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# Photoexcited Electron Capture by Ionized and Neutral Shallow Impurities in Silicon at Liquid-Helium Temperatures*

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The capture rates for photoexcited electrons due to ionized phosphorus, arsenic, antimony, and bismuth donors as well as neutral boron, aluminum, gallium, and indium acceptors in silicon have been determined in the liquid-helium temperature region, using combined optical and paramagnetic-resonance techniques. The ionized-donor capture rates exceed by about an order of magnitude the values predicted from the theories of Lax and of Ascarelli and Rodriguez for capture of thermalized electrons. The capture rates are independent of temperature between 1 and 4°K, at variance with both theories, and their dependence on the ionization energy of the different donors also does not conform to the theoretical predictions. These results, as well as photoconductivity measurements as a function of charged-impurity concentration, demonstrate the inadequacy of any existing model of the low-temperature donor capture process for photoexcited electrons in silicon. Possible explanations of the results in terms of nonrandom impurity clusters or capture from hot-electron states are presented. The neutral-acceptor rates are about two orders of magnitude smaller than those of the ionized donors, are also independent of temperature between 1 and 4°K, and show a small dependence of about $I^{1/2}$ on the hole ionization energy of the impurities, compared with expected $T^{1/2}$ and $I^{-3/2}$ dependences from the theory for thermalized-electron capture by neutral centers. As in the case of the ionized donors, no presently available model appears adequate to explain the results.

## I. INTRODUCTION

IONIZED shallow donors in silicon have very large capture rates for electrons at temperatures in the liquid-helium region. They are of the order of $10^{-5}$ cm$^3$/sec at 1°K, which would correspond to capture cross sections of about $10^{-11}$ cm$^2$ if the electrons were thermalized, and have been named "giant traps" by Lax,[1] who first offered a detailed theoretical treatment of the capture process. The theory was subsequently modified by Ascarelli and Rodriguez,[2,3] who obtained cross-section magnitudes comparable to those obtained by Lax, but different temperature and ionization energy dependences. Neutral acceptors also serve as fairly efficient electron-capture centers in silicon, with capture rates about two orders of magnitude smaller than those of ionized donors. This smaller magnitude results from their attractive polarization potential in contrast to the Coulomb potential associated with the ionized impurities. The case of neutral acceptors[1] was also treated by Lax, who calculated the magnitude, temperature dependence, and ionization-energy dependence of the capture cross sections for thermalized electrons. At low temperatures, these two types of centers usually dominate the capture process.

The photoexcited electron-capture rates of ionized phosphorus impurities in silicon have previously been determined by Levitt and Honig,[4] using combined optical and paramagnetic-resonance techniques on double-doped *n*-type silicon. They obtained a result about an order of magnitude greater than the theoretically calculated value for thermalized electrons at 4°K, and a temperature dependence in the liquid-helium-temperature region at variance with the theory. A determination of the neutral-boron capture rate[5,6] has also previously been reported. In the present work, similar measurement techniques have been employed and capture-rate measurements have been extended to all of the shallow impurities in silicon. These include ionized phosphorus, arsenic, antimony, and bismuth donors, and neutral boron, aluminum, gallium, and indium acceptors. The impurity concentrations of the samples are in the vicinity of $5\times10^{15}$/cm$^3$ and the temperature range investigated is between 1.1 and 4.2°K. The dependence of the capture rates on impurity ionization energy is compared with the various theories. In addition, the kinetics of the optically induced charge transfer among the impurities and the consequent time-dependent photoconductivity are discussed. Some more complicated capture processes involving a distribution of trapping lifetimes due to impurity clusters and trapping from hot-electron states are considered in an attempt to account for the experimental results.

## II. MEASUREMENT OF ELECTRON CAPTURE RATES AND CAPTURE CROSS SECTIONS

### A. Samples

Experiments were performed on *n*-type silicon samples double-doped with shallow-donor and shallow-acceptor impurities. Sample impurity concentrations were determined at 4.2°K by a combined optical and paramagnetic resonance technique[5] which is illustrated

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[1] M. Lax, Phys. Rev. **119**, 1502 (1960).

[2] G. Ascarelli and S. Rodriguez, Phys. Rev. **124**, 1321 (1961).

[3] G. Ascarelli and S. Rodriguez, Phys. Rev. **127**, 167 (1962).

[4] R. S. Levitt and A. Honig, J. Phys. Chem. Solids **22**, 269 (1961).

[5] A. Honig, in *Proceedings of the International Conference on Semiconductor Physics, 1960* (Academic Press Inc., New York, 1961), p. 610.

[6] A. Honig and R. Levitt, Phys. Rev. Letters **5**, 93 (1960).

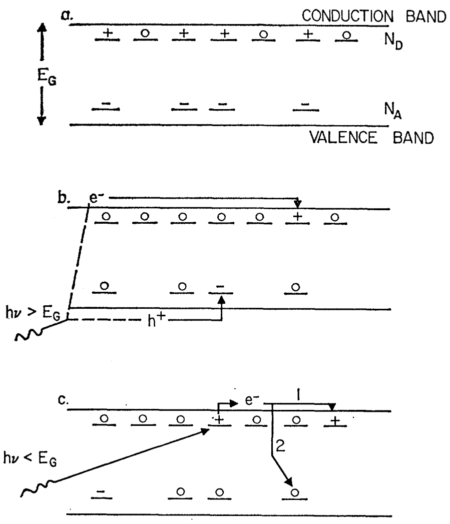

FIG. 1. Optical pumping and delocalized electron transfer in $n$-type compensated silicon. (a) Equilibrium charge state. (b) Intrinsic optical pumping process. (c) Extrinsic photon absorption-delocalized electron captured by either (1) charged donor or (2) neutral acceptor.

schematically in Fig. 1. The equilibrium impurity charge state is shown in Fig. 1(a). In this state, the electron-spin-resonance signal is proportional to $N_D - N_A$, where $N_D$ is the donor-impurity concentration and $N_A$ is the acceptor-impurity concentration. In Fig. 1(b), the change in charge state of the impurities brought about by intrinsic irradiation is illustrated. The intrinsic radiation generates electrons and holes which are captured primarily on the ionized donors and ionized acceptors, respectively, since the charged impurity capture rates are much larger than the neutral impurity capture rates. With the sample thus fully optically "pumped," the electron-spin-resonance signal is proportional to $N_D$. The resonance measurements at 4.2°K thus determine the ratio $N_D/(N_D - N_A)$. Combining this ratio with a room-temperature-resistivity measurement which yields $(N_D - N_A)$ results in the determination of the impurity concentrations to an accuracy of about 5%, for the concentration region corresponding to that of most of our samples. The impurity concentrations of the samples used in this work are listed in Table I.

TABLE I. Characteristics of compensated $n$-type silicon samples used in this study.

| Impurities | $\rho$ (Ω cm) | $N_A/N_D$ | $N_D$ (cm$^{-3}$) | $N_A$ (cm$^{-3}$) | Sample designation |
|---|---|---|---|---|---|
| P-B | 1.35 | 0.33 | $6.0\times10^{15}$ | $2.0\times10^{15}$ | P-B-Si 6.0-2.0-15 |
| P-Al | 1.42 | 0.50 | $7.6\times10^{15}$ | $3.8\times10^{15}$ | P-Al-Si 7.6-3.8-15 |
| P-Ga | 2.24 | 0.62 | $6.1\times10^{15}$ | $3.8\times10^{15}$ | P-Ga-Si 6.1-3.8-15 |
| P-In | 1.71 | 0.50 | $6.2\times10^{15}$ | $3.1\times10^{15}$ | P-In-Si 6.2-3.8-16 |
| As-B | 0.89 | 0.28 | $8.4\times10^{15}$ | $2.4\times10^{15}$ | As-B-Si 8.4-2.4-15 |
| Sb-B | 1.40 | 0.44 | $6.8\times10^{15}$ | $3.0\times10^{15}$ | Sb-B-Si 6.8-3.0-15 |
| Bi-B[a] | 0.7–2.0 | ~0.6 | $\sim1.4\times10^{16}$ | $\sim8\times10^{15}$ | Bi-B-Si |
| P-B | 25 | 0.10 | $1.9\times10^{14}$ | $0.2\times10^{14}$ | P-B-Si 1.9-0.2-14 |
| P-B | 1.04 | 0.63 | $1.4\times10^{16}$ | $0.85\times10^{16}$ | P-B-Si 1.4-0.85-16 |

[a] Owing to strong impurity-concentration gradients in the bismuth sample, it was not possible to make accurate determinations of $N_D$ and $N_A$.

### B. Capture by Ionized Donors

The principal technique used for determining ionized-donor capture rates consists of determining with a photo-Hall measurement the steady-state electron concentration under a known photon flux. The technique has been described in detail by Levitt and Honig.[4] Briefly, upon irradiating a sample in its equilibrium charge state with extrinsic radiation ($\lambda \cong 2\,\mu$), electrons are excited from the neutral donors into the conduction band and are subsequently captured by the charged donors, of which there are $N_A$. The steady-state conduction-electron concentration is given by

$$n_e = S N_D{}^0 t_l\,, \tag{1}$$

where $N_D{}^0$ is the concentration of neutral donors, $S$ is the ionization rate per neutral donor due to the extrinsic light flux, and a unique capture lifetime[7] $t_l$ is assumed. $S$ is determined by measuring the electron-spin interchange rate[8] in a separate resonance experiment under the same extrinsic light flux[9] as used in the photo-Hall measurements. Measurements of photocurrent and of the photo-Hall voltage then yield $n_e$ and hence $t_l$, through Eq. (1). The charged-donor capture-rate constant $d$ is given by

$$d = 1/t_l N_D{}^+\,, \tag{2}$$

where $N_D{}^+$ is the concentration of charged-donor centers. The experimentally determined capture-rate constant is related to the energy-dependent electron-capture cross section $\sigma(E)$ and the electron velocity $v$ by

$$d = \langle \sigma(E) v \rangle\,, \tag{3}$$

and an effective electron-capture cross section $\sigma_c$ is defined as

$$\sigma_c = \langle \sigma(E) v \rangle / \langle v \rangle\,. \tag{4}$$

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[7] A necessary condition for the capture lifetime to be independent of extrinsic light intensity, namely $n_e \ll N_D{}^0$, is easily satisfied in all of our experiments. Nevertheless, the concept of a unique trapping lifetime will be seen to be inconsistent with some of our results. Impurity clustering and capture from hot-electron states can lead to a distribution of $t_l$. This is treated in Secs. IV and V.

[8] The electron-spin interchange rate is described in detail for phosphorus donors (nuclear spin $I = \frac{1}{2}$) in Ref. 4. Essentially, it is the rate at which different initial electron magnetizations associated with the $(2I+1)$ donor hyperfine components are equalized as their electrons are transferred among the donors via the conduction band, under extrinsic light irradiation. It is measured from the paramagnetic-resonance amplitudes of the hyperfine components as a function of time. For $I = \frac{1}{2}$, this rate gives directly the quantity $S$, and for $I > \frac{1}{2}$, $S$ is simply obtained, especially for simple initial magnetization inequalities which can be produced by selective saturation of particular hyperfine components.

[9] See Ref. 4 for a description of how the light flux in the resonance and Hall samples are made to correspond.

Most of the experimental results are discussed in terms of capture-rate constants rather than capture cross sections, since in the case of photoexcited carriers at low temperatures, the carriers' velocity distribution is frequently not known.

The relative magnitudes of the capture-rate constants $d$ for the various charged-donor impurities can be measured by a distinct method, which serves as a check on the directly measured values. The method consists of measuring the ratio $a/d$, where $a$ is the neutral-acceptor electron-capture-rate constant and $d$ is the ionized-donor electron-capture-rate constant. By using double-doped samples containing different donors but a common acceptor impurity, the relative values of $d$ follow for all of the donors. The technique for measuring $a/d$ is described in the next section, since it also provides the method by which neutral-acceptor capture rates are determined.

Two other less precise means for obtaining the relative capture rate constants for the various charged-donor impurities have also been used. The accuracy of these methods is estimated as only about 50%, but we present them because they are relevant to an analysis of the time-dependent intrinsic photoconductivity and because the bismuth-doped sample was of such great spatial inhomogeneity in its impurity concentration that photo-Hall measurements were not interpretable, thereby precluding the direct-measurement technique used for the other donors. We define $I_{2\mu}$ and $I_{1\mu}^0$, respectively, as the extrinsic photocurrent in the unpumped[10] sample and the *initial* intrinsic photocurrent in the pumped sample. Initial intrinsic photocurrent is specified because the intrinsic photocurrent changes with time under irradiation because of the neutralization of the charged donors and the consequent increase in carrier lifetime (see Fig. 2). Letting the intrinsic carrier generation rate be denoted by $G$, in the steady state the carrier lifetime is given by $t_l = n_e/G$; and since $n_e = I_{1\mu}^0/K\mu_e$, where $\mu_e$ is the electron mobility and $K$ is a constant depending on the sample geometry and lead contacts, one finds

$$t_l = I_{1\mu}^0/KG\mu_e. \tag{5}$$

Combining Eq. (5) with Eq. (2), and noting that $N_D^+ = N_A$ in the unpumped state, it follows that

$$d = KG\mu_e/I_{1\mu}^0 N_A. \tag{6}$$

Since $\mu_e$ was shown[4] to be proportional to $N_A^{-1/3}$, one can finally write

$$d = K'G/I_{1\mu}^0 N_A^{4/3}, \tag{7}$$

where $K'$ is another constant dependent only on sample geometry. $G$ is measured by the time taken to neutralize a known number of charged-donor impurities, as is illustrated in Fig. 2(a), and $I_{1\mu}^0$ is measured directly. To the extent that the samples are geometrically similar, the proportionality constant $K'$ is the same and the relative $d$ values for the shallow donors can be obtained. The effect of hole current is neglected in view of the lower hole mobility and the comparable capture rates of holes and electrons.

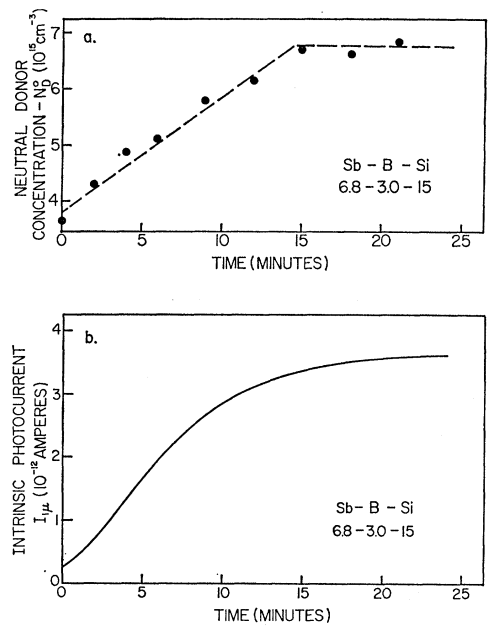

FIG. 2. Growth of (a) neutral-donor concentration and (b) photocurrent under 1-$\mu$ intrinsic illumination. $T = 4.2$°K.

From $I_{2\mu}$ measurements, a similar analysis starting from $t_l = n_e/SN_D^0$ leads to

$$d = K'SN_D^0/I_{2\mu}N_A^{4/3}. \tag{8}$$

$S$ is again determined from the electron interchange rate. The inaccuracy of these two methods arises principally from the fact that $K'$ is not identical for the various samples because of inhomogeneous impurity concentrations and variation in contact areas of the sample leads.

### C. Capture by Neutral Acceptors

The neutral-acceptor capture rates are measured on double-doped samples containing a common donor, in our case always phosphorus. The capture rate of the ionized donor (phosphorus) is independently known by means of the experiments described in the previous section, and the technique of delocalized electron transfer[5,6] yields the $a/d$ ratio, i.e., the ratio of the neutral-acceptor capture rate constant to that of the ionized donor. A brief outline of the delocalized-electron-transfer method follows. In the fully pumped sample [see Fig. 1(b)], spontaneous electron transfer from a neutral donor to a neutral acceptor can occur wlth the emission of a photon and phonons.[11] The rate of this spontaneous

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[10] Unpumped is taken to mean equilibrium charge state, i.e., prior to charge transfer due to optical pumping by intrinsic light.

[11] A. Honig and R. Enck, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965).

TABLE II. Ionized donor capture rates of photoexcited electrons.

| | | | $d$ (cm$^3$/sec) | | | |
|---|---|---|---|---|---|---|
| Donor | Donor ionization energy[a] (eV) | Acceptor | Photo-Hall | Delocalized electron transfer | 1-$\mu$ current ratio | 2-$\mu$ current ratio |
| P | 0.045 | B | $6.9\times10^{-6}$ | $6.9\times10^{-6}$ | $6.9\times10^{-6}$ | $6.9\times10^{-6}$ |
| As | 0.054 | B | $7.2\times10^{-6}$ | $5.2\times10^{-6}$ | $4.9\times10^{-6}$ | $8.6\times10^{-6}$ |
| Sb | 0.043 | B | $1.6\times10^{-6}$ | $1.8\times10^{-6}$ | $2.9\times10^{-6}$ | $2.6\times10^{-6}$ |
| Bi | 0.071 | B | $\cdots$ | $3.4\times10^{-5}$ | $1.0\times10^{-5}$ | $1.4\times10^{-5}$ |

[a] See, for example, G. W. Ludwig and H. H. Woodbury, *Solid State Physics* (Academic Press, Ltd., London, 1962), Vol. 13, p. 250.

process is a very strong function of impurity concentration, decreasing very rapidly as the overlap between wave functions of the donor and acceptor impurities becomes small. For the concentrations used in this study, i.e., $N_D\sim5\times10^{15}/\text{cm}^3$ and $N_A\sim2.5\times10^{15}/\text{cm}^3$, it has been shown[5] that the spontaneous transfer rate is extremely small for the bulk of the impurities, and an almost fully pumped state can persist for hours. By delocalizing the electrons from the neutral donors with extrinsic radiation, however, [see Fig. 1(c)] the electron transfer can be effected at a rate depending on the $a/d$ ratio, the impurity concentrations, and the incident light intensity. We are able to neglect the hole delocalization process in the treatment, because near 2 $\mu$, which is the wavelength of the extrinsic radiation employed, there is an optical absorption peak for the electrons[12] so that many more electrons than holes are generated. The equations governing the electron transfer are

$$dN_D{}^0/dt=-SN_D{}^0+dN_D{}^+n_e\,, \tag{9a}$$

$$dn_e/dt=SN_D{}^0-dN_D{}^+n_e-aN_A{}^0n_e\,, \tag{9b}$$

where $N_A{}^0$ is the concentration of neutral acceptors and the other quantities have already been defined. Typical electron lifetimes in the samples studied are $\sim10^{-10}$ sec, so that on a time scale of the order of seconds which is associated with the electron-transfer processes, steady-state conduction-electron concentrations can be used. In this approximation, one obtains for the $a/d$ ratio and for the time dependence of $n_e$

$$2\frac{a}{d}St=\ln\left\{\left[\frac{N_DN_A-(N_D+N_A)N_D{}^++(N_D{}^+)^2}{N_DN_A-(N_D+N_A)(N_{D,i}{}^+)+(N_{D,i}{}^+)^2}\right]\times\left[\frac{(N_D{}^+-N_D)(N_{D,i}{}^+-N_A)}{(N_{D,i}{}^+-N_D)(N_D{}^+-N_A)}\right]^{(N_D+N_A)/(N_D-N_A)}\right\}, \tag{10a}$$

$$n_e=S(N_D-N_D{}^+)/(dN_D{}^++aN_A{}^0)\,, \tag{10b}$$

where $N_{D,i}{}^+$ is the initial value of $N_D{}^+$ and has a value near zero in the fully pumped sample. In a resonance experiment, $N_D{}^0$ (and thus $N_D{}^+$, which equals $N_D-N_D{}^0$) is measured as a function of time while the sample is uniformly illuminated with extrinsic ($\sim2\,\mu$) radiation. A fit of Eq. (10a) to the experimental resonance decay curve yields $a/d$, after $S$ is determined from the electron interchange rate.

## III. RESULTS ON CAPTURE RATES

The charged-donor capture rates determined by the methods of Sec. IIB are summarized in Table II. The direct determinations appear in the column labeled photo-Hall measurements. The capture rates are temperature-independent in the 1.1–4.2°K range studied. It should be remarked that the photo-Hall measurements yield $n_e$ within a factor $r_H$, called the Hall factor. The values in the table are based on an assumed value of 1 for $r_H$. It has been shown[4] that under the conditions of our experiment, $\sim1\leq r_H<2$, so that there is a possibility of a systematic error whereby the $d$ values in the photo-Hall column could be as much as a factor of 2 too large. Aside from this possible systematic error, the random errors in $d$ associated with the spin interchange measurement and the impurity concentrations amount to about 20%. No value is given for the bismuth-doped sample because the crystal from which it was cut had a very marked impurity concentration gradient and the photo-Hall results could not be interpreted in a reliable way. The values of $d$ listed in the other columns are based on relative magnitudes of $d$ as obtained from the methods indicated by the column headings and discussed in Sec. IIB. The value for phosphorus is taken as a standard from the photo-Hall measurements. The reliability of the delocalized electron-transfer method is about 20%, whereas the current ratio techniques should not be reliable to better than ~50%. The bismuth-doped sample shows respective resistivity values on its two faces perpendicular to the growth direction of 0.7 and 2.2 Ω cm. For purposes of assigning representative impurity concentration, a value of 1.0 Ω cm was chosen; this is deliberately biased toward the low-resistivity end since that is the region of highest donor concentration and therefore accounts for most of the resonance signal. This resistivity value combined with the unpumped and optically pumped resonance signal yields approximate concentrations of $1.4\times10^{16}/\text{cm}^3$ Bi and $0.8\times10^{16}/\text{cm}^3$ B. The magnitudes should vary by not more than a factor of 2 from these throughout the sample. The delocalized electron transfer also requires measurement of the spin-interchange rate $S$, which may easily be in error by a

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[12] W. Spitzer and E. Y. Fan, Phys. Rev. **108**, 268 (1957).

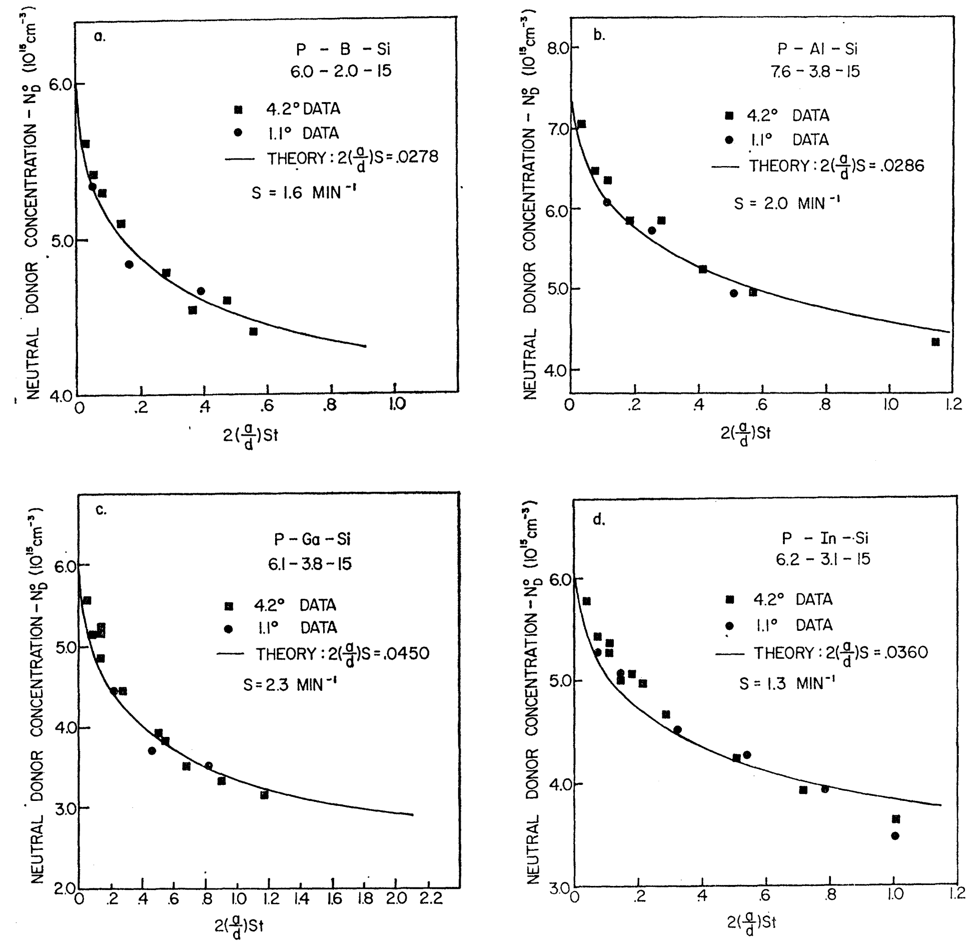

FIG. 3. Delocalized-electron-transfer curves for determining the ratio of the capture rate of neutral acceptors to that of ionized phosphorus donors. Theoretical curves are based on Eq. (10a).

factor of 2 because of the inhomogeneity. Thus, the value of $d$ given for bismuth is only a rough indication, easily subject to an error of a factor of 3. The 1-$\mu$ current-ratio value for bismuth is of little worth because it arises largely from the less concentrated portion of the sample. The 2-$\mu$ current ratio is better because it depends on the concentrated portion of the sample, as do the impurity-concentration measurements.

The electron-capture-rate constants $a$ of the neutral acceptors, measured as described in Sec. IIC, are given in Table III, as well as the acceptor hole ionization energies,[13] for later reference. The rates are temperature-independent in the 1.1 to 4.2°K temperature region which was investigated. The resonance decay curves are shown in Fig. 3, from which the $a/d$ values were determined by the best fit to the theoretical equation (10a). The ordinate $N_D{}^0$ is directly proportional to the amplitude of the resonance signal, and the dimensionless abscissa units are naturally suggested from Eq. (10a). The relative errors of the $a$ values in Table III come about principally from the measurements of $S$ and of the concentrations, and amount to about 20%. Any error in the magnitude of $d$ for ionized phosphorus is of course passed on as a systematic error in the magnitude of each of the $a$ values, but does not affect the relative values. The $a/d$ ratio for the phosphorus-boron sample is about 4 times smaller than the measurement previously reported.[6] The discrepancy may be due to room-temperature infrared radiation leakage in the earlier experiments.

## IV. DISCUSSION OF CAPTURE RATES

### A. Ionized Donors

Some of the discussion presented by Levitt and Honig[4] for the case of phosphorus-boron double-doped silicon is applicable here. One recalls that the Lax theory involves

TABLE III. Neutral-acceptor capture rates of photoexcited electrons.

| Donor | Acceptor | $a/d$ ratio | $a$ (cm$^3$/sec) | Hole ionization energy (eV) |
|---|---|---|---|---|
| P | B | 0.0075 | $5.2\times10^{-8}$ | 0.0439 |
| P | Al | 0.0063 | $4.3\times10^{-8}$ | 0.0685 |
| P | Ga | 0.0099 | $6.8\times10^{-8}$ | 0.0723 |
| P | In | 0.014 | $9.7\times10^{-8}$ | 0.1554 |

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[13] H. V. Hrostowoski and R. H. Kaiser, J. Phys. Chem. Solids 4, 148 (1958).

initial trapping into very highly excited states while the Ascarelli and Rodriguez theory involves initial trapping into lower lying excited states. Neither theory accounted for the observed temperature dependence of the ionized-phosphorus capture rate, and both theories yielded capture rates for thermalized carriers about an order of magnitude smaller than what was observed at 4.2°K. This situation holds also for the electron-capture rates of ionized arsenic, antimony, and bismuth impurities. The additional element of obtaining the dependence of trapping rate on impurity ionization is of no help in reconciling experiment with theory. In particular, Lax's theory does not depend on donor ionization energy since initial trapping and sticking probabilities involve only the very high excited states which are independent of the particular shallow donor. The Ascarelli-Rodriguez theory does lead to an ionization energy dependence, since the sticking probability in relatively low-lying excited states depends to some extent on the transition probability directly to the ground state. This transition probability from a state of principal quantum number $n$ to the ground state contains a term $E_i^{-5}$, where $E_i$ is the ionization energy of the donor, and thus the sticking probability is expected to be smaller for donors having larger ionization energy. Thus it is seen that the Ascarelli-Rodriguez theory predicts a decreasing capture rate as the donor ionization energy increases, the opposite of the experimental measurements.

This disparity between theory and experiment for the ionized-donor capture rates may result from several aspects of the capture process. One possibility is that in double-doped samples, the impurities tend to cluster rather than take on a random distribution. There is evidence to this effect from other experiments on concentration-dependent spin relaxation in double-doped silicon[14] and from the photocurrent growth curves, to be discussed in Sec. V. If clustering does occur, it could account for the observed temperature independence of the trapping rates because of a cutoff mechanism suggested by Lax[1] in which overlap between the highest trapping excited states of the donors prevents the capture radius from exceeding half the interimpurity distances. Thus, trapping occurs in lower excited states where the sticking probability is high and the temperature dependence is thus reduced. This cluster hypothesis may be attractive for impurity concentrations of about $5\times10^{15}/\text{cm}^3$ which we have employed in this study, but it is difficult to reconcile with the almost identical capture-rate-constant results obtained in much purer phosphorus-boron silicon samples, as has been previously reported.[4] Batches of clusters of interimpurity separation of about $2\times10^{-6}$ cm would have to be present in dilute samples in the $10^{14}/\text{cm}^3$ range. In addition, the proportionality of $t_l$ to $(N_D^+)^{-1}$ over a large range of concentrations, also previously reported,[4] would seem to be fortuitous for a model strongly dependent on cluster formation. Despite these difficulties, the cluster model cannot be excluded and it is probably of great importance in connection with the intrinsic photocurrent growth curves, which are discussed in Sec. V.

We consider now another possibility in which the ionized-donor capture process could be radically modified because of the relatively high energy state in the conduction band to which the electrons are initially photoexcited. Two separate situations require consideration. In the first, the lifetime of the conduction electrons would be given by the time for the electrons to cascade down to thermal energies, after which the electrons would almost immediately become captured. In the second, the time for thermalization is long compared to the time for the hot electrons to be captured by the impurities. The first case, in which the cascading time is the bottleneck, could give a temperature-independent trapping time and an $(N_D^+)^{-1}$ dependence, if the cascading would occur via inelastic ionized-impurity scattering accompanied by phonon emission. However, cascading times for energy losses up to 0.06 eV (approximately the optical phonon energy) of $10^{-10}$ sec at $N_D^+$ concentration of $10^{15}/\text{cm}^3$ would be required. Such short cascading times, though not impossible, are not very likely.[15,16] Moreover, the time for capture by impurities would have to be still shorter than that, and $10^{-10}$ sec for $N_D^+=10^{15}/\text{cm}^3$ is already an order of magnitude shorter than the theories predict for thermalized electrons at 4°K. The second case of direct capture of hot electrons by the impurities would not easily explain the temperature-independent capture rates since the trapping would presumably be into large orbits, just as in the case of capture of thermalized electrons, and the temperature dependence which arises from the sticking probability in the large orbits would still be expected. Also, it has already been noted that the observed capture rate is an order of magnitude larger than the theory predicts at 4°K for thermalized electrons. Even allowing for proportionality of the capture rate to the velocity, and an average electron temperature of 500°K, the results would imply a comparable capture cross section for the hot and the thermalized electrons, contrary to the prediction of any of the theories. The dependence of the capture rates on the ionization energy of the donors might conceivably under certain circumstances stem from the dependence of the conduction electrons' energy on the ionization energy of the donors. Since a fixed photon energy ($\lambda\cong2\,\mu$) was used, the deeper lying donors would yield photoexcited electrons of lower kinetic energy. However, this explanation in our case is unlikely, because the variation of ionization energy among the donors is small, and the

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[14] G. Yang and A. Honig (to be published).

[15] B. C. Rollin and J. M. Rowell, Proc. Phys. Soc. (London) **76**, 1001 (1960).

[16] H. J. Stocker, C. R. Stannard, Jr., H. Kaplan, and H. Levinstein, Phys. Rev. Letters **12**, 163 (1964).

monochromator bandwidth used in the photoexciting light was of the order of the optical phonon energy (0.06 eV). For the neutral capture dependence on hole ionization energy, no consideration like this is even relevant, since a common donor is employed in all the experiments.

### B. Neutral Acceptors

According to Lax's theory[1] of electron trapping by a neutral center, the attractive potential has an $r^{-4}$ dependence, due to the induced polarization of the neutral center by the electron. The theory gives an $I^{-3/2}$ and $T^{-1}$ dependence for the neutral-acceptor capture cross section for thermalized electrons, where $I$ (in our case) is the ionization energy of the hole associated with the neutral acceptor. We find that the capture rates for all of the neutral acceptors are temperature-independent in the 4.2 to 1.1°K range. The ionization energy dependence is shown in Fig. 4 which is a logarithmic plot of neutral-acceptor capture rate against $I$. One notes that the dependence on $I$ is small (of the order of $I^{1/2}$) and in a contrary sense to that of the theory. The same type arguments as given above for ionized donors, namely the complications due to clusters and to trapping from hot-electron states, may be applicable to the case of neutral acceptors.

Pokrovskii and Svistunova[17,18] have reported measurements of neutral-acceptor capture cross sections of boron, gallium, and indium in silicon in the temperature range of about 20 to 50°K. To connect our 4°K capture data with their 20°K data, even allowing for the possibility that our electrons are at about 500°K before capture and their electrons are thermalized, would require at least a $T^{-3}$ dependence of the neutral-acceptor capture rate. Such a temperature dependence does not agree with theoretical or experimental evidence on neutral center capture rates. Their method of determining the capture rates was to observe the decay of intrinsic photoconductivity, and then assume that the decay occurs because of capture of electrons from the conduction band onto neutral-acceptor sites. The experiments were carried out on $n$-type silicon samples having, for example, $2.7\times10^{16}/\text{cm}^3$ antimony and $1.5\times10^{15}/\text{cm}^3$ acceptors. It is known[5,11] that in this concentration region spontaneous localized electron transfer from donor to acceptor sites occurs rapidly and probably independently of temperature. It is likely that below about 40°K in such samples, the donor-acceptor electron-transfer process becomes more probable than electron capture by neutral acceptors out of the conduction band. Thus, the intrinsic photoconductive decay time probably yields the radiative lifetime associated with donor-acceptor electron transfer. This would be consistent with the temperature-independent time constants observed[17] below about 40°K.

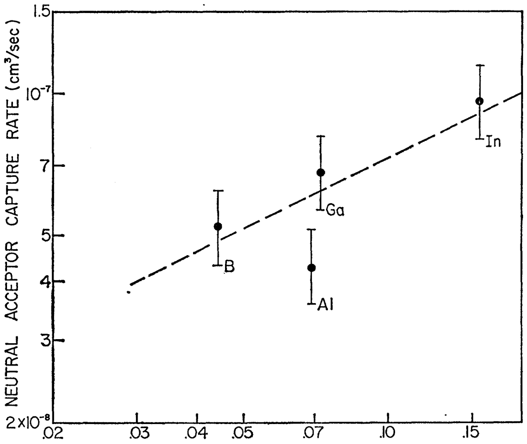

FIG. 4. Logarithmic plot of neutral-acceptor capture rates against hole ionization energy of the acceptors. Dashed line indicates an $I^{1/2}$ dependence. Temperature range is 1.1 to 4.2°K.

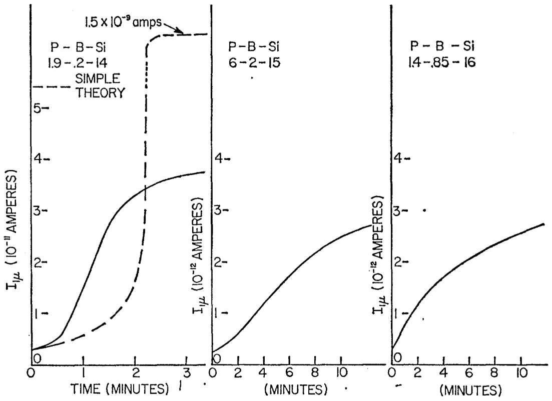

FIG. 5. Intrinsic photocurrent growth curves for three P-B-Si samples at widely varying impurity concentrations. In (a), theoretical curve is based on Eq. (10b). $T=4.2$°K.

## V. INTRINSIC PHOTOCURRENT GROWTH CURVES

The framework within which the experimental data were interpreted was that of isolated capture centers and a unique electron-capture lifetime. This assumption is approximately valid, becoming better as impurity concentration decreases and as any hot-electron distribution becomes more monoenergetic. It is supported by the consistency of capture rates resulting from different methods. However, it has already been suggested that the lack of agreement of the capture rates with theory may in part be due to impurity clusters or hot-electron capture processes, either of which would modify the simple model. Especially dependent on the unique lifetime model are the time variations of the

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[17] Ya. E. Pokrovskii and K. I. Svistunova, Fiz. Tverd. Tela **5**, 1880 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1373 (1963)].

[18] Ya. E. Pokrovskii and K. I. Svistunova, Fiz. Tverd. Tela **6**, 19 (1964) [English transl.: Soviet Phys.—Solid State **6**, 13 (1964)].

extrinsic and intrinsic photocurrents, associated, respectively, with delocalized electron transfer [see Eq. (10b)] and with optical pumping [see Fig. 2(b)]. Discrepancies in the current responses were already apparent in prior work,[6] and further attention is given to the intrinsic photocurrent growth process here.

The simple model based on an electron lifetime proportional to $(N_D{}^+)^{-1}$ and a mobility proportional to $(N_D{}^+)^{-1/3}$ fails to explain the outstanding features of the intrinsic photocurrent curves, even in dilute samples. This can be seen in Fig. 5, which shows the growth of intrinsic photocurrent as a function of time for three samples of different impurity concentrations. It is seen that the initial rise of intrinsic current is much too fast, and that the ratio of the final intrinsic photocurrent to the initial intrinsic photocurrent is at least a factor of 30 smaller than predicted by the simple model. The departure from the theory increases with increasing impurity concentration. What is needed to explain this current growth curve is an average capture lifetime that in the beginning increases rapidly as charged donors are neutralized, and later increases slowly with further donor neutralization. One way a model with these properties can be constructed is by assuming a capture rate per impurity that is a function of interimpurity distance. In addition, a nonrandom distribution of relatively closely spaced impurity clusters would be necessary for appreciable effects to be observable on dilute samples ($\sim 10^{14}/\text{cm}^3$), as they have been. A certain proportion of the donors and neighboring acceptors ought to be close enough so that the electron-transfer rate[11] from donor to acceptor is fast enough to keep these impurities always charged. It is easily seen that such a model produces a faster initial rate of rise of intrinsic photocurrent, since the more efficient capturing centers do the main part of the initial carrier capturing and upon being thereby neutralized give rise to a sharp increase in the carrier lifetime. The impurities which are close enough so that they are always charged serve to limit the final/initial intrinsic photocurrent ratio. The distribution of impurity separations, even with nonrandom clusters, is probably continuous, as is also the distribution of donor to acceptor electron transfer rates, or recombination rates $R$. The impurities that will remain charged are those for which the $R$ value exceeds the portion of the generation rate $G$ which neutralizes them. The model is sufficiently indefinite, especially with regard to the dependence of the donor capture rate $d$ on impurity separation, that it is instructive and not unduly restrictive to consider only 3 cluster categories ($i=1, 2, 3$) of concentrations $N_i$, $N_i^+$, capture rate constants $d_i$ and recombination rates $R_i$. The dynamics of the impurity charging process are then governed by the set of equations

$$dN_i^+/dt=(-d_iN_i^+/\textstyle\sum_j d_jN_j^+)G+R_i(N_i-N_i^+)\,. \qquad i,j=1,2,3\,. \quad (11)$$

For certain choices of $d_i$, $R_i$, and $N_i$, which allow a large degree of arbitrariness because of our ignorance of the detailed relationship between $d_i$ and $R_i$, curves very similar to the experimental ones can be generated. The choice incorporates an appreciable fraction of the impurities with small $R_i$ and with $d_i$ several times the value it has in isolated centers, an appreciable fraction of impurities with large $R_i$, and the isolated centers with $R_i=0$. It is also possible that other effects may help limit the final/initial intrinsic photocurrent ratio, such as, for example, the possibility of electrons cascading to lower velocities in the greater $t_l$ available as charged centers become neutralized; this could be accompanied by an increase in capture rate.

It is difficult to see how the photocurrent growth curves could result from a variable lifetime model other than one involving the configuration of impurities. For example, if the variable lifetime of carriers resulted only from a carrier energy distribution in the conduction band, it would require an extraordinary relation between that energy distribution and the charge state of the impurities to yield the initial intrinsic photocurrent growth curves.

## VI. CONCLUSIONS

Photoexcited electron-capture rates due to ionized shallow donors and neutral shallow acceptors in silicon have been determined. The capture rates are large, typical of the picture of giant traps proposed by Lax, but the temperature and ionization energy dependences do not agree with the capture theories for thermalized electrons. There is a strong possibility that impurity clusters play an important role in the capture process, and it is probable that capture occurs from hot-electron states, for which situation the present theory of electron capture may not be satisfactory. Further experiments on capture of monochromatically excited electrons are warranted to clarify the capture process.