

Recombination and Trapping Processes of the Injected Carriers in Gold-Doped Silicon at Low Temperatures

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Steady-state recombination and trapping processes of the injected carriers in gold- and phosphorus-doped silicon have been studied for the case that the doping and temperature range are such that the equilibrium carrier densities are small compared with the impurity density. The fluctuation of the charge in the impurity centers as a result of injection is taken into account in the charge-neutrality condition. The relationship between the injected carriers (electrons and holes) for charge neutrality is established in the form of power laws (i.e., $\Delta p = \Gamma \Delta n^\alpha$) that hold in different ranges of injection. Numerical analyses of Δp versus Δn and τ_n versus Δn are presented for the case of n -type silicon overcompensated and undercompensated by the gold impurities.

I. INTRODUCTION

In steady-state injection, the emission and capture of carriers (electrons and holes) by impurity centers cause the charge states in these centers to change from their thermal equilibrium value. Therefore, the density of carriers trapped in the flaws is, in general, a function of the injection. If the density of impurity centers is larger than the injected carrier density, then the charge in them will play an important role in preserving charge balance under steady-state injection. In the present paper, we shall show that the charged impurity centers are dominant in controlling charge-neutrality except at very high injection.

The Shockley-Read¹ (SR) and the Sah-Shockley² (SS) statistics are used to interpret the interaction of the phosphorus and gold impurity centers with the injected carriers in silicon at low temperatures (below 100°K). The trapping of the injected carriers in these centers is included in a generalized charge-neutrality equation for arbitrary injection levels and flaw densities. The formulation yields the relationship between injected hole and electron densities that preserve charge neutrality.

Specific results of the trapping and recombination processes as a function of injection are obtained for the case of n -type silicon doped with gold impurity at low temperatures. It is shown that a simple power-law relationship between injected electrons and holes can be defined over specific injection range.

II. GENERALIZED CHARGE BALANCE

The assumption of charge neutrality is valid when the actual net charge density necessary to satisfy the requirements of transport is very small compared with the total opposing variable charge densities. In order to describe these, we need to consider first the details of the models for the impurities.

In Fig. 1 we show the energy-band model for silicon. The impurity centers for gold and phosphorus are shown in their possible charge states.

The emission and capture statistics of the phosphorus level can be characterized by the SR model.¹ In their

development, Shockley and Read found the probability of occupancy of a single level impurity under steady-state injection. This gives the density of electrons in the phosphorus level as¹

$$n_D = N_D \frac{C_{nD}n + C_{pD}p_{1D}}{C_{nD}(n + n_{1D}) + C_{pD}(p + p_{1D})}, \quad (1)$$

where C_{nD} and C_{pD} are the electron and hole capture rate at the donor level, respectively; n_{1D} and p_{1D} are the electron and hole density when the Fermi level coincides with the donor level, respectively; n and p are electron and hole density, respectively.

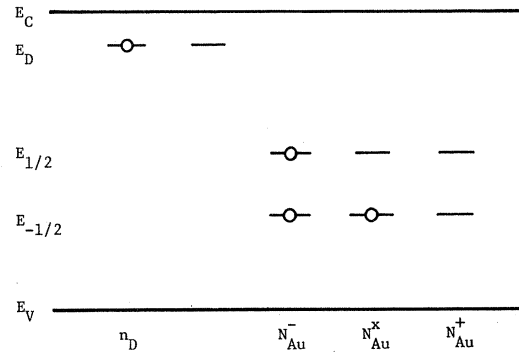


FIG. 1. Localized states introduced by gold and phosphorus in the energy-band gap for silicon. N_{Au}^- denotes density of negative gold acceptor centers, N_{Au}^0 for neutral gold centers, and N_{Au}^+ for positive gold donor levels.

There is experimental evidence³ suggesting that the cross section of electron capture by phosphorus is about 1000 times larger than that of hole capture. This is reasonable, since electron capture by phosphorus is by a Coulomb attractive center requiring small energy transfer, whereas hole capture is by a neutral center requiring a large energy transfer. These considerations allow us to neglect the interaction of the phosphorus level with the valence band by setting C_{pD} to zero. The resulting density of electrons in that level is then reduced to

$$n_D = N_D [n / (n + n_{1D})]. \quad (2)$$

Sah and Shockley's statistics² give the ratios of the densities of a multilevel impurity in consecutive charged states. Applied to gold in silicon, this gives

$$N_{\text{Au}}^-/N_{\text{Au}}^x = (nC_n^x + p_{1/2}C_p^-)/(n_{1/2}C_n^x + pC_p^-), \quad (3)$$

$$N_{\text{Au}}^+/N_{\text{Au}}^x = (n_{-1/2}C_n^+ + pC_p^x)/(nC_n^+ + p_{-1/2}C_p^x), \quad (4)$$

where C_n^x and C_p^- are the electron and hole capture rate at the gold acceptor level, respectively; C_n^+ and C_p^x are the electron and hole capture rate at the gold donor level, respectively; $n_{1/2}$ and $p_{1/2}$ are the electron and hole density at the gold acceptor level; $n_{-1/2}$ and $p_{-1/2}$ are the electron and hole density at the gold donor level, respectively. These two ratios, along with the requirement that

$$N_{\text{Au}}^+ + N_{\text{Au}}^- + N_{\text{Au}}^x = N_{\text{Au}} \quad (5)$$

can be solved for the densities of the individual charged states of the gold centers. These densities are functions of the injected carrier densities.

We can now write the generalized charge balance equation for gold- and phosphorus-doped silicon:

$$p + (N_D - n_D) + N_{\text{Au}}^+ - N_{\text{Au}}^- - n = 0, \quad (6)$$

or, subtracting the thermal equilibrium contributions, we have excess density

$$\Delta p + \Delta N_{\text{Au}}^+ = \Delta n + \Delta n_D + \Delta N_{\text{Au}}^-, \quad (7)$$

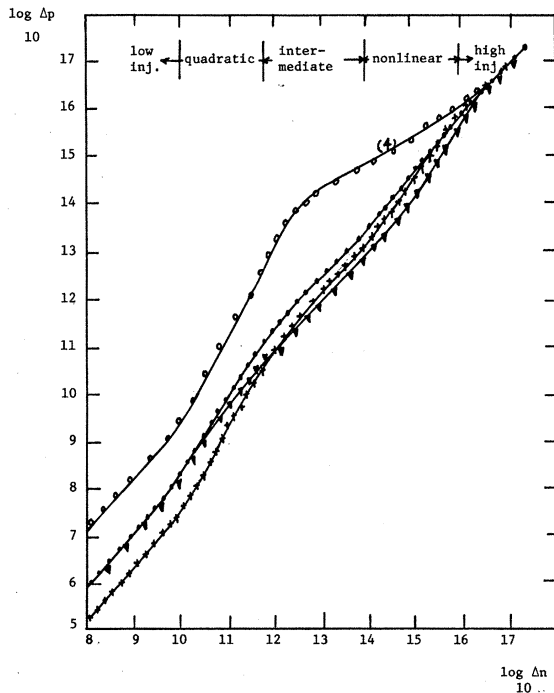


FIG. 2. Δp versus Δn obtained from the charge-balance condition in n -type silicon undercompensated with gold at low temperatures (i.e., $n_0 \ll N_{\text{Au}}$). The assumed values are $N_D = 2 \times 10^{17} \text{ cm}^{-3}$, $N_{\text{Au}} = 10^{16} \text{ cm}^{-3}$, and $n_0 = 10^{10} \text{ cm}^{-3}$. ● curve for $\gamma_{1/2} = 100$, $\gamma_{-1/2} = 0.1$; ▼ curve for $\gamma_{1/2} = 100$, $\gamma_{-1/2} = 1$; + curve for $\gamma_{1/2} = 500$, $\gamma_{-1/2} = 0.1$; ○ curve 4 for $\gamma_{1/2} = 5$, $\gamma_{-1/2} = 0$.

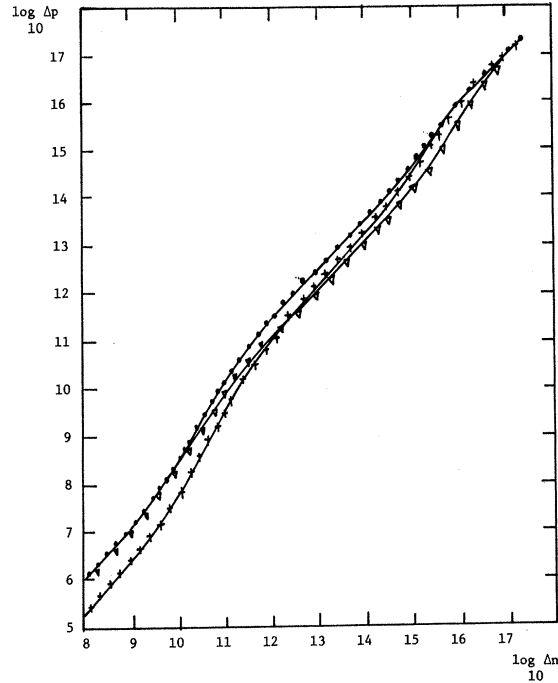


FIG. 3. Δp versus Δn in n -type silicon overcompensated with gold at low temperatures. The assumed values are $N_D = 10^{16} \text{ cm}^{-3}$, $N_{\text{Au}} = 2 \times 10^{16} \text{ cm}^{-3}$, and $n_0 = 10^{10} \text{ cm}^{-3}$. ● curve for $\gamma_{1/2} = 100$, $\gamma_{-1/2} = 0.1$; ▽ curve for $\gamma_{1/2} = 100$, $\gamma_{-1/2} = 1$; + curve for $\gamma_{1/2} = 500$, $\gamma_{-1/2} = 0.1$.

where $p = p_0 + \Delta p$ and $n = n_0 + \Delta n$. Each term in Eq. (7) is a function of Δp and Δn only; therefore the equation gives an implicit relationship that the injected carrier densities have to satisfy for charge balance.

The procedure outlined above applies to n -type silicon either overcompensated or undercompensated by gold. In fact, this approach could be applied in any case in semiconductors where a shallow impurity is compensated by a deep single or multilevel impurity. The details of the results are very sensitive to the level of compensation and the capture parameters. There is a general tendency which can be very useful. Under certain conditions, one can define ranges of injection where the excess carrier densities satisfy the charge-balance equation by obeying a power law. In other words, one can define the parameters Γ and α such that

$$\Delta p = \Gamma \Delta n^\alpha \quad (8)$$

holds with Γ and α approximately constant within a specified range of Δn and Δp , and α is either 1 or 2.

III. RESULTS AND DISCUSSION

A. Undercompensated Case

Consider the undercompensated case at temperatures low enough that the material is extrinsic n type and the equilibrium electron density is small compared to the

TABLE I. Approximate solutions of the charge-balance equation in n -type silicon compensated by gold. The constants below define the relationship $\Delta p = \Gamma \Delta n^\alpha$ which the injected carrier must satisfy for charge balance.

Doping and equilibrium carrier density	Γ	α	$\Delta n \gg$	$\Delta n \ll$
Undercompensated				
$N_D > N_{Au}$	$(N_D - N_{Au}) / N_D \gamma_{1/2}$	1	0	n_0
$n_0 > N_{Au}$	$(N_D - N_{Au}) / N_D \gamma_{1/2} n_0$	2	n_0	$[N_D n_0 / (N_D - N_{Au})] (\gamma_{1/2} / \gamma_{-1/2})^{1/2}$
$n_0 \ll N_{Au}$	$(\gamma_{1/2} \gamma_{-1/2})^{-1/2}$	1	$[N_D n_0 / (N_D - N_{Au})] (\gamma_{1/2} / \gamma_{-1/2})^{1/2}$	N_{Au}
$n_0 \simeq 0$	1	1	N_{Au}	∞
Overcompensated				
$N_D < N_{Au}$	$(N_{Au} - N_D) / N_D \gamma_{1/2}$	1	0	$[(N_{Au} - N_D) / N_{Au}] n_{1D}$
$n_0 < N_{Au}$	$N_{Au} / N_D \gamma_{1/2} n_{1D}$	2	$[(N_{Au} - N_D) / N_{Au}] n_{1D}$	$(N_D n_{1D} / N_{Au}) (\gamma_{1/2} / \gamma_{-1/2})^{1/2}$
$n_0 \simeq 0$	$(\gamma_{1/2} \gamma_{-1/2})^{-1/2}$	1	$(N_D n_{1D} / N_{Au}) (\gamma_{1/2} / \gamma_{-1/2})^{1/2}$	N_{Au}
$n_0 \simeq 0$	1	1	N_{Au}	8

gold concentration. This can be achieved with $N_{Au} > 10^{14} \text{ cm}^{-3}$, and $N_D > N_{Au}$, at temperatures below 30°K . At these temperatures, the equilibrium carrier density is given by⁴:

$$n_0 \approx N_C [(N_D - N_{Au}) / N_{Au}] \exp[(E_D - E_C) / kT]. \quad (9)$$

Here we let E_D represent the degeneracy of the donor level in the manner described by SR.¹ Also, at these low temperatures, $n_{1/2}$, $p_{1/2}$, $n_{-1/2}$, $p_{-1/2}$, and p_0 are negligibly small and n_{1D} can be expressed in terms of n_0 . Using the definition of n_{1D} and Eq. (9) we find that⁵

$$n_{1D} = [N_{Au} / (N_D - N_{Au})] n_0. \quad (10)$$

From Eqs. (3)–(5) we find that

$$N_{Au}^x = N_{Au} [n \Delta p / (\Delta p^2 \gamma_{-1/2} + n \Delta p + n^2 / \gamma_{1/2})]. \quad (11)$$

Finally, realizing that at thermal equilibrium

$$(N_D - n_D)|_{\text{th.eq.}} = N_{Au} \quad (12a)$$

and

$$(N_{Au}^-)|_{\text{th.eq.}} = N_{Au}, \quad (12b)$$

the charge-balance equation can be rewritten as

$$\begin{aligned} \Delta p + N_{Au} \frac{2\Delta p^2 \gamma_{-1/2} + n \Delta p}{\Delta p^2 \gamma_{-1/2} + n \Delta p + n^2 / \gamma_{1/2}} \\ = \Delta n + N_{Au} \Delta n \left(\frac{N_D}{N_D - N_{Au}} n_0 + \Delta n \right)^{-1}, \end{aligned} \quad (13)$$

where

$$\gamma_{1/2} = C_p^- / C_n^x$$

is the ratio of the hole and electron capture rate at negative and neutral gold acceptor levels, respectively, and

$$\gamma_{-1/2} = C_p^x / C_n^+$$

is the ratio of the hole and electron capture rate at the neutral and positive gold centers.

Equation (13) can be solved for Δp as a function of Δn , with the impurity concentrations and the capture rate ratios as the parameters. This solution has been computed for assumed values of the γ 's and the results are plotted in Fig. 2. In this graph, we can identify five ranges of injection as follows:

(1) At low injection, the equilibrium distribution is perturbed only slightly, and we obtain a linear range.

(2) The low-injection nonlinear range occurs when the injected carrier densities are comparable or greater than the equilibrium density. In this range the density of electrons trapped in the flaws changes strongly with injection.

(3) The intermediate linear range results when the donors become saturated with electrons. In this range the change in the gold centers remains invariant with respect to injection, maintaining a constant ratio of free carriers.

(4) The high-injection nonlinear range results as the injected carriers themselves begin to contribute directly to charge balance.

(5) In the high-injection linear range, the carrier densities are simply so large that they dominate and the charge-balance condition is $\Delta p = \Delta n$.

The case of compensation by a single-deep-level impurity can be obtained by setting $\gamma_{-1/2}$ to zero. Curve 4 in Fig. 2 is plotted with this assumption. This case differs from the two-level impurity in that the intermediate linear range is eliminated. The high-injection linear range remains unchanged, showing that the gold donor level has negligible effects in this range of injection.

The assumed values of the γ 's were chosen according to the following criterion. We assume $\gamma_{1/2} \gg 1$ because it is the ratio of an attractive to a neutral capture rate. Similarly, we assume that $\gamma_{-1/2} \leq 1$.⁶ However, the experimental data available do not establish these ratios accurately. Therefore, we arbitrarily chose a low and a high value for the γ 's ($\gamma_{1/2} = 500, 100$; $\gamma_{-1/2} = 1, 0.1$) in our solutions. The γ 's determine the boundaries and the factors of proportionality for each range of injection. This can be observed in Fig. 2 and will be substantiated in the power laws obtained later in this paper. The exponents of the power laws are not affected except for the extreme case where the range is too restricted to make a power law valid. This situation can be observed in Fig. 2 for $\gamma_{1/2} = 100$ and $\gamma_{-1/2} = 1$; the nonlinear range following the low-injection linear range is not a power law of 2 as in the other cases.

B. Overcompensated Case

Let us consider the overcompensated case ($N_{Au} > N_D$) at low temperatures. The thermal-equilibrium densities are

$$n_D|_{th.eq.} = 0, \quad (14a)$$

$$N_{Au}^-|_{th.eq.} = N_D, \quad (14b)$$

$$N_{Au}^x|_{th.eq.} = N_{Au} - N_D, \quad (14c)$$

and

$$N_{Au}^+|_{th.eq.} = 0. \quad (14d)$$

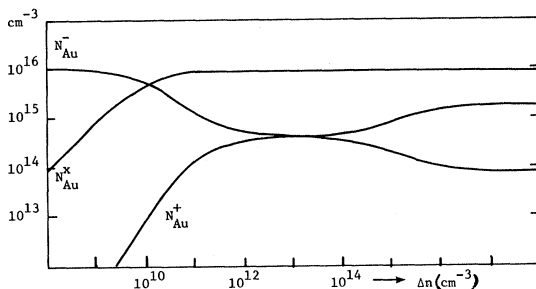


FIG. 4. Density of the charged and neutral gold centers as a function of excess electron concentration for the undercompensated case. The assumed values are $N_D = 2 \times 10^{17} \text{ cm}^{-3}$, $N_{Au} = 10^{16} \text{ cm}^{-3}$, $n_0 = 10^{10} \text{ cm}^{-3}$, $\gamma_{1/2} = 100$, and $\gamma_{-1/2} = 0.2$.

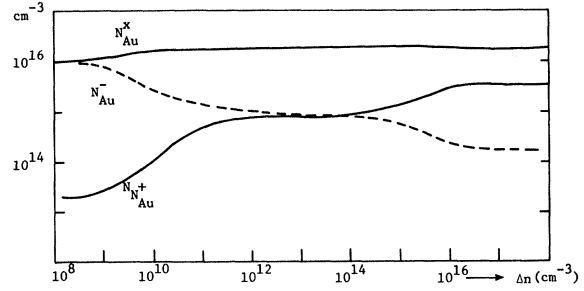


FIG. 5. Density of the charged and neutral gold centers as a function of excess electron concentration for the overcompensated case. The assumed values are $2N_D = N_{Au} = 2 \times 10^{16} \text{ cm}^{-3}$, $n_{1D} = 10^{10} \text{ cm}^{-3}$, $\gamma_{1/2} = 100$, and $\gamma_{-1/2} = 0.2$.

With this we write the charge-balance equation for this case as follows:

$$\Delta p + \frac{(N_{Au} + N_D) \Delta p^2 \gamma_{-1/2} - (N_{Au} - N_D) \Delta n^2 / \gamma_{1/2} + N_D \Delta n \Delta p}{\Delta p^2 \gamma_{-1/2} + \Delta n \Delta p + \Delta n^2 / \gamma_{1/2}} = \Delta n + N_D \Delta n (n_{1D} + \Delta n)^{-1}. \quad (15)$$

The equilibrium carrier densities are essentially zero because the Fermi level is locked at the gold acceptor level and it is not practical to represent n_{1D} in terms of n_0 in this case.

We have obtained numerical solutions of Eq. (15) for Δp versus Δn for assumed values of the parameters. The results are plotted in Fig. 3. Again, five ranges of injection can be identified and the γ 's have the same effect as discussed for the undercompensated case.

The low-injection range in this case is limited by n_{1D} . For Δn small compared to n_{1D} , the equilibrium distribution is only slightly disturbed, resulting in the low-injection linear range. When Δn becomes comparable to and larger than n_{1D} , the trapped carrier densities change strongly with injection, and the low-injection nonlinear range is obtained. For higher injection, the donors saturate. The explanation for the intermediate linear and the high-injection ranges follows the same reasoning as for the undercompensated case.

We can obtain approximate solutions of the charge-balance equations, giving Δp in terms of Δn in some of these ranges. These approximations take the form of power laws, i.e.,

$$\Delta p = \Gamma \Delta n^\alpha. \quad (16)$$

The values of the constants Γ and α are listed in Table I, along with the boundaries of the corresponding range injection.

The small signal quadratic ranges have a single representation valid from zero injection to the upper bound of the quadratic range. These are

$$\Delta p = [(N_D - N_{Au}) / N_D \gamma_{1/2}] [\Delta n + (\Delta n^2 / n_0)] \quad \text{for } N_D > N_{Au} \quad (17)$$

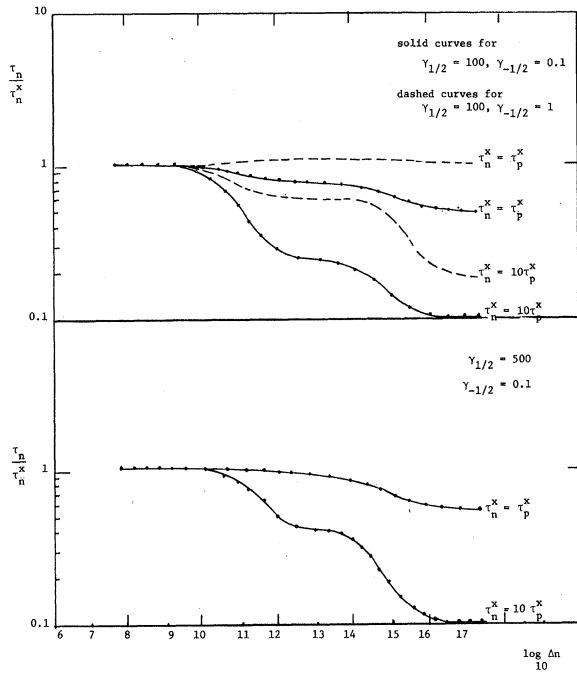


FIG. 6. Normalized electron lifetime τ_n/τ_n^x as a function of excess electron density for undercompensated case and for different values of τ_n^x/τ_p^x , $\gamma_{1/2}$, and $\gamma_{-1/2}$. The assumed values are $N_D = 2 \times 10^{17} \text{ cm}^{-3}$, $N_{Au} = 10^{16} \text{ cm}^{-3}$, and $n_0 = 10^{10} \text{ cm}^{-3}$.

and

$$\Delta p = [(N_{Au} - N_D)/N_D \gamma_{1/2}] \Delta n + (N_{Au}/N_D n_{1D} \gamma_{1/2}) \Delta n^2 \quad \text{for } N_D < N_{Au}. \quad (18)$$

We have obtained the relationship between the injected electron and hole densities for charge balance and have shown that there exist different ranges of injection where this relationship reduces to a simple power law (i.e., $\Delta p = \Gamma \Delta n^\alpha$). The exponent in this law varies between about $\frac{1}{2}$ to 2, and under certain conditions a power law can extend over more than one order of magnitude of injection.

IV. RECOMBINATION

The recombination rate through the gold centers is given by²

$$R = (np - n_i^2) \left[\frac{(N_{Au}^- + N_{Au}^x) C_n^x C_p^-}{C_n^x (n + n_{1/2}) + C_p^- (p + p_{1/2})} + \frac{(N_{Au}^x + N_{Au}^+) C_n^+ C_p^x}{C_n^+ (n + n_{-1/2}) + C_p^x (p + p_{-1/2})} \right]. \quad (19)$$

In the previous charge-balance analysis, we found the density of impurities in each charged state. Therefore, charge balance gives all the information we need to evaluate the recombination rate. At low temperatures,

Eq. (19) reduces to

$$R = \Delta n / \tau_n = n \Delta p \left[\frac{(N_{Au}^x + N_{Au}^-) / N_{Au}}{n / \gamma_{1/2} + \Delta p} \frac{1}{\tau_n^x} + \frac{(N_{Au}^x + N_{Au}^+) / N_{Au}}{n + \Delta p \gamma_{-1/2}} \frac{1}{\tau_p^x} \right], \quad (20)$$

where $\tau_n^x = 1/C_p^x N_{Au}$ is the electron lifetime at the neutral gold acceptor level and $\tau_p^x = 1/C_p^x N_{Au}$ is the hole lifetime at the neutral gold donor level.

From the charge neutrality, Eqs. (13) and (15), the density of the charged and neutral gold centers can be computed as a function of excess electron density. This is demonstrated in Figs. 4 and 5, assuming that the hole and electron capture rate ratio at the gold acceptor center $\gamma_{1/2} = 100$, and the hole and electron capture rate ratio $\gamma_{-1/2} = 0.2$ for both undercompensated and overcompensated cases. The curves in these figures were obtained numerically during the computations leading to Figs. 2 and 3. Note that the charged and neutral gold density versus injection curves (Figs. 4 and 5) are insensitive to the change in the values of $\gamma_{1/2}$ and $\gamma_{-1/2}$.

The electron lifetime τ_n as a function of excess electron density can now be computed by using Eq. (20). The result is shown in Figs. 6 and 7, assuming that $\gamma_{1/2} = 100$ and $\gamma_{-1/2} = 0.1$ and for different τ_n^x and τ_p^x

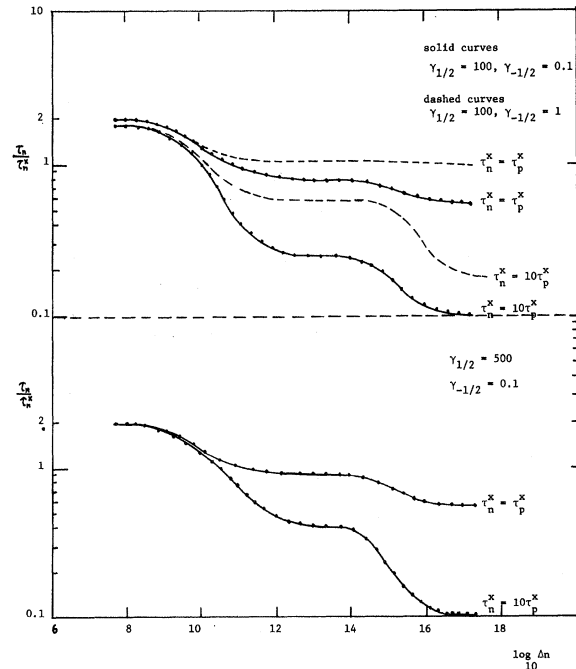


FIG. 7. Normalized electron lifetime τ_n/τ_n^x as a function of excess electron density for overcompensated case and for different values of τ_n^x/τ_p^x , $\gamma_{1/2}$ and $\gamma_{-1/2}$. The assumed values are $N_{Au} = 2N_D = 2 \times 10^{16} \text{ cm}^{-3}$, $n_{D1} = 10^{10} \text{ cm}^{-3}$.

ratio. It is interesting to note that the five injection ranges appeared in Figs. 2 and 3 are also apparent in Figs. 4-7. In the low-injection linear range, most of the gold centers are in the thermal-equilibrium configuration and the lifetime is constant. In the quadratic range, the charge in the gold centers changes and most of these become neutral in the upper end of the range. The decrease of the lifetime is mostly due to the increase in hole density. In the intermediate linear range the distribution of charge in the gold centers and the lifetime are essentially constant. In the high-injection region the charge distribution changes to the high-injection linear range values and the electron lifetime again reaches a constant value. It is also noted from Figs. 6 and 7 that the normalized electron lifetime τ_n/τ_n^x versus injection (Δn) depends strongly on the ratio of τ_n^x and τ_p^x .

V. CONCLUSIONS

The Shockley-Read and the Sah-Shockley statistics were used to describe the interaction of gold and phosphorus centers with injected carriers in silicon. The most significant effect of these centers on the injected electron and hole densities is that their equality is destroyed by the charge-balance requirement. The

relationship between the injected carriers for charge neutrality is established in the form of power laws (i.e., $\Delta p = \Gamma \Delta n^\alpha$) that hold in different ranges of injection.

The power-law relationship between Δp and Δn is linear (i.e., $\alpha=1$) in three ranges: at very low or very high injection and in an intermediate injection range. The low and intermediate ranges are joined by a well-defined quadratic range (i.e., $\alpha=2$). We have found the constants Γ and α that define these power laws in four defined ranges of injection. Also, numerical analysis was used to plot Δp versus Δn for all injections satisfying the neutrality condition (Figs. 2 and 3). Application of the present theory to the photomagnetolectric effect in gold-doped silicon at low temperatures has shown good agreement with experimental observation.⁵ Another application of the present theory to the diffusion of photoexcited carriers in semiconductors will be reported in a later publication.

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High-Field Distribution Function and Mobility in *n*-Type Cadmium Sulphide

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The energy distribution function of carriers in *n*-type cadmium sulphide is calculated considering acoustic (both deformation-potential and piezoelectric), impurity, and polar optical modes of scattering. The drift velocity obtained from a rigorous solution of the Boltzmann equation is compared with the high-carrier-concentration case where strong carrier-carrier scattering imposes a displaced Maxwellian distribution on the carriers.

I. INTRODUCTION

The transport properties of *n*-type cadmium sulphide at high electric fields have received the attention of several workers.¹⁻⁵ The scattering process in this semiconductor is quite complex; in addition to the electron-electron and electron-ionized-impurity scattering, the carriers also interact with the acoustic phonons (both deformation- and piezoelectric-potential modes) and the polar optical phonons. In materials of low resistivity the application of a high electric field results in an appreciable disturbance in the acoustic-phonon distribu-

tion. This gives rise to an acoustoelectric current,⁶ which flows in a direction opposite to the normal drift current and gives rise to current saturation and oscillation when the applied field exceeds a certain critical value. For higher-resistivity materials, however, the phonons remain in equilibrium, and the experimental results should be explained satisfactorily by conventional hot-electron theory neglecting the acoustoelectric effect.

Hot-carrier conduction phenomena in semiconductors can be studied theoretically by solving the Boltzmann