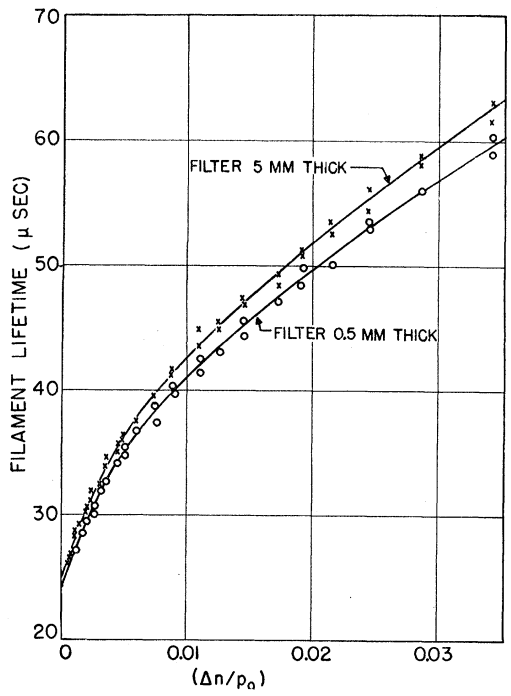

FIG. 2. Photoconductive decay lifetime in a filament of p-type silicon 2.5 mm thick as a function of excess electron density, at $T=297$°K. Free hole density $=1.2\times10^{14}$ cm^{-3} in this material.

[4] J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).
[5] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 323.
[6] Reference 5, p. 320.
[7] G. G. MacFarlane and V. Roberts, Phys. Rev. **98**, 1865 (1955).
[8] Integration of (2) through the depth suggested that the photoconductance of a sample should vary with filter thickness as $\ln(1+d/a)$, or a more complex expression with the same tendency if multiple reflections are allowed for. This was found experimentally to be correct; thus with a sample 6 mm thick and filters of 1.07, 2.29, and 4.15 mm, signals were in the ratios 1.00:0.74:0.50, in good agreement with the expected ratios of 1.00:0.70:0.49.

$-\Delta n(dt/d\Delta n)$ was obtained by matching the decay when the photoconductance was down to half the peak value.

When the 5-mm filter was used, the surface recombination rate was $\nu_s \sim 2000$ sec^{-1}. For the conditions of the thin filter a small reduction in bulk recombination was computed, but since the over-all lifetime was smaller, the surface rate must have increased by ~ 3000 sec^{-1}. This is by no means a negligible change if meaningful results are to be obtained.

III. SHOCKLEY-READ RECOMBINATION

(a) Single Type of Recombination Center

In this paper we are concerned with a p-type semiconductor which in thermal equilibrium contains p_0 free holes per unit volume but virtually no electrons. When disturbed from equilibrium, the hole and electron densities increase by amounts Δp and Δn; these are equal if the recombination center density N_t is small. If this is so, then in steady state the electron lifetime is

$$\tau_n = \frac{\tau_0 + (\tau_{n0}+\tau_{p0})(\Delta n/p_0)}{1+\Delta n/p_0}, \tag{3}$$

following the terminology and reasoning of Shockley and Read.[2] The appropriate form for τ_0 depends on the location of E_t in the intrinsic gap. If this lies in the upper half of the gap, then

$$\tau_0 = \tau_{n0} + \tau_{p0}\left(\frac{n_1}{p_0}\right) = \tau_{n0} + \tau_{p0}\left(\frac{N_c}{p_0}\right)\exp\left(\frac{E_t - E_c}{kT}\right), \tag{4}$$

while for recombination levels nearer to the valence band the appropriate expression is

$$\tau_0 = \tau_{n0}\left[1+\frac{p_1}{p_0}\right] = \tau_{n0}\left[1+\left(\frac{N_v}{p_0}\right)\exp\left(\frac{E_v - E_t}{kT}\right)\right]. \tag{5}$$

In the analysis of experimental data, the variation of τ_n with Δn and temperature will normally show one of (4) or (5) to be impossible. This approach was followed by Bemski,[1] who found $\tau_n(1+\Delta n/p_0)$ to vary linearly with $(\Delta n/p_0)$ for his samples of p-type silicon, in accordance with (3). The strong variation was consistent with $\gamma = \tau_{n0}/\tau_{p0} = 0.025$. The values for τ_0 were fitted to the sum of a constant term and one which varied as $\exp(-0.20/kT)$ as expected from either (4) or (5), and Bemski chose the latter representation on the grounds that the coefficient of the temperature-dependent term was too small by a factor of 3000 to permit comparison with (4). But he did not note that this coefficient was still too small by a factor of 30 for a proper identification of his results with (5). This factor could be accounted for by assuming that the recombination levels move further from the valence band on heating, but several alternative explanations are possible if the variation of $\tau_n(1+\Delta n/p_0)$ with $(\Delta n/p_0)$ was not precisely linear at low modulation levels. Bemski's measurements, like those presented in this paper, were made using a transient rather than steady-state method, and transient decay departs more easily from the form of (3) and (5) than does steady-state recombination; nevertheless, even for steady-state conditions (3) is an approximation.

Thus Δn and Δp are rarely exactly equal, the difference comprising the change in the population of the recombination centers $\Delta n_t = \Delta p - \Delta n$. The importance of this depends on the density and energy level of these centers, and on whether transient or steady-state conditions are under discussion. In the latter case, the situation of a p-type semiconductor with centers in the lower half of the gap [previously described by (3) and (5)] must now be generalized to

$$\tau_n = \left\{\frac{\tau_{n0}(1+p_1/p_0)+(\Delta n/p_0)[\tau p_0+\tau_{n0}(\Delta p/\Delta n)]}{1+(\Delta n/p_0)(\Delta p/\Delta n)}\right\}, \tag{6}$$

which evidently gives the same result as before for $\Delta n = 0$ or ∞, but will be different for finite modulation if $(\Delta p/\Delta n) \neq 1$. Fortunately, it develops that N_t must be several times larger than (p_0+p_1) to make a serious difference,[9] and this complication can be neglected for crystals with moderately long lifetime.

The influence of carriers trapped at recombination centers on the form of a transient decay is more acute. The equations governing decay are

$$-\tau_{p0}N_t\frac{dp}{dt} = \Delta p\left[p_0+p_1+\frac{p_1N_t}{p_0+p_1}\right] - \Delta n(p_0+p_1)+(\Delta p^2-\Delta n\Delta p), \tag{7}$$

$$-\tau_{n0}N_t\frac{dn}{dt} = \Delta n\left[n_0+n_1+\frac{p_0N_t}{p_0+p_1}\right] - \Delta p(n_0+n_1)+(\Delta n^2-\Delta n\Delta p), \tag{8}$$

and the terms involving Δn and Δp can be separated to give highly nonlinear second-order equations for Δn and Δp as functions of time. An adequate discussion of the solutions to this problem has not been published and it is proposed to remedy this deficiency soon.[10] Sandiford[11] has examined the much simplified situation of very small excess carrier density [ignoring the second-order terms in (7) and (8)], but for some reason he avoided discussion of the most interesting case, that in which the density and energy of the

[9] With low-lying recombination levels as discussed above, we have

$$\frac{\Delta p}{\Delta n} = \frac{(p_0+p_1)(p_0+p_1+\Delta p+\Delta n/\gamma)+N_tp_0/\gamma}{(p_0+p_1)(p_0+p_1+\Delta p+\Delta n/\gamma)+N_tp_1}.$$

Unless N_t is very large, $\Delta p/\Delta n$ will not depart far from unity except for centers where γ is very small, and in this case the value of $\Delta p/\Delta n$ does not affect the result for τ_n very much.

[10] K. C. Nomura and J. S. Blakemore (to be published).

[11] D. J. Sandiford, Phys. Rev. **105**. 524 (1957).

centers are appropriate for trapping most of the minority carriers. Clarke[12] considered the transition to a trapping character, but he too discussed only the solutions for infinitesimal modulation. Wertheim[13] has recently approached the question of extension to finite modulation, but only for rather special cases.

The general problem posed by (7) and (8) cannot be solved in closed form for many of the possible cases. In p-type silicon we can start by supposing that only terms appropriate for centers in the lower half of the gap need be retained, so that the excess electron decay follows as

$$\tau_{p0}\left[\frac{d^2\Delta n}{dt^2}-\frac{(1-\gamma)}{\Delta n}\left(\frac{d\Delta n}{dt}\right)^2\right]+\frac{d\Delta n}{dt}\left[\frac{p_1+2p_0}{p_1+p_0}+\frac{p_1+p_0+\Delta n(1+1/\gamma)}{N_t}\right]+\frac{\Delta n}{\tau_{n0}}\left[\frac{p_0}{p_0+p_1}+\frac{p_0+\Delta n}{N_t}\right]=0. \quad (9)$$

This can be solved exactly for small modulation in the form

$$\Delta n=\Delta n_0\exp\left[\frac{-tp_0}{\tau_{n0}(p_0+p_1)}\right]\times\left\{1+C\exp\left[\frac{-t}{\tau_{p0}}\left(\frac{p_0+p_1}{N_t}+\frac{p_1}{p_0+p_1}\right)\right]\right\}^{1/\gamma}. \quad (10)$$

This looks formidable, but note that $C=0$ if the initial conditions are $\Delta n=\Delta p$ at time $t=0$ (which is true if the decay follows a very short period of illumination). Then the low-level lifetime is exactly as given by Eq. (5), even for large N_t.

The extension to finite modulation can be made by perturbation methods; the apparent complexity of the result disguises a basic similarity for the dependence of τ_n on Δn with that of the simple steady-state theory. But this is not the complete story if lifetime is measured by photoconductive decay, where the signal is influenced by the separate contributions of electrons and holes. From the increase of conductivity can be deduced the quantity $\Delta\bar{n}=(\Delta p+b\Delta n)/(1+b)$ (where b is the ratio of electron to hole mobility), but $\Delta n=\Delta p=\Delta\bar{n}$ only for small recombination center densities. With centers having energies in the lower half of the intrinsic gap, the densities and decay time constants of excess minority electrons and majority holes are different if N_t is comparable with or larger than $\bar{N}=\gamma(p_0+p_1)^2/(p_0-\gamma p_1)$. We are concerned mainly with donor-like centers where $\gamma\ll 1$; then the critical center density may be considerably smaller than p_0 at rather low temperatures.

For center densities comparable with $\bar{N}$ the linearity of the relationship between $\tau_n(1+\Delta\bar{n}/p_0)$ and $(\Delta\bar{n}/p_0)$ is modified in that the apparent lifetime increases more rapidly with $\Delta\bar{n}$ for small modulation than for large, the initial slope being up to $(1+b)$ times larger than the final slope for heavy modulation. Since this sounds qualitatively similar to the behavior of the specimen in Fig. 2, it is important to note the other attributes of this model. Thus, the curvature of the lifetime-modulation characteristic becomes less marked at higher temperatures, since the ratio $(N_t/\bar{N})$ declines as p_1 increases. Moreover, the larger N_t is for material of a given resistivity, the more marked and more persistent with heating is this curvature. As a further corollary, the larger the free hole density for a given N_t, the less prominent should this curvature be at the lower temperatures.

It might be noted at this point that the results of Sec. IV do not accord with the expected temperature dependence of the above model, and it is useful to consider another possible extension of the Shockley-Read model, that corresponding to recombination via more than one kind of center.

(b) Several Types of Recombination Center

In the preliminary presentation of data on p-type silicon,[3] it was noted that the dependence of τ_n on Δn could be fitted to a model supposing two species of recombination center. Ludwig and Watters[14] remarked

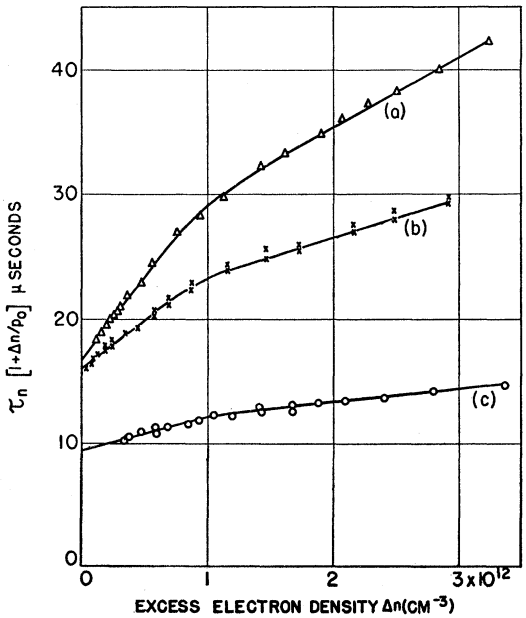

FIG. 3. Dependence of lifetime, expressed as $\tau_n[1+\Delta n/p_0]$, on excess electron density for three boron-doped silicon crystals, at $T=300°$K. (a) Specimen 1, $p_0=10^{14}$ cm^{-3}. (b) Specimen 2, $p_0=2.5\times10^{14}$ cm^{-3}. (c) Specimen 3, $p_0=1.1\times10^{15}$ cm^{-3}.

[12] D. H. Clarke, J. Electronics **3**, 375 (1957).
[13] G. K. Wertheim, Phys. Rev. **109**, 1086 (1958).
[14] R. L. Watters and G. W. Ludwig, J. Appl. Phys. **27**, 489 (1956).

that the temperature dependence they found for τ_0 was not suitable for representation by a single Shockley-Read process, and other recent reports on the intensity dependence of lifetime have similarly been ascribed by their authors[15] to the influence of more than one kind of center.

Kalashnikov[16] has discussed the theory of recombination through several kinds of center for the limiting case of small carrier disturbance. He showed that if one kind of center is present in sufficiently large numbers, then the total recombination rate is not equal to the sum of the contributions each kind would make seperately; but the center density required for this complication must be much larger than $\bar{N}$ if the semiconductor is extrinsic.

Then for two kinds of center each present in a density smaller than $\bar{N}$ it seems reasonable to expect the lifetime to follow

$$\tau_n=[\nu_1+\nu_2]^{-1}, \tag{11}$$

where

$$\nu_1=\frac{1+\Delta n/p_0}{\tau_{01}+(\tau_{n01}+\tau_{p01})(\Delta n/p_0)}, \tag{12}$$

with a similar expression for the second set of centers. It will readily be appreciated that if the factor $(\tau_{n0}+\tau_{p0})/\tau_0$ is larger for one set of centers than for the other, a variety of forms for the dependence of lifetime on excess carrier density become possible. Some of the results given later are fitted to expressions of this kind.

As a further theoretical possibility, we might consider recombination via a divalent impurity center which can lose either one or both electrons. Champness[17] has discussed the somewhat academic case of the Fermi level in a semiconductor containing divalent donors but no other impurities. Two more recent papers[18] consider the general principles of steady-state recombination via multivalent defects. We have examined the statistics of divalent centers with arbitrary Fermi level and nonequilibrium conditions. Recombination is more complicated than for separate sets of levels since now the concentrations of the two levels are interdependent. There are many possible cases, but for a p-type semiconductor with a first donor recombination level above the mid-point of the gap and the second in the lower half of the gap, the electron lifetime can be expressed in the form of Eq. (11) where now

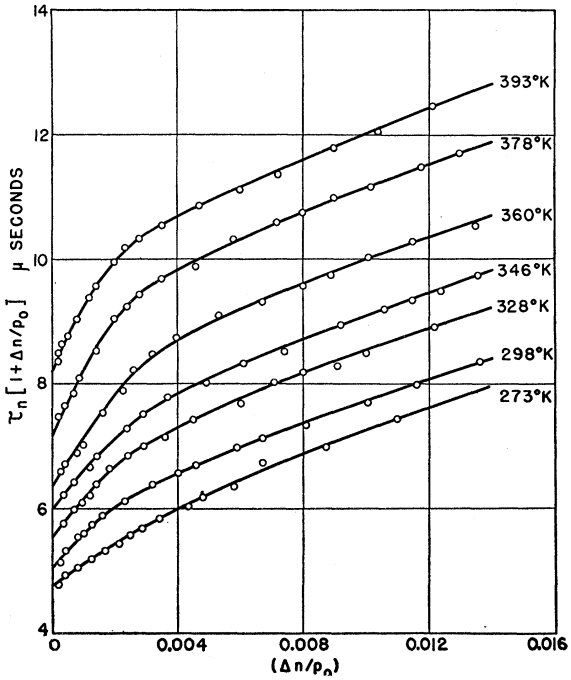

FIG. 4. Variation of lifetime with modulation at various temperatures for specimen 4 ($p_0=6.0\times10^{14}$ cm^{-3}).

$$\nu_1=\frac{(1+\Delta n/p_0)}{\left[\tau_{n01}\left(1+\frac{\Delta n}{p_0}\right)+\tau_{p01}\left(\frac{n_1}{p_0}\right)\right]\left[1+\frac{\tau_{n02}(p_0+\Delta n)}{\tau_{p02}\Delta n+\tau_{n02}p_2}\right]+\tau_{p01}\left(\frac{\Delta n}{p_0}\right)}, \tag{13}$$

and

$$\nu_2=\frac{(1+\Delta n/p_0)}{\tau_{n02}\left(1+\frac{p_2}{p_0}\right)+\frac{\Delta n}{p_0}\left\{\tau_{p02}+\tau_{n02}+\tau_{p01}\left[\frac{\tau_{n02}p_2+\tau_{p02}\Delta n}{\tau_{n01}p_0+\tau_{p01}n_1}\right]\right\}}. \tag{14}$$

These expressions are discussed in Sec. IV in relation to the experimental results obtained.

IV. RESULTS AND DISCUSSION

The typical form of variation between lifetime and excess electron density is illustrated in Fig. 3. These specimens came from crystals doped with boron in varying amounts, yet all showed a change in the characteristic slope for about the same electron density, $\Delta n\sim10^{12}$ cm^{-3}. A thought occurred that the connecting link might be the quasi-Fermi level for electrons: this would be important if recombination were via a single

[15] M. S. Ridout, *Report of the Meeting on Semiconductors* (Physical Society, London, 1956), p. 33; E. B. Dale and R. W. Beck, Electrochemical Society Meeting at Buffalo, October, 1957 (unpublished).
[16] S. G. Kalashnikov, J. Tech. Phys. (U.S.S.R.) **26**, 241 (1956).
[17] C. H. Champness, Proc. Phys. Soc. (London) **B69**, 1335 (1956).
[18] P. T. Landsberg, Proc. Phys. Soc. (London) **B70**, 282 (1957); C. T. Sah and W. Shockley, Phys. Rev. **109**, 1103 (1958).

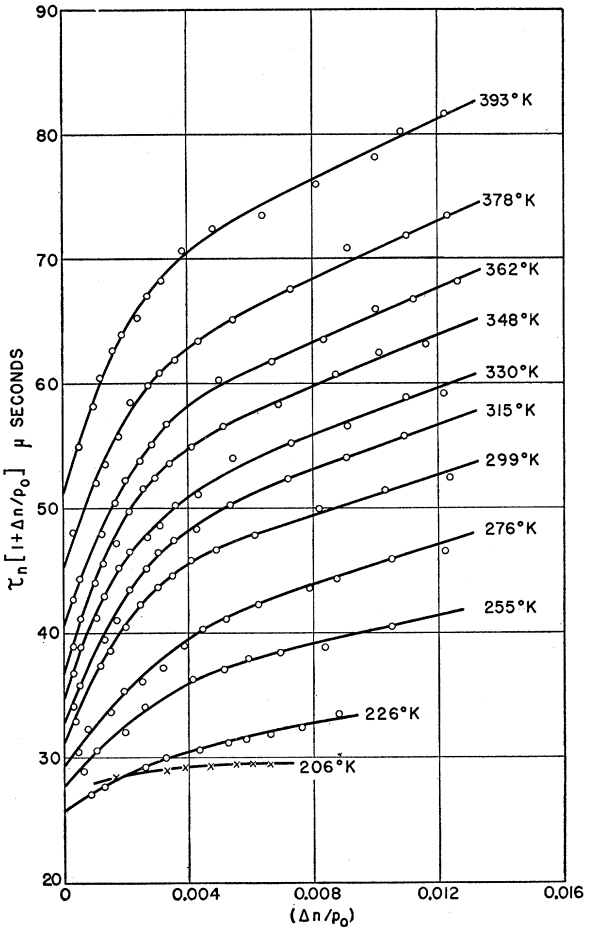

FIG. 5. Variation of lifetime with modulation at various temperatures for specimen 5 ($p_0=6.6\times10^{14}$ cm^{-3}).

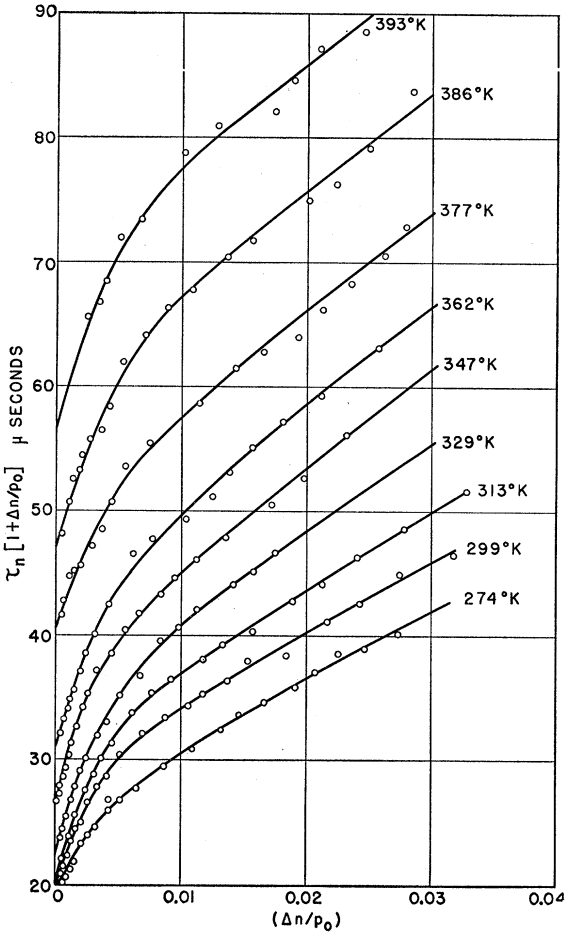

FIG. 6. Variation of lifetime with modulation at various temperatures for specimen 6 ($p_0=9.0\times10^{13}$ cm^{-3}).

agency which did not obey Fermi statistics when strongly charged, such as a set of dangling bonds on a dislocation.[19] But dislocation densities were small in these samples, and not correlated with lifetime.

As remarked in III(a), curvature of the characteristic between lifetime and modulation will occur with a single set of recombination centers whose density is comparable with $\bar{N}$. The applicability of this model can be tested through observations of lifetime at various temperatures. Typical sets of temperature characteristic are shown in Figs. 4–6; these curves provide comparison between specimens of similar resistivity but different lifetime, and between specimens of similar lifetime but different resistivity. In the case of specimen 5, measurements are illustrated down to 206°K, but the curves for the lowest temperatures may be affected by the onset of slow trapping. In any event, the range 273–393°K gives ample room for comparisons.

The model discussed in III(a) is not supported by the curves for our various specimens. Thus the model predicts that isothermals should be more nearly linear at high temperatures, which is patently not so. The model further requires that for two samples of similar resistivity but different lifetime, the one of higher lifetime should show more nearly linear isothermals; but comparison of Figs. 4 and 5 shows that this is not necessarily so. The predictions for comparison between specimens of different majority carrier density are not borne out either. Moreover, in none of our specimens does τ_0 vary with temperature in accordance with (5), as expected for a single-level recombinative model. Typically, for specimen 4, the data for the extreme temperatures must be ignored to force a mediocre fit to

$$\tau_0=4.65\left[1+0.0053\left(\frac{N_v}{p_0}\right)\exp\left(\frac{-0.18}{kT}\right)\right]\mu\text{sec}. \quad (15)$$

This can be reconciled with $\tau_0=\tau_{n0}[1+p_1/p_0]$ only by supposing that the recombination level moves rapidly away from the valence band on heating, $(E_t-E_v)=(0.18+4.5\times10^{-4}T)$ ev, a rather unlikely situation.

[19] W. T. Read, Jr., Phil. Mag. **45**, 775 (1954); S. R. Morrison, Phys. Rev. **104**, 619 (1956).

Thus it seems desirable to examine other possible explanations of the experimental results. For two independent sets of centers, lifetime would be expected to follow (11) and (12). An attempt to fit the behavior of a typical specimen in this manner is illustrated by Fig. 7. The solid curve follows

$$\tau_n\left[1+\frac{\Delta n}{p_0}\right]=\left\{\frac{1}{39.2+760(\Delta n/p_0)}+\frac{1}{83+25\,000(\Delta n/p_0)}\right\}^{-1}\mu\text{sec}, \quad (16)$$

so that if this is a legitimate way to represent the behavior of the specimen, most recombination occurs in a set of donor-like centers for which $\gamma=\tau_{n0}/\tau_{p0}$ is approximately 0.05. The other centers, which become prominent at low modulation levels, are much more strongly donor-like with γ approximately 0.003.

This feature encourages examination of models for recombination via divalent donors, where strong asymmetry of capture cross sections is to be expected. But no definite conclusions have been reached in attempts to compare experiment with expressions such as (13) and (14), or the corresponding ones for both levels in the same half of the gap. The comparison is difficult since so many unknown parameters are involved, but tentatively it may be remarked that the arrangement of these parameters which permits the best fit with experiment is also that which minimizes the distinction from the behavior of two separate systems. Accordingly, the following discussion is pertinent to recombination via two independent sets of centers, such that

$$\tau_n\left[1+\frac{\Delta n}{p_0}\right]=\left\{\frac{1}{\tau_{01}+(\tau_{n01}+\tau_{p01})(\Delta n/p_0)}+\frac{1}{\tau_{02}+(\tau_{n02}+\tau_{p02})(\Delta n/p_0)}\right\}^{-1}. \quad (17)$$

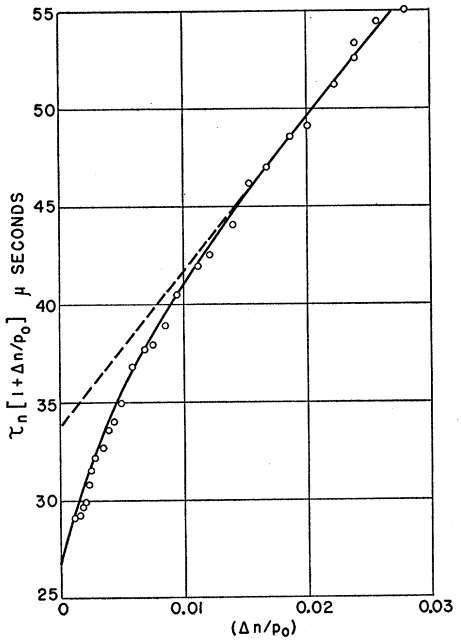

FIG. 7. Variation of $\tau_n[1+\Delta n/p_0]$ with $(\Delta n/p_0)$ at 300°K for specimen 7, in which $p_0=1.5\times10^{14}$ cm^{-3}. The solid curve follows Eq. (16), based on two separate recombination processes.

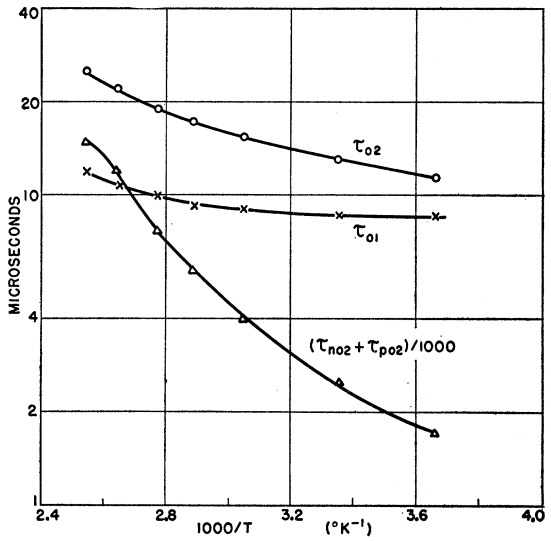

FIG. 8. Temperature dependence of τ_{01}, τ_{02}, and $(\tau_{n02}+\tau_{p02})/1000$ for specimen 4, when the results of Fig. 4 are fitted by Eq. (17). $(\tau_{n01}+\tau_{p01})$ is constant at 120 μsec.

Data for a number of specimens have been fitted to this form at various temperatures, as described above for specimen 7 at a single temperature. In doing so, $(\tau_{n01}+\tau_{p01})$ and $(\tau_{n02}+\tau_{p02})$ as well as τ_{01} and τ_{02} were optimized for each temperature. For although the original Shockley-Read theory makes no allowance for temperature dependence of τ_{n0} or τ_{p0}, such dependencies have been noted in germanium[20] and may be anticipated here.

The subscript 1 is used to distinguish the process involving only moderate asymmetry of capture cross sections. These type 1 centers, which account for rather more than half the recombination in all our samples, demonstrate fairly repeatable characteristics from one crystal to another. For specimen 4 (Fig. 4) the optimum value of $(\tau_{n01}+\tau_{p01})$ is 120 μsec over the whole temperature range, while τ_{01} varies with temperature (Fig. 8) in accordance with the following relation:

$$\tau_{01}=8.5\left[1+0.36\left(\frac{N_v}{p_0}\right)\exp\left(\frac{-0.34}{kT}\right)\right]\mu\text{sec}. \quad (18)$$

This indicates levels some 0.34 ev above the valence

[20] J. F. Battey and R. M. Baum, Phys. Rev. **100**, 1634 (1955); R. G. Shulman and B. J. Wyluda, Phys. Rev. **102**, 1455 (1956).

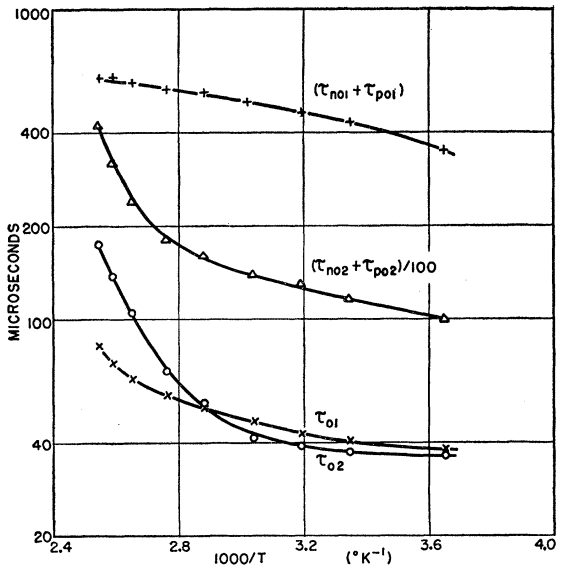

FIG. 9. Temperature dependence of τ_{01}, τ_{02}, $(\tau_{n01}+\tau_{p01})$, and $(\tau_{n02}+\tau_{p02})/100$ for specimen 6, in order to fit the results of Fig. 6 with Eq. (17).

band for which $\tau_{p01}=111\,\mu$sec and $\tau_{n01}=8.5\,\mu$sec, whence $\gamma_1=0.077$. The data for other crystals indicate centers of similar asymmetry and energy level, though rather more complex behavior is evident in a few samples, including specimen 6 (Figs. 6 and 9). For these samples $(\tau_{n01}+\tau_{p01})$ falls off at the lower temperatures while a variation of τ_{01} continues down to lower temperatures than expected; yet the high-temperature behavior is in excellent accord with centers of $\gamma_1=0.077$ at $(E_t-E_v)=0.34$ ev. It is suspected that these crystals contain a few centers with energies closer to the valence band in addition to the normal type 1 centers: the complication does not arise in specimens for which τ_{n01} is less than about 25 μsec.

The type 1 centers are tentatively identified with gold, which provides a donor level 0.35 ev above the valence band,[21] active in recombination. The capture cross sections reported for gold by Bemski and Struthers[22] bear a ratio not wholly consistent with the asymmetry reported above, but on the other hand these authors describe experiences with heat treatment effects on lifetime in gold-contaminated silicon which are in good accord with observations on some of our samples.

[21] Collins, Carlson, and Gallagher, Phys. Rev. **105**, 1168 (1956).
[22] G. Bemski and J. D. Struthers, Electrochemical Society Meeting at Buffalo, October, 1957 (unpublished).

It is much more difficult to attribute to a single kind of center the highly asymmetric process designated by the subscript 2. Since the properties adduced very markedly from one crystal to another, it seems likely that several chemical residues are present in various proportions: in this way it is possible to explain the considerable temperature dependence which our fitting procedure prescribes for $(\tau_{n02}+\tau_{p02})$ in many specimens (Figs. 8 and 9). Moreover, in some specimens, such as 4, it is not possible to resolve τ_{02} into the sum of a constant term and one which varies exponentially with T^{-1}. This is fortunately not so for all specimens; thus in specimen 5 the quantity $(\tau_{n02}+\tau_{p02})$ is independent of temperature and τ_{02} varies as follows:

$$\tau_{02}=80+7500\left(\frac{N_c}{p_0}\right)\exp\left(\frac{-0.54}{kT}\right)\mu\text{sec}. \quad (19)$$

The expression is written to facilitate comparison with Eq. (4), and indicates a donor level some 0.54 ev below the conduction band. While for specimen 6 some variation of $(\tau_{n02}+\tau_{p02})$ with temperature appears necessary, the low-level lifetime does conform with the postulation of a donor level in the same position, following the relation

$$\tau_{02}=37+2460\left(\frac{N_c}{p_0}\right)\exp\left(\frac{-0.54}{kT}\right)\mu\text{sec}. \quad (20)$$

Several impurity levels are reported at the above-mentioned energy which could contribute to the recombination.[23] Of the rapidly-diffusing transition elements, both iron[24] and manganese[14,25] provide levels at the appropriate energy which interact more readily with electrons than with holes. Traces of these elements up to approximately 10^{12} cm^{-3} (sufficient to explain the observed results) could occur in silicon grown by the Czochralski method.

V. ACKNOWLEDGMENTS

It is a pleasure to express appreciation to J. D. Heaps for assistance with the measurements, and to K. C. Nomura with whom many valuable discussions were held. The crystals used in this work were grown by T. J. Davies.

[23] The existence of an acceptor level for gold 0.54 ev below the conduction band can only be a coincidence, since the recombinative action implies a strongly donor-like nature.
[24] C. B. Collins, Bull. Am. Phys. Soc. Ser. II, **1**, 49 (1956).
[25] R. O. Carlson, Phys. Rev. **104**, 937 (1956).

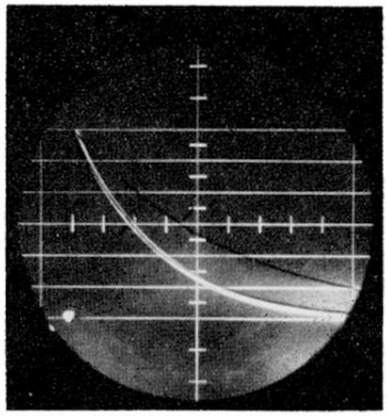

FIG. 1. Oscilloscope trace of photoconductive decay in p-type silicon. The time base is adjusted for coincidence between a portion of the trace and one of the two black exponential marker curves.