Trapping of Minority Carriers in Silicon. I. *P*-Type Silicon

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(Received October 11, 1954)

Experimental evidence of temporary trapping of electrons in the volume of *p*-type silicon in two different traps is presented. The evidence is shown to lead to a multiple trapping model the kinetics of which explains the data. The trap parameters are determined by the fit of experimental data to the theory. The trap density, energy level, cross section for capture, S, and the time which an electron spends in a trap, τ_0, are determined for both traps. For the deeper traps, $S\tau_0$, a property of the trap itself, is shown to have the probable value $0.81\pm0.25\times10^{-13}$ cm^2 sec with $\tau_0\cong0.3$ sec for all specimens examined. In low-resistivity crystals there is evidence for a loss mechanism for electrons (recombination) from the deeper traps at a rate found proportional to the square of the hole concentration. The deep-trap concentration is found to be roughly proportional to the sample conductivity.

INTRODUCTION

RECENT experiments[1-3] indicate that minority carriers in silicon and germanium may be trapped, that is temporarily imprisoned, at what must be special sites or imperfections in the crystal lattice. Trapping in silicon is readily observed at room temperature, whereas in germanium it is seen at $\sim-80°$C and lower temperatures. It is the primary purpose of this paper to present (1) evidence for the existence of two sets of volume traps for electrons in *p*-type silicon and (2) a model for the kinetics of trapping which appears to be entirely consistent with the experimental observations. A further report, Part II, will be forthcoming shortly on hole traps in *n*-type silicon.

EVIDENCE FOR TRAPPING—MOBILITY EXPERIMENTS

The existence of trapping centers (other than recombination or "deathnium" centers) for minority carriers was first indicated by drift velocity experiments employing a time-of-flight technique. In this type of experiment a short pulse of minority carriers is injected by a point into a germanium or silicon rod on which is impressed a small longitudinal electric field. The carriers drift in the electric field along the rod and at the same time diffuse and also recombine with majority carriers. A second point contact placed downstream is used to measure the concentration of the minority carriers in the immediate neighborhood of the point as a function of the time and also distance from the injection point. Arrival of the minority carriers at the collector is shown schematically in Fig. 1, assuming that a short pulse of minority carriers was injected into the rod at the emitter at zero time. If the rod is germanium at room temperature, the minority carrier pulse as measured by the collector, shown by the broken line in Fig. 1, spreads out with time and distance from the emitter and decreases in amplitude with time and distance. Recombination and diffusion explain[4] these effects quantitatively. In *p*-type silicon at room temperature and *n*-type germanium *circa* $-80°$C and lower temperatures the pulse shape is different as shown by the solid line in Fig. 1. A straggling is observed as if some of the carriers suffer an additional time delay in their transit between the two points. The straggle can be eliminated, also as shown by the broken line in Fig. 1, by increasing sufficiently the ambient light falling on the crystal. In silicon the areas under the two curves are the same within the experimental error of measurement.

An interpretation of these results can be given qualitatively in terms of temporary traps. For low external illumination some of the carriers are caught in traps where they sit for a time and then are ejected back into the conduction stream. High external illumination, however, creates sufficient electron-hole pairs to keep the traps filled. Thus the injected minority carriers are not aware of the existence of the traps, and a pulse shape with no straggle is observed. The experiment, then, is evidence for the existence of temporary trapping centers for minority carriers in which recombination does not occur prominently, since the areas under the curves are the same. The experiment suggests that the mean time a carrier spends in a trap before release is

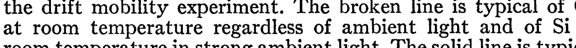

FIG. 1. Collector signal (schematic) as a function of time in the drift mobility experiment. The broken line is typical of Ge at room temperature regardless of ambient light and of Si at room temperature in strong ambient light. The solid line is typical of *p*-type Si in weak ambient light when some trapping of minority carriers occurs.

[1] J. R. Haynes and W. C. Westphal, Phys. Rev. **85**, 680 (1952).
[2] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).
[3] Gebbie, Nisenoff, and Fan, Phys. Rev. **91**, 230(A) (1953).
[4] Transistor Teachers Summer School, Phys. Rev. **88**, 1368 (1952).

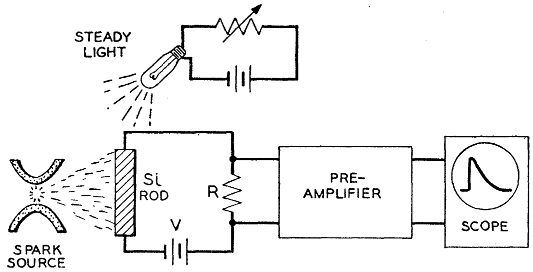

FIG. 2. Schematic diagram of circuit used to measure the lifetime of minority carriers and to study the trapping of minority carriers.

the order of tens of microseconds, i.e., the order of the minimum decay time of the straggling effect.

EVIDENCE FOR TRAPPING—LIFETIME EXPERIMENTS

Further evidence for the trapping of electrons in *p*-type silicon[5] has been obtained from experiments in which the lifetime of injected electrons in the material is observed directly. This experiment may be described as follows (Fig. 2).

A semiconductor sample in the form of a rod (dimensions $0.2\times0.2\times2$ cm) with plated electrodes at either end is connected in series with a resistor and a battery. A short pulse of light[6] approximately 0.2 μsec in duration illuminates the crystal. This creates very suddenly a pulse of additional electron hole pairs. The resulting change in conductivity produces a voltage change that is measured as a function of time by means of high-gain, wide-band (8-megacycle) amplifiers and an oscilloscope. Clearly, the change in voltage across the specimen, which is proportional to the increase in conductivity, will persist as long as a detectable number of added electron-hole pairs remain in the specimen. Sufficiently low electric fields are impressed on the rod so that the added pairs disappear mainly through recombination rather than drift to the electrodes. Under these circumstances the decay in photoconductivity observed is a direct measure of the apparent lifetime of the minority carriers.

If the sample is germanium at room temperature, the time constant of the decay agrees very well with the lifetime for minority carriers measured by other methods.[7] At about $-80°$C and lower temperatures in *n*-type germanium, the decay time appears to cease decreasing with temperature and, in fact, to reverse its variation with temperature. Under these conditions shining additional light on the specimen causes the decay time to shorten just as in the mobility experiment additional light causes the straggle to disappear. By using sufficient light so that the decay is independent of light intensity, the decay time has been measured as a function of temperature down to liquid nitrogen temperature. It is found to decrease monotonically with temperature and approach a constant, limiting value as predicted[8] for the variation of recombination time with temperature.

These results we interpret as additional evidence for the existence of temporary trapping centers in *n*-type germanium at low temperature. The implication is that the minority carriers are trapped unless sufficient electron-hole pairs are created (by the dc light) to keep the traps filled. Thus we interpret the decay time under strong external illumination as the recombination time (or lifetime) and the longer decay time as representative of some combined property of the temporary traps and recombination centers.

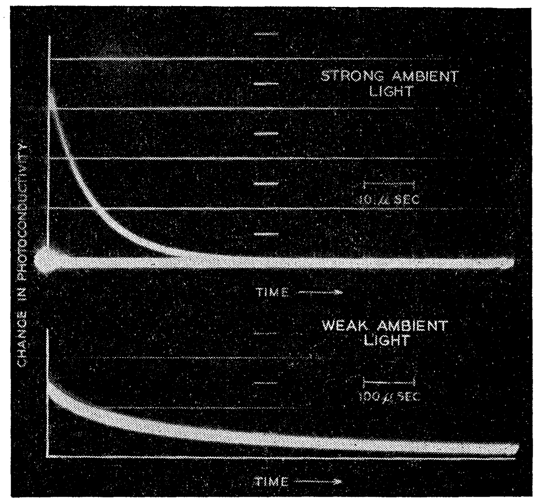

FIG. 3. Photographs of the oscilloscope trace in the experiment shown in Fig. 2. Top—with strong ambient light falling on a *p*-type silicon specimen, no trapping is observed and the decay in photoconductivity as a function of time represents the true lifetime of the added electrons. Bottom—without ambient light trapping occurs, and it controls the decay in photoconductivity.

At room temperature *p*-type silicon shows the same trapping effects in this experiment, *viz.*, a long decay time that can be changed by external dc light. Measurements of the recombination time (as described above) in this material quantitatively agree with other methods of measuring lifetime, whereas the observed decay time with weak or zero external light may be orders of magnitude longer. These effects are shown in Fig. 3. The upper part of Fig. 3 is reproduced from a photograph of the cathode ray tube trace with strong ambient illumination (light from a $1\frac{1}{2}$ volt flashlight bulb). The lower trace was photographed when light from a semi-darkened room was falling on the sample. We note that

[5] *N*-type silicon and germanium show similar effects.

[6] The light source is described by J. A. Hornbeck, Phys. Rev. **83**, 374 (1951).

[7] One common practice is to measure the diffusion length $l_\tau=(D\tau)^{\frac{1}{2}}$ where D is the diffusion coefficient of the minority carriers and τ is the mean lifetime before recombination. It should be emphasized that l_τ will, in general, be unaffected by temporary trapping.

[8] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

both the initial amplitude and time constant of decay can be affected by the external light.

On the basis of a trapping hypothesis it is possible to predict quantitatively the amplitude change that is observed. The experimental observation is that first the decay time increases for a while with decreasing ambient light without the initial amplitude being affected. With a further decrease in ambient light the amplitude begins to decrease and the decay time continues to increase as before. When the amplitude has decreased to one-third its initial value, a further decrease in ambient light leaves the amplitude unchanged although the decay time continues to increase.

This variation of initial deflection with dc light intensity can be explained in the following way. With all of the traps filled by the external light the initial deflection should be proportional to the change in conductivity, i.e., to the number of hole-electron pairs formed by a single light pulse and to the sum of the electron and hole mobilities: $\Delta\sigma = nq(\mu_+ + \mu_-)$, where n is number of pairs formed, q is the electronic charge, and the μ's are the mobilities of holes and electrons. As the ambient light is decreased the number of empty traps increases and the mean free time before trapping (τ_t) of an electron from the conduction band decreases. At some point τ_t will become the order of the response time of the apparatus (pulsed light source plus video amplifiers), and the initial response will fall off because those electrons that are trapped before the measuring system can "see" them give no observable conduction. For still lower light intensities (and larger number of unfilled traps), τ_t will be so short that essentially all the electrons are trapped before they are detected, and the initial amplitude should remain unchanged at that value contributed by the holes alone; since for each trapped electron there is, due to the requirement of space charge neutrality, one free hole. Thus in this limit $\Delta\sigma = nq\mu_+$. The ratio of the two limiting values of initial amplitude is $(\mu_+ + \mu_-)/\mu_+$. Rough measurements on a particular silicon specimen (223*B*) gave 3 for this ratio. If we take the values from recent mobility studies[9] $\mu_+ = 500$ cm²/volt-sec and $\mu_- = 1200$ cm²/volt-sec, we should predict a ratio of 3.4, which agrees within the accuracy of the present ratio measurement.

For this specimen the mean lifetime of electrons in the conduction band was measured as $\tau_r = 20$ μsec. Since the response time of the measuring system was $\sim 10^{-7}$ sec, we would conclude that when most of the traps are empty τ_t is less than or the order of 10^{-7} sec. Thus with the traps empty an electron in the conduction band is much more likely to be trapped in a temporary trap than to recombine, i.e., to be trapped at an ordinary recombination center. We are therefore led to the concept of multiple trapping: an electron is trapped, emitted by thermal action back into the conduction band, retrapped, re-emitted, etc., until it is finally removed from the conduction band by recombination with a free hole at a recombination (deathnium) center. The continuing increase in the decay time as the external dc illumination is decreased is further evidence for the multiple trapping process.

[9] M. B. Prince, Phys. Rev. **93**, 1204 (1954).

EXPERIMENTAL EVIDENCE FOR TWO SETS OF TRAPS

We shall present next experimental evidence for the existence of two sets of traps in *p*-type silicon. The evidence comes primarily from the observation of the change in photoconductivity as a function of time after external illumination is removed from a specimen. This observation is similar to the pulsed photoconductivity measurement described previously, but differs in that the light source is intense enough to saturate the traps before it is turned off.

Two variations in the experimental setup were employed to gain improved low-frequency response. In the first variation the spark light source was replaced by a battery-operated tungsten lamp and sectored disk light "chopper" as a shutter; the video amplifiers by a direct coupled preamplifier followed by either a dc oscilloscope (DuMont 304) or additional amplifiers and a Sanborn pen recorder. As connected, the high-frequency response of the setup with the oscilloscope was about 20 kc/sec and the sensitivity 10^{-3} volts/cm deflection. With a Sanborn recorder the high-frequency response was 100 cps and the detection limit about 200 μv. In the second variation for measuring very long time constants a bridge arrangement was used with an L and N dc amplifier (50-μv full scale) coupled to a G.E. pen recorder. Thus the combination of these three experimental arrangements together with the wide-band equipment described above was capable of measuring photoconductivity changes over a time range from about 10^{-7} sec to 10^3 sec or longer.

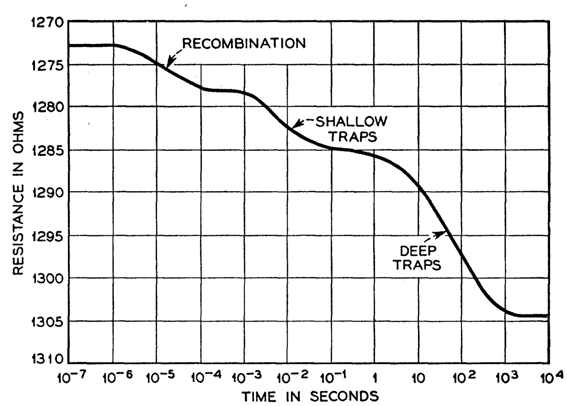

FIG. 4. Change with time of the resistance of *p*-type Si rod 223-*B* after a strong light has been removed from the specimen. The photoconductivity of the rod decays in three well-defined steps, the first (in sequence of time) is attributed to recombination of electrons in the conduction band; the second is attributed to the emptying of shallow traps; and the third is attributed to the emptying of deep traps.

With this apparatus the change in conductivity *versus* time shown in Fig. 4 was obtained for a particular silicon specimen (*223B*) after a strong source of light was suddenly removed from the specimen by interposing the sectored disk. Figure 5 is a reproduction of a photograph of an oscilloscope trace which shows all three decay components. Here change in conductivity is shown as a function of time. Consider the highest trace. At zero time the shutter is closed cutting off the light reaching the silicon specimen. The conductivity drops immediately because of recombination in the conduction band (this time constant is not resolved on the photograph). There follows a slower decay which takes place in tens of milliseconds. The remaining traces, photographed at the times indicated, show a much slower decay in conductivity which takes place in tens of seconds.

If the experiment is repeated successively under conditions such that the intensity of the pulsed light is decreased each time, one observes that first the amplitude of the fast component ($\tau \sim 20\ \mu$sec) decreases and disappears; next the amplitude of the 10^{-2} sec component decreases and subsequently disappears; and then with lower initial light intensities the initial amplitude of the 260-sec component decreases.

Almost the reverse of this sequence can be brought about by starting as before but, instead of decreasing the source light intensity, gradually increasing the dc ambient light falling on the crystal. Ordinary room light is sufficient to prevent the observation of the 260-sec component. Additional light is needed to prevent detection of the 10^{-2}-sec component. There was no evidence, however, that the fast component could be eliminated.

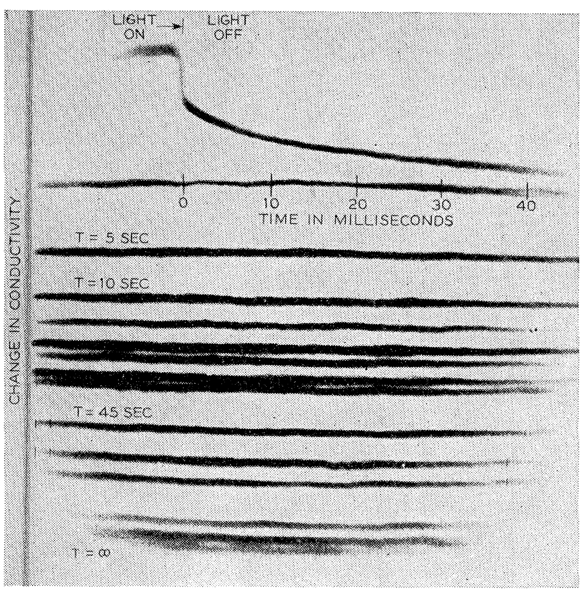

FIG. 5. Photograph of an oscilloscope pattern showing the three decay components in *p*-type Si (specimen *223B*). The external light source is turned off (by a shutter) at $t=0$. The immediate decay in photoconductivity, seen in the highest trace, is attributed to recombination of electrons in the conduction band which is fast compared with the shutter speed. This is followed by a slow decay which takes place in tens of milliseconds. The remaining traces, photographed at the times indicated, show a much slower decay component which takes place in tens of seconds.

This last series of experiments demonstrates, we believe, that two distinct sets of traps for electrons are present in the silicon sample at room temperature. The fast (20-μsec) decay we have already associated with recombination from the conduction band, that is normal lifetime, before either of the sets of traps unloads appreciably. The intermediate component (10^{-2} sec) we associate with the decay of a set of relatively shallow traps. The slowest component (260 sec) we associate with the decay of a set of deeper traps.

The conclusion previously reached that multiple trapping occurs in the *p*-type specimen applies so far only to the shallow traps, for the effects observed in the drift mobility experiments could only be associated with the shallow traps. Under the conditions of that experiment the deep traps were filled by room light, and in any case the mean time an electron spends in a deep trap, as we shall see, is so long that it could not be observed in that experiment.

An independent experiment indicates that the deep traps also decay by a multiple trapping process. A third electrode was attached to the center of a silicon rod, and it was mounted in a bridge circuit, Fig. 6, so that the rod made up two arms of the bridge. Light was then shone for a second or two on part of the silicon rod comprising the left arm of the bridge. This unbalanced the bridge, as shown at the bottom of Fig. 6, in the direction expected for higher conductivity in that arm. In a time *the order of tens of seconds, after the light was cut off*, however, the bridge became unbalanced in the opposite direction indicating that the right arm was then of higher conductivity than the left arm. We interpret this experiment as direct evidence that electrons initially trapped in the left arm were moved due to the applied electric field into the right arm and became trapped there. Thus, multiple trapping occurs in the deep traps. This experiment also is evidence that recombination does not remove all the electrons from the deep traps.

The shape of the two trapping components of the decay curve, Fig. 4, is additional evidence of multiple trapping in both sets of traps. The components are not simple exponential functions of time as would be the case if the electrons were trapped but once.

VOLUME OR SURFACE EFFECT

By masking off the electrodes from the incident light it is rather easy to show that the delayed photoconductivity (trapping) effects are associated with the body of the semiconductor rods and not with some spurious effect at the electrodes. Also these rods show no rectification effects when the current direction is reversed.

There remains the question as to whether we are observing a surface or volume effect, or a combination of the two. It is conceivable that the entire resistivity change occurs in the narrow region within a Debye length ($\sim 10^{-4}$ cm in 20-ohm-cm silicon) of the surface. The evidence against this hypothesis is twofold. First, the decay curves (Fig. 4) are the same when the electron-hole pairs are formed (by "penetrating" light) rather uniformly throughout the volume as when they are formed preponderantly at the surface. Second, the decay curves are the same when the surface of the rod is highly polished, when it is etched, or when the specimen is sandblasted. Sandblasting increases the surface area by a factor of two or more, and the depth of the surface pits is greater than a Debye length.[10]

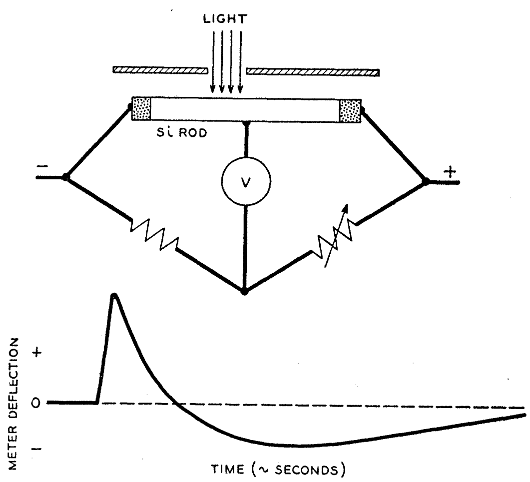

FIG. 6. Schematic representation of experiment which shows that electrons are trapped more than once in the deep traps in p-type silicon. The bridge is balanced initially with no light falling on the specimen. Light shining on part of the specimen comprising the left arm of the bridge unbalances the bridge because of electron trapping, and the meter deflects in the positive direction. The subsequent reversal of the meter which occurs tens of seconds after removal of the light shows that at a later time more electrons are trapped in the right arm than in the left arm.

The decay curves do change markedly, however, between different crystal specimens. We therefore conclude that these traps are located in the volume of the silicon.

DETERMINATION OF THE TRAPPING PARAMETERS—RESULTS

There remains to illustrate the degree of quantitative agreement between experiment and the multiple trapping model, which is treated mathematically in the Appendix. There are two sets of quantities that can be measured: amplitudes of the components and time constants. From the saturated initial amplitudes the number of normally unfilled traps is obtained, and from the decay rates come the constants of the traps.

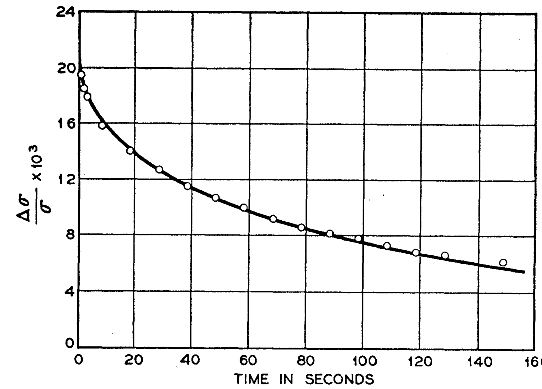

FIG. 7. The decay in photoconductivity as a function of time caused by the deep traps in p-type Si 223B. The ordinate is the fractional change in conductivity, and zero time on the abscissa is the instant the light is removed from the specimen. The open circles are experimental points, and the solid line is a fit of Eq. (10), Appendix, to these points. The values of the parameters in the equation that are determined by the fit are given in the text.

Let us first consider the deep traps in a particular p-type specimen. In Fig. 7 the open circles are experimental points taken from a record made by a pen recorder of the fractional change in conductivity of silicon specimen 223B as a function of time. This is quite obviously not a simple exponential but one in which the decay rate decreases progressively with time. According to the analysis of the multiple trapping model given in the Appendix the effective time constant of decay τ at any time t is given by Eq. (13):

$$\tau = \tau_g + \tau_r \tau_g N S v (1-y),$$

where τ is defined by $\tau^{-1} = -(1/y)dy/dt$, τ_g is the mean time that an electron spends in a trap, τ_r is the mean lifetime of electrons in the conduction band, N is the density of normally unfilled traps, S is the cross section for capture of electrons in traps, v is the arithmetic mean thermal velocity, and y is the fraction of traps filled. The solid line of Fig. 7 is a fit of Eq. (13) to these experimental data. The values of the parameters determined by the fit are: density of normally unfilled deep traps, $N = 1.0 \times 10^{13}/\text{cm}^3$, the time constant at infinite time, as given by Eq. (6) of the Appendix, $\tau_\infty = \tau_r \tau_g N S v = 260$ sec, $\tau_g \simeq 1$ sec, and $\tau_r = 20 \times 10^{-6}$ sec. The thermal velocity v for a particle having the mass of a free electron at room temperature is 1.07×10^7 cm/sec. Substituting these values into Eq. (6) we may estimate the capture cross section of the deep traps $S \simeq 10^{-13}$ cm^2.

The data for the shallow traps in specimen 223B shown in Fig. 5 are not accurate enough to warrant a careful fit to Eq. (13). Instead we have measured directly the time constant for the shallow trap τ_∞ and the initial conductivity (when all the traps are filled). From these we find the concentration of shallow traps not normally filled $N = 2 \times 10^{12}/\text{cm}^3$ and $\tau_\infty = 10^{-2}$ sec. From the drift velocity experiment mentioned earlier

[10] We are indebted to W. Shockley for discussions of this point.

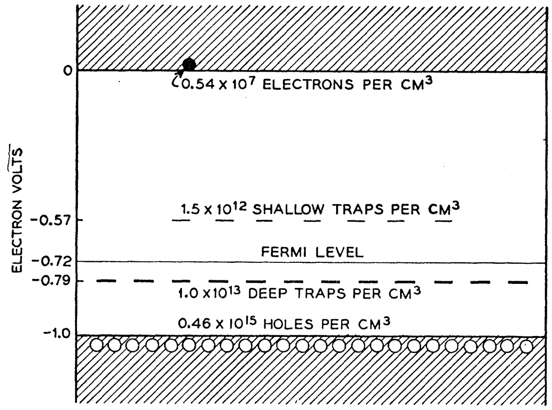

FIG. 8. Diagram depicting the number and relative energy of the traps for electrons in p-type Si 223B. Zero of energy is the bottom of the conduction band. The numbers given were computed assuming the specimen to be at room temperature.

we obtain τ_g for the shallow traps[11] $\simeq 50\times10^{-6}$ sec. Since $\tau_r=20\times10^{-6}$ sec, we find using Eq. (6) that the time before trapping in a shallow trap $\tau_t=1.2\times10^{-7}$ sec and the capture cross section of a shallow trap $S=4\times10^{-13}$ cm^2.

It is evident that the cross sections associated with the trapping of electrons in deep and shallow traps are large on an atomic scale. Wannier of these Laboratories has estimated[12] a limiting value for τ_t (not cross sections directly) by assuming that the trapping process involves emission of a phonon by a very slow electron. He finds that the free time before trapping of electrons in silicon $>10^{-9}$ sec. This limit is two orders of magnitude less than the trapping time $(NSv)^{-1}$ for either the deep or shallow traps, and therefore lends credibility to the large values obtained for their capture cross sections.

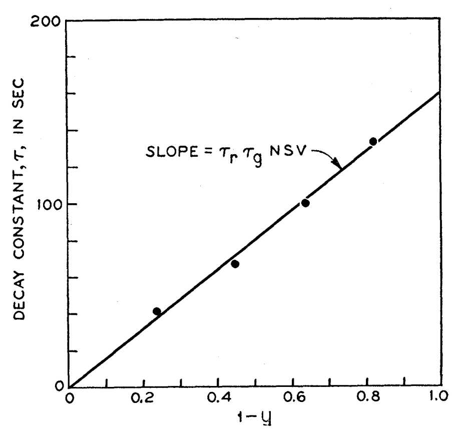

FIG. 9. Plot of the apparent time constant τ as a function of $(1-y)$, the fraction of deep traps empty (specimen VI-550-1, $\rho=17$ ohm cm). According to the simple multiple-trapping model Eq. (13), this plot should be a straight line with intercept at $y\equiv n_2/N=1$ equal to τ_g. The quantity τ_g is too small to be resolved on this time scale.

[11] The mean time in a shallow trap, τ_g, should be the decay time of the "straggle effect" in the drift velocity experiment when the electrons have a small probability of being trapped once in traveling from emitter to collector and therefore a very small or negligible change of being trapped twice. This can be arranged experimentally by having enough ambient (dc) light falling on the specimen to fill all the shallow traps, and then reduce the ambient light intensity just a little so that some trapping occurs.

[12] G. H. Wannier, Phys. Rev. **91**, 207(A) (1953).

DEPTH OF TRAPS

A well-known argument involving detailed balance, based upon the assumption of thermal equilibrium, permits us to estimate the depth[13] of the traps below the conduction band. This formula[14] in a form useful for the present calculations is

$$\exp[-(E_c-E_T)/kT]=N_c\tau_g/N\tau_t.$$

Here E_c-E_T equals the energy difference between the traps and the conduction band, k is Boltzmann's constant, T is the absolute temperature, $N_c=2.41\times10^{19}/\text{cm}^3$ at room temperature is the so-called equivalent density of states in the conduction band, assuming a spherical, nondegenerate band, and τ_g, τ_t, and N refer to the traps as previously defined. Here we have ignored the statistical weight of the traps since it will not affect things much. Since closely $\tau_g/\tau_t=\tau/\tau_r$, the ratio τ_g/τ_t is known much more accurately from these experiments than either of the quantities is known by itself. Upon substituting the known quantities in the detailed balance equation we find, $E_c-E_{T1}=0.57$ ev for the shallow traps and $E_c-E_{T2}=0.79$ ev for the deep traps. From the measured resistivity of specimen 223B, *viz.*, $\rho=27$ ohm cm, (E_c-E_F), where E_F is the Fermi level, is $\sim$0.72 ev. Thus the deep traps lie about $3kT$ below the Fermi level. The thermal equilibrium situation in this specimen for room temperature is given in Fig. 8. The numbers given are computed assuming that the electron mass is the mass of a free electron.

By definition, N, the number of normally empty trapping sites, is given by $N=N_0(1-f)$ where N_0 is the total number of trapping centers and

$$f=[1+\exp(E_T-E_F)/kT]^{-1}$$

is the Fermi factor. Thus the number of deep trapping centers is $\sim1.7\times10^{14}/\text{cm}^3$, whereas the number of shallow trapping centers very closely equals the number of normally empty shallow traps.

RESULTS FOR A NUMBER OF SPECIMENS AND RECOMBINATION IN THE DEEP TRAP

Since, as we have seen, the multiple-trapping model appears to agree quantitatively with experiments on specimen 223B, the question arises as to whether the analysis is generally applicable to p-type silicon. It will be shown in this section that this is the case for the

[13] Efforts to observe the trap depth by the change in photoconductivity associated with the absorption of infrared radiation have been unsuccessful. The sensitivity of the apparatus was such that the change in conductivity with light which was observed could be accounted for by a change in temperature of the silicon rod of about 0.001°C.

[14] A further discussion of the relationship and justification for its use will be found in Part II of this report.

deep traps provided that an additional loss mechanism for electrons is added to the model,[15] *viz.*, recombination of a trapped electron directly from the deep trap.

A convenient way to analyze a multiple-trapping decay curve, such as that in Fig. 7, is to plot the apparent time constant τ as a function of $(1-y)$, the fraction of traps empty. According to Eq. (13), this plot should be a straight line with intercept τ_g at $(1-y)=0$ and of slope $\tau_r\tau_g NSv$. Such a plot is given in Fig. 9 for specimen (VI-550-1) which is p-type with $\rho=17$ ohm cm. In this case the intercept τ_g is not resolved, since there is so much multiple trapping.

In higher-conductivity material straight-line plots of τ *vs* $(1-y)$ are not obtained, indicating a deviation from the model as presented. An example of this is shown in Fig. 10 for silicon specimen (VI-277), $\rho=1.9$ ohm cm. This deviation can be accounted for quantitatively by assuming that an electron in a trap has a certain probability of recombining with a hole without first returning to the conduction band. If the decay

TABLE I. Summary of data on deep traps in p-type silicon analyzed by assuming the multiple trapping model with recombination.

Sample	Conductivity (ohm cm)$^{-1}$	Trap concentration[a] cm^{-3}	τ_∞ sec	τ_r μsec	τ_b sec	$S\tau_g=\tau_\infty/\tau_r Nv$ cm^2 sec
259-*H*	1.02	1.48×10^{14}	41.6	~0.5	32	0.5×10^{-13}
323-*D*	0.625	2.83×10^{14}	516	4	78	0.43×10^{-13}
277	0.524	0.92×10^{14}	526	11	111	0.49×10^{-13}
546-1	0.14	1.88×10^{13}	435	20	∞	1.1×10^{-13}
550-1	0.0599	1.00×10^{13}	161	19	∞	0.79×10^{-13}
223-*B*	0.0373	1.00×10^{13}	260	33	∞	0.74×10^{-13}
568*A*-3	0.0369	3.82×10^{12}	150	26	∞	1.41×10^{-13}
509-2	0.021	1.35×10^{12}	0.7	1.1	∞	0.46×10^{-13}
580*A*-3	0.0178	7.1×10^{11}	23	23	∞	1.32×10^{-13}
580*A*-1	0.015	6.65×10^{11}	19	29	∞	0.91×10^{-13}

[a] Corrected for variation in mobility with conductivity.

rate from the trap through this process is $(1/\tau_b)$, then it is easily shown that the observed $\tau(y)$ is given by [see Eq. (31) of the Appendix],

$$(1/\tau)=(1/\tau_b)+(1/\tau)_{old},$$

where $(1/\tau)_{old}$ is that defined by Eq. (13). If there is sufficient multiple trapping so that τ_g is negligible compared with the other term in $(1/\tau)_{old}$, then according to the above equation a plot of $(1/\tau)$ *versus* $(1-y)^{-1}$ should yield a straight line of slope $(\tau_r\tau_g NSv)^{-1}$ and intercept at $(1-y)^{-1}=1$ of $[\tau_b^{-1}+(\tau_r\tau_g NSv)^{-1}]$. The data of Fig. 10 are replotted in this way in Fig. 11. The indication that this analysis is correct comes not only from the fact that the data plot in a straight line. In addition, the value of $S\tau_g$, which is a property of the deep trap itself, turns out to be within experimental error just that which is obtained in higher-resistivity specimens for which $1/\tau_b$ is negligible.

[15] J. A. Hornbeck and J. R. Haynes, Phys. Rev. **94**, 1437(A) (1954).

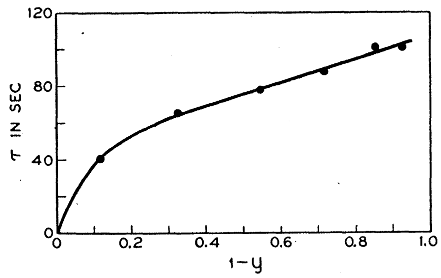

FIG. 10. Plot similar to that in Fig. 9 showing a deviation from the simple multiple-trapping model (Specimen VI-277, $\rho=1.9$ ohm/cm).

Data for a number of different specimens derived from analyses as described above are summarized[16] in Table I.

From Table I, we have computed the most probable value of $S\tau_g$ and find it equal to $(0.81\pm0.25)\times10^{-13}$ cm^2 sec, which corresponds to a single deep-trapping level 0.78 ev below the conduction band. Specimen (509-2) was carefully chosen because in it τ_∞ is the same order of magnitude as τ_g, so there is a measurable intercept when its decay curve is plotted as in Fig. 9. From this we obtain $\tau_g\simeq0.3$ sec, whence $S\simeq3\times10^{-13}$ cm^2.

The consistency of the results in Table I gives us some confidence in the analysis, and we therefore feel justified in pursuing further recombination in the deep trap as characterized by τ_b. These data from Table I together with data for higher-conductivity specimens with single exponential decays (because τ_b predominates) are shown in Fig. 12, where the rate $1/\tau_b$ is plotted as a function of the hole concentration. Within the experimental error, $1/\tau_b$ is found to be proportional to the square of the majority carrier concentration, and the rate of the recombination is low as if "forbidden" by a selection rule. We do not know what the recombination mechanism is, and we shall not speculate on it at this time.

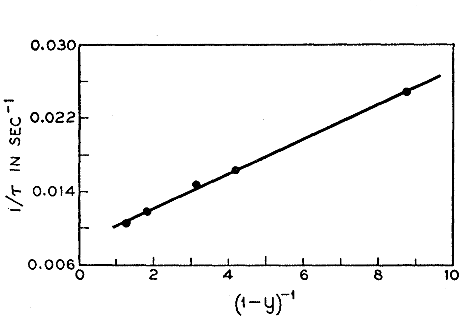

FIG. 11. Replot of the data, Fig. 10, as suggested by Eq. (31) which is derived on the assumption that, in addition to simple multiple-trapping, recombination in the trap also occurs.

[16] In studying the deep traps, it is particularly important to keep stray light from falling on the sample. Not only does this affect the measurement of the trap density, but also the values of the trapping parameters. See Appendix, Case IV.

CORRELATION BETWEEN DEEP-TRAP CONCENTRATION AND SAMPLE CONDUCTIVITY

A correlation has been found between the deep-trap concentration and conductivity of the *p*-type silicon specimens. This is shown in Fig. 13. A semiquantitative interpretation of these results is that the material has nearly a constant number ($\sim 10^{15}$ cm^{-3}) of trapping centers and that the number of "cocked" or empty traps varies with the position of the Fermi level, which itself is a function of conductivity. Recently[17] it has been found that the trap concentration can be reduced if when the single crystal is grown, the seed is not rotated. We have no explanation for this effect, nor do we know at this time what causes the deep or shallow traps.

ACKNOWLEDGMENTS

We wish to thank many of our colleagues for considerable help during the course of this investigation. These include H. R. Moore, who guided the instrumentation, E. Buehler, who supplied silicon crystals, W. C. Westphal, who assisted us generally, W. Shockley, C. Herring, G. H. Wannier, and P. A. Wolff, who supplied valuable discussions, and M. D. Underwood, who made some of the measurements of trap concentrations.

APPENDIX: TRAPPING KINETICS

With the multiple-trapping model suggested by experiment, we shall now consider the parameters that enter into this volume process and deduce for comparison with experiment the mathematical form of the decay curves on the basis of the model.[18] In these calculations we shall be concerned with deviations from thermal equilibrium.

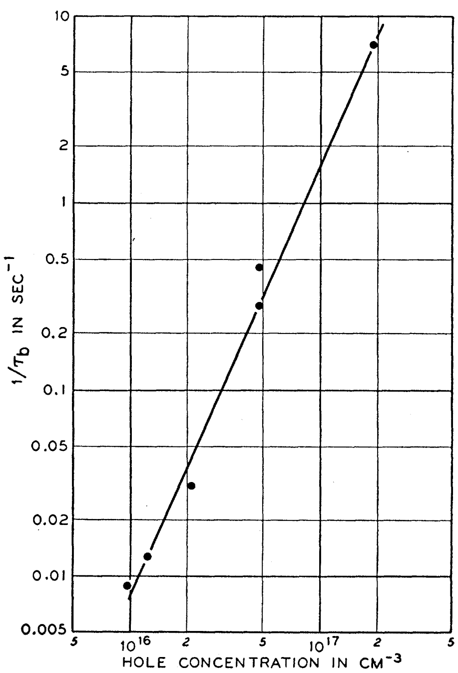

FIG. 12. Plot of the rate of recombination in the deep traps, $1/\tau_b$, as a function of the majority carrier concentration. Within the experimental error, the slope of the line equals 2.

[17] Hannay, Haynes, and Shulman, Phys. Rev. **96**, 833 (1954).

Let n = the excess density of electrons in the conduction band, n_1 = the excess density of electrons in traps, $r \equiv 1/\tau_r$ = rate of recombination of excess electrons in the conduction band, $g \equiv 1/\tau_g$ = rate of generation of electrons from traps, S = cross section for capture of electrons in traps, N = density of normally unfilled traps, v = arithmetic mean thermal velocity, l = rate of generation of electron-hole pairs per cm^3 by external light, and $NSv \equiv 1/\tau_t$ = rate of trapping of electrons when all traps are empty. With these definitions we may immediately write down the differential equations which follow for the case in which there is a single set of volume traps. We shall see later that it is unnecessary to consider in detail the case of two sets of traps because the time constants of the traps in *p*-type silicon usually are so well separated.

$$dn/dt = l - rn + gn_1 - n(N - n_1)Sv,$$
$$dn_1/dt = -gn_1 + n(N - n_1)Sv. \quad (1)$$

In all the following cases the observed change in conductivity for a *p*-type specimen is given by

$$\Delta\sigma = nq(\mu_- + \mu_+) + n_1 q\mu_+. \quad (2)$$

As we shall see, the first term of Eq. (2) is negligible compared to the trapping term except (a) at very high values of l and (b) for a short time (the order of the recombination time, τ_r) after the light is turned off. Thus $\Delta\sigma = n_1 q\mu_+$ and is a direct measure of n_1, the number of trapped electrons.

Case I. Steady State

In the steady state, $dn/dt = dn_1/dt = 0$, and the solution of (1) is[19]

$$n = l/r,$$
$$n_1/N = (1 + g/nSv)^{-1}. \quad (3)$$

Case II. Transient Solution for No External Light

Suppose that external light is shone on the crystal, and at $t = 0$ the light is turned off, i.e., for $t < 0$, $l = l_0$ and for $t \geq 0$, $l = 0$. We shall consider first the asymptotic form of the solution. For sufficiently large t, n_1 will become small compared to N and Eqs. (1) become

[18] H. Y. Fan, Phys. Rev. **92**, 1424 (1953), independently has considered parts of this same problem.

[19] The equivalent steady-state solution of the problem when two sets of traps are considered is $n = l/r$, $n_1/N_1 = (1 + g_1/nS_1v)^{-1}$, and $n_2/N_2 = (1 + g_2/nS_2v)^{-1}$. Here the subscripts (1) refer to one set of traps and the subscripts (2) to the same quantities for the second set of traps. Physically, the important point here is that the fraction of the traps of either set filled in the steady state by light is independent of the existence of the other set.

linear, i.e., for large t

$$dn/dt \simeq -rn + gn_1 - (NSv)n,$$
$$dn_1/dt \simeq -gn_1 + (NSv)n. \quad (4)$$

It is easy to show that the solution of (4) is given to a good approximation by[20]

$$n \propto \exp(-t/\tau_\infty),$$
$$n_1 \propto \exp(-t/\tau_\infty), \quad (5)$$
$$\tau_\infty = \tau_r + \tau_g + \tau_r\tau_g NSv.$$

Thus the decay curve approaches asymptotically a single exponential of time constant τ_∞. It turns out that in almost all cases for p-type silicon $(\tau_r+\tau_g) \ll \tau_r\tau_g NSv$, so that[21]

$$\tau_\infty \simeq \tau_r\tau_g NSv \equiv \tau_r\tau_g/\tau_t, \quad (6)$$

where $\tau_t = (NSv)^{-1}$ is the mean free time an electron spends in the conduction band before trapping when all the traps are empty.

Because the recombination rate is small compared to NSv, as approximate solution of (1) for $l=0$ can be obtained. This solution can easily be more exact than the experimental error in measurement. We shall normalize Eqs. (1) in order to illustrate the extent of the approximation. We define some dimensionless parameters as follows:

$$T = (rg/NSv)t, \quad G = g/NSv, \quad R = r/NSv, \quad x = nSv/g, \quad y = n_1/N. \quad (7)$$

Then for $l=0$ Eqs. (1) become

$$Gdx/dt = -x + R^{-1}[y - x(1-y)], \quad (8a)$$

$$dy/dT = -R^{-1}[y - x(1-y)]. \quad (8b)$$

As we shall demonstrate later, G is the order of 10^{-6} for the deep traps and 2×10^{-3} for the shallow traps, whereas R^{-1} may be greater than ten and usually $|Gdx/dT| \ll |dy/dT|$. Thus we set $Gdx/dT=0$ in Eq. (8),[22] i.e.,

$$x = y(1+R-y)^{-1}, \quad (9)$$

[20] Figure 4 helps in arriving at the equivalent solution to Eqs. (5) for a two-trap model. According to Fig. 4, the shallow traps all unload before the number of electrons in the deep traps changes appreciably. Thus we have to consider only the effect of the vacant shallow traps on the decay while the deep traps are unloading. To begin with, we don't expect much of an effect because decay times associated with the shallow traps are several orders of magnitude smaller than those associated with the deep traps. It is easy, however, to obtain an approximate solution for the two-trap case if one assumes (a) that the shallow traps are substantially empty, and (b) that the fraction of the deep traps filled is small, *viz.*, $(n_2/N_2 \ll 1)$. For this case the exponential decay time of the system $\tau_{\infty 2}$ is given by

$$\tau_{\infty 2} = \tau_r + \tau_{g1} + \tau_{g2} + \tau_r\tau_{g1}/\tau_{t1} + \tau_r\tau_{g2}/\tau_{t2}.$$

For the case in hand, the last term of this expression turns out usually to be at least 100 times as large as any of the other terms, and it comes from a single-trap model.

[21] This formula is given by J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).

[22] We are indebted to Dr. R. W. Hamming for pointing out this approximation. A more complete justification for this approximation is given in this Appendix, Case III.

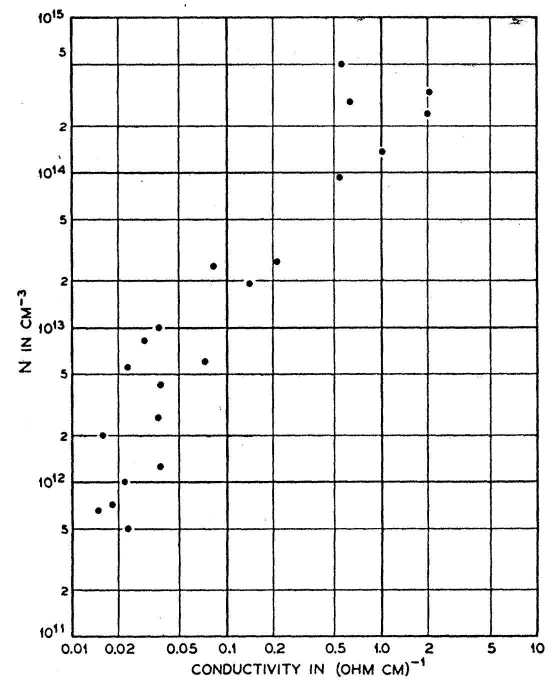

FIG. 13. Plot of the number of empty (deep) traps *vs* sample conductivity showing a rough correlation which can be accounted for largely by the position of the Fermi level if the number of trapping centers in each specimen is roughly constant.

and integrate. This yields, for the initial condition that $y=y_0$ at $t=0$,

$$\exp-[T/(1+R)] = (y/y_0)\exp[(y_0-y)/(1+R)]. \quad (10)$$

According to Eq. (10), for sufficiently large t, y decays exponentially with a time constant τ_∞ given by

$$\tau_\infty = \tau_g + \tau_r\tau_g NSv, \quad (11)$$

which differs only by the negligible quantity τ_r from Eq. (5).

We wish to emphasize particularly one property of the multiple-trapping equation (10) above which is quite useful in reducing experimental data. We first define the apparent time constant of decay, τ, at any time t to be

$$1/\tau = -(1/y)dy/dt. \quad (12)$$

Now using Eq. (10), we find

$$\tau = \tau_g + \tau_r\tau_g NSv(1-y). \quad (13)$$

In practice, from an experimental decay curve $y(t)$ τ is obtained and plotted *vs* $(1-y)$, the fraction of traps empty. This plot (in the absence of any recombination directly in the trap—see Appendix Case V) is a straight line of slope $\tau_r\tau_g NSv$ and intercept at $t=0$ and $y=1$, of τ_g.

Case III. Solution Near Zero Time and Value of $x = nSv/g$

It has been stated without proof that the contribution to the added conductivity of the conduction-band electrons is negligible compared with the contribution of the holes associated with trapped electrons. We shall now examine the range of validity of this statement and the approximation made in the last section leading to Eq. (10).

If external light has been shining on the crystal long enough for a steady state to be established, then from Eqs. (3),

$$(n_0/N)\equiv Gx_0=l/Nr,\quad (n_{10}/N)\equiv y_0=(1+1/x_0)^{-1}. \tag{14}$$

If the external light is turned off at $t=0$, then for all time both dx/dT and dy/dT are negative, i.e., both the concentration of electrons in the conduction band and the concentration of trapped electrons decay with time. This is shown in the second part of this section. From Eqs. (8), a direct consequence of this is that for all time,

$$-x+R^{-1}[y-x(1-y)]<0,\quad -R^{-1}[y-x(1-y)]<0. \tag{15}$$

The relationships (15) may be expressed as the following inequality:

$$\frac{y}{1-y}>x>\frac{y}{1-y+R}. \tag{16}$$

As will be seen, for both deep and shallow traps $R=r/NSv\sim 0.005$ in the silicon specimen *223B*. Thus for time greater than that at which $(1-y)$ is several times R, i.e., $(1-y)\simeq 0.02$, there is no appreciable difference between $(1-y)$ and $(1-y+R)$, and quite accurately $x=y(1-y+R)^{-1}=y(1-y)^{-1}$. In this region Eqs. (9) and (10) are the solution. The expression for x can be written in the following form, making use of the inequality (16)

$$n/N\leq Gy/1-y.$$

For the shallow traps $G\simeq 2\times 10^{-3}$ and for the deep traps $G\simeq 10^{-7}$. Thus when $(1-y)\geq 0.02$, $n/n_1<0.1$ for the shallow traps and for the deep traps, $n/n_1<0.5\times 10^{-4}$; when $(1-y)\geq 0.1$, $n/n_1<0.02$ for the shallow traps. We conclude, then, that over almost the entire decay curve for either deep or shallow traps $n_1\gg n$ and $\Delta\sigma\simeq n_1 q\mu_+$.

Next we shall consider the solution to Eqs. (8) for the shallow traps in the region near $t=0$, when the approximate solution given by Eqs. (9) and (10) is invalid. Equation (8) above is generally satisfactory for the deep traps. For time in the immediate vicinity of $t=0$ we expect that $dx/dT\gg dy/dT$. If $dy/dT\simeq 0$, then from Eq. (8a) $Gdx/dT\simeq -x$. This suggests that we try a solution of the form

$$x=x_0\exp(-T/G)+f(T),$$

whence

$$Gdx/dT=x_0\exp(-T/G)+df/dT \tag{17}$$

and

$$-Rdy/dT=y-(1-y)[x_0\exp(-T/G)+f]. \tag{18}$$

At $T=0$, $f(T)=0$; in some region $x_0e^{-T/G}\gg f$. Let us solve Eq. (18) in this region by neglecting f, i.e., letting $T/G\equiv T_r\equiv rt$, and $G/R\equiv\lambda$,

$$-\lambda^{-1}dy/dT_r\simeq y-(1-y)x_0\exp(-T_r). \tag{19}$$

It follows directly that

$$y\simeq\lambda x_0F^{-1}(T_r)\int e^{-T_r}F(T_r)dT_r+AF^{-1}(T_r), \tag{20}$$

where A is a constant of integration and $F(T_r)$ is

$$F(T_r)\equiv\exp[\lambda(T_r-x_0e^{-T_r})]. \tag{21}$$

Successive integration by parts expands Eq. (20) into the following asymptotic series

$$y\simeq 1-(e^{T_r}/x_0)+(1+\lambda^{-1})(e^{T_r}/x_0)^2-(1+\lambda^{-1})(1+2\lambda^{-1})(e^{T_r}/x_0)^3+\cdots+(-1)^n\times\left(1+\frac{n-1}{\lambda}\right)\left(1+\frac{n-2}{\lambda}\right)\left(1+\frac{n-3}{\lambda}\right)\cdots\times(1)(e^{T_r}/x_0)^n+\cdots+AF^{-1}. \tag{22}$$

The solution comprising the first two terms of Eq. (22), it turns out, is valid for large enough values of T_r so that it overlaps the region in which the solution given by Eqs. (9) and (10) is valid. We must, however, adjust the arbitrary constant in Eq. (10) so that the two solutions fit together continuously. Our final result is for $0<T_r\leq T_{rc}$, where $T_r=T/G$,

$$x=x_0e^{-T_r},\quad y=1-x_0^{-1}e^{T_r}. \tag{23}$$

For $GT_{rc}=T_c\leq T<\infty$,

$$x=y(1-y+R)^{-1},\quad \frac{y}{y_c}\exp\left(\frac{y_c-y}{1+R}\right)=\exp\left(\frac{-(T-T_c)}{1+R}\right), \tag{24}$$

where

$$T_{rc}=\ln(x_0\sqrt{G}),\quad x_c=1/\sqrt{G},\quad y_c=1-\sqrt{G}. \tag{25}$$

The critical values, *viz.*, x_c, y_c, and T_c, are chosen such that to within a negligible error both the slopes and absolute magnitudes of the two expressions (23) and (24) for y are equal.

We now can see the range in which the series (22) needs to be valid: The relations (25) state that the maximum value of $(e^{T_r}/x_0)=\sqrt{G}$, and this is independent of x_0 and, therefore, the initial light intensity except that x_0 must be greater than x_c. If $x_0<x_c$, the solution Eq. (10) holds for all T; this is the case for the deep traps and any reasonable intensity of light prior to $T=0$. Although the series (22) eventually diverges if too many terms are retained, the error incurred by

keeping only the first two terms is less than the absolute magnitude of the next term.[23] By a similar argument for the case $T_r=0$, it can be shown that the term AF^{-1} is negligible, i.e., $A=0$. Since F^{-1} decreases with increasing T_r, AF^{-1} is negligible at all times in which we are interested.

We should point out that at $T_r=0$, Eqs. (23) give

$$\left.\frac{dy/dT_r}{dx/dT_r}\right|_0=\frac{1}{x_0^2},$$

which for large x_0 is consistent with our previous assumption in setting up this solution. Note also that at $T_r=0$, both derivatives are negative, which confirms an earlier assertion. It is easy to show, also, that $f(T)$ defined by Eq. (17) is very small and negligible.

Case IV. Transient Solution with Steady External Light

Another feature of the multiple-trapping model that can be tested by experiment is the variation of the decay curves with arbitrary ambient illumination. This in particular emphasizes the nonlinear character of the decay and illustrates the importance of stray light in affecting the values of the trap parameters as deduced from experiment.

Equation (14) states that steady illumination l_0 maintains an additional number of electrons n_0 in the conduction band and n_{10} in traps, where

$$n_0=l_0/r,$$
$$n_{10}/N=[1+g/n_0Sv]^{-1}. \tag{14}$$

Let us now consider deviations from this steady state due to a second light source which is turned off at $t=0$. The deviations u and u_1 in n and n_1, respectively are defined by

$$u=n-n_0,\qquad u_1=n_1-n_{10}. \tag{26}$$

On substitution of (26) into (1) we obtain

$$du/dt=-ru+(g+n_0Sv)u_1-u[(N-n_{10})-u_1]Sv,$$
$$du_1/dt=-(g+n_0Sv)n_1+u[(N-n_{10})-n_1]Sv. \tag{27}$$

Clearly Eqs. (27) have the same form as the normalized Eqs. (8) if we replace the parameters as indicated below:

$$\begin{aligned}&N\rightarrow N(1-n_{10}/N),\\ &g\rightarrow g(1-n_{10}/N)^{-1},\\ &x\rightarrow\frac{uSv}{g}(1-n_{10}/N),\\ &y\rightarrow u_1[N(1-n_{10}/N)]^{-1},\\ &T\rightarrow T(1-n_{10}/N)^{-2}.\end{aligned} \tag{28}$$

The relations (28) predict, for example, that the asymptotic decay constant τ_∞ will vary as the square of the fraction of traps that are not filled by the steady illumination. In the case of the deep traps, this has been checked quantitatively.

The kinetics associated with filling the traps, i.e., the case in which the traps are empty and at $t=0$ the external light is turned on, will not be discussed here because this case is not essential in establishing the trapping model. It may be pointed out that if the probability of an electron being trapped is substantially larger than the probability that it recombine, the electrons formed by the light will tend to fill up the traps before building up the steady-state concentration in the conduction band. If, however, the recombination rate greatly exceeds the trapping rate, then after the light is turned on, the steady-state concentration in the conduction band will build up (in the order of the recombination time) before appreciable trapping occurs.[24]

Case V. Trapping Kinetics with Recombination in the Trap

We now introduce a second loss mechanism for electrons, *viz.*, recombination in (or from) the trap. For the case $l=0$ (no external light), Eqs. (1) become

$$dn/dt=-rn+gn_1-n(N-n_1)Sv,$$
$$dn_1/dt=-(g+b)n_1+n(N-n_1)Sv. \tag{29}$$

Here $b\equiv1/\tau_b$ is the rate of recombination from the trap just as r is the rate of recombination from the conduction band. Now we make the same approximation that was used to solve Eqs. (8), and again we can handle the problem. We find

$$e^{-bt}=y^{(1+R)/(1+R+PR)}\left[\frac{1+R+PR-y}{R(1+P)}\right]^{PR/(1+R+PR)}, \tag{30}$$

for the approximate initial condition that for $t=0$, $y=1$. Here the notation is that defined by (7) with the addition that $P\equiv g/b$.

In the limit that $b\rightarrow0$, i.e., no recombination in the trap, Eq. (30) becomes Eq. (10), as it should. In the other limit, $b\gg g$, Eq. (30) approaches the limit $y=\exp(-bt)$, as it should. This case also is realized experimentally for material of sufficiently high conductivity (see, for example, Fig. 12).

As suggested in the text, analysis for the recombination effect τ_b is facilitated by plotting from the experimental data $\tau^{-1}\equiv-(1/y)(dy/dt)$ *vs* $(1-y)^{-1}$. From Eq. (30) we find

$$1/\tau\equiv-(1/y)(dy/dt)=1/\tau_b+1/[\tau_g+\tau_r\tau_gNSv(1-y)]. \tag{31}$$

This result justifies the procedure utilized in separating τ_b from the multiple trapping effects, e.g., Fig. 11, since the decay rate $1/\tau_b$ adds directly to the old rate defined by Eq. (13).

[23] We are indebted to Dr. R. W. Hamming for a discussion of asymptotic series.

[24] We have evidence for this latter case in n-type silicon at 300°K.

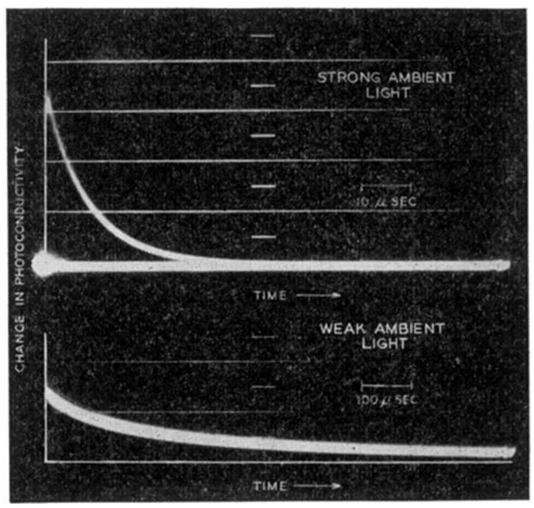

FIG. 3. Photographs of the oscilloscope trace in the experiment shown in Fig. 2. Top—with strong ambient light falling on a *p*-type silicon specimen, no trapping is observed and the decay in photoconductivity as a function of time represents the true lifetime of the added electrons. Bottom—without ambient light trapping occurs, and it controls the decay in photoconductivity.

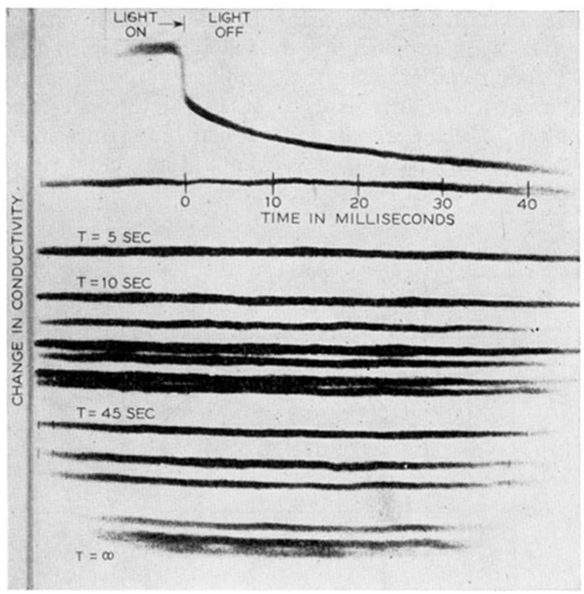

FIG. 5. Photograph of an oscilloscope pattern showing the three decay components in *p*-type Si (specimen 223*B*). The external light source is turned off (by a shutter) at $t=0$. The immediate decay in photoconductivity, seen in the highest trace, is attributed to recombination of electrons in the conduction band which is fast compared with the shutter speed. This is followed by a slow decay which takes place in tens of milliseconds. The remaining traces, photographed at the times indicated, show a much slower decay component which takes place in tens of seconds.