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Analysis of Recombination of Excitons Bound to Deep Neutral Donors and Acceptors

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On the basis of the plausibility arguments and experimental results of previous workers on shallow-donor and -acceptor levels, the recombination of bound excitons at deep-neutral-donor and -acceptor sites via an Auger process appears to be a likely candidate for a nonradiative or "killer" mechanism in luminescent material. We analytically investigate the effects of this center in a p-type semiconductor (the results can be extended in a straightforward manner to n-type material) with the goal of uncovering experimentally verifiable properties. The analysis specializes in several specific examples. The first case is that in which the competing nonradiative-recombination mechanism is a shallow exciton bound to an acceptor. For this case the strength of the nonradiative recombination goes through a maximum as a function of temperature, and this effect would be experimentally observed as a minimum in the radiative efficiency of the semiconductor. Such an effect is reported in GaP(Zn, O) in an accompanying paper. Furthermore, on the basis of numerical calculations presented in this paper we consider it unlikely that the silicon acceptor, which has been suggested as a possible nonradiative center in GaP, is a strong recombination site. The second example considered is that of an exciton bound to a neutral donor. Since this situation involves capture of two minority carriers by the donor, the concentrations of the captured electrons are expected to depend nonlinearly on excitation intensity. These effects are easily observed if electrons in either state give rise to a detectable radiative band. In the accompanying paper the intensity variation of the oxygen-donor infrared band in GaP(Zn, O) with excitation level is interpreted in terms of the above model. An approximate time-dependent solution is obtained for the deep-level population which yields an initial fast decay at high-excitation levels. This fast component, which is due to two-electron-recombination processes, has also been observed in the GaP oxygen-donor infrared band.

I. INTRODUCTION

There is abundant theoretical[1] and experimental[2–7] evidence demonstrating the existence and stability of hole and electron pairs bound as excitons to neutral donors and acceptors. Because there are three bound particles present in this configuration, nonradiative recombination through an Auger process is highly probable and, in fact, is observed to be orders of magnitude greater than the accompanying radiative recombination.[4,6,7] (The low radiative efficiency of these centers contrasts with the high efficiencies obtained from excitons bound to isoelectronic centers, for example, nitrogen[8] and the zinc-oxygen nearest-neighbor complex[9,10] in GaP, where only two particles are bound, thus precluding the possibility of an intrinsic Auger process.) It has furthermore been suggested that the Auger process would render *deep* donors or acceptors particularly effective as nonradiative centers because of the large overlap of the bound-particle wave functions.[7] In this paper we analyze the recombination kinetics associated with such deep sites and attempt to identify experimentally verifiable clues which can be utilized to uncover these usually unwanted centers. Some experimental evidence of these effects has recently been observed for the oxygen donor in GaP, and these results are presented in an accompanying paper.[11]

II. ANALYSIS

For clarity the analysis will be specialized to p-type material, but the results can be carried over to n-type material in a straightforward manner. Deep centers are expected to be of most interest, but the activation energy of the first bound

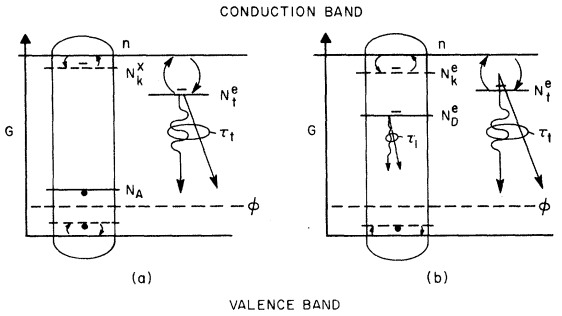

FIG. 1. (a) Schematic representation of recombination of minority electrons in a p-type semiconductor. Two centers are shown, a radiative center with concentration N_t and a nonradiative center with concentration N_A. The nonradiative center is a deep-acceptor level which first binds a hole, then a second hole, and finally a minority electron which forms an exciton with the second hole. (b) Same as in (a) except that the nonradiative center is now a deep donor, which first binds a minority electron, then a second electron, and finally a hole which forms an exciton with the second electron.

particle for the most part does not enter into our analysis and the centers are deep by implication only; the understanding being that thermalization of the first bound particle is not important at room temperature and that the Auger recombination rate increases rapidly with increasing activation energy. [An empirical expression for the Auger time, $\tau_A \approx (E_A/60)^{-4.5} \times 10^{-7}$ sec was obtained in Ref. 7 for a series of five acceptors in GaP, where E_A, the acceptor level, is given in meV. The expression was justified from considerations of increasing wave-function overlap with increasing acceptor energy.]

The systems to be discussed are schematically depicted in Figs. 1(a) and 1(b). The arrangement in Fig. 1(a) is simpler to analyze in that, with the exception of saturation effects, the recombination kinetics is described in terms of linear equations. In this figure the total concentration of deep acceptors is represented by N_A. A shallow-acceptor state, not shown, determines the position of the Fermi level φ, and hence the deep acceptors are assumed to be neutral. The neutral acceptor can capture a second hole[1] into a shallow level which is indicated by the unlabeled dashed line. If this shallow state is in rapid thermal communication with the valence band its population can be evaluated through Fermi statistics. Once a hole occupies a shallow state the center is again charged and can capture an electron to form a bound exciton (concentration N_k^x). The three-particle configuration is circled to emphasize that all particles are bound to the same center. A radiative center with an electron concentration N_t^e is also indicated and a prime goal of this paper is to determine what experimentally observable effects the specific nonradiative centers considered here have on the detectable radiation.

The arrangement shown in Fig. 1(b) is similar to the one in Fig. 1(a) except that the donor captures two rather than one minority carrier and therefore the relative values of the deep-donor-electron concentration N_D^e, the shallow-donor-electron concentration N_k^e, and the radiative center electron concentration N_t^e, depend nonlinearly upon the minority-carrier concentration n and hence nonlinearly upon the generation rate G. Analogous to the deep-acceptor example, the second electron must be captured before a hole can be captured to form a bound exciton. A deep-donor radiative-decay process is also depicted in Fig. 1(b) and, as with the radiation from the efficient center, specific attention will be directed toward uncovering effects of the bound-exciton nonradiative system that are displayed in the time, temperature, or intensity dependence of this radiation. In contrast with radiation from the deep-donor level, radiative recombination of the bound exciton is neglected. Observation and study of this luminescence is in itself sufficient evidence to identify the bound-exciton Auger process and this has been the route of previous investigations.[2-7] However, to date only shallow centers have been studied, the luminescence is very inefficient, and moreover it becomes increasingly inefficient for deeper centers.[6,7] For the more effective nonradiative centers we expect this radiation would be extremely difficult to detect.

To maintain physical insight and avoid an exercise in algebraic manipulation, a number of simplifying assumptions are made: Systems with three or more competing centers are not considered, and conductivity modulation, diffusion, and surface effects are neglected. A constant generation rate is utilized rather than one of the form $e^{-\alpha x - r^2/l^2}$, for instance, that may be found experimentally. The diffusion and surface effects can be important at high intensities even when absorption lengths are many times greater than diffusion lengths; these effects have been considered elsewhere in the context of a related problem.[12] The utilization of a nonuniform generation rate would tend to smooth out the intensity-related curves presented here. A convolution of these curves with a nonuniform generation function can be performed without much difficulty.

Despite the simplifications, we are left with many parameters and the treatment given here is by no means comprehensive. Rather, a few limiting cases are considered and in each situation the emphasis is placed on a different variable—temperature, intensity, or time.

Section II A treats the deep-acceptor system; the efficiency of the radiative center is followed as a function of temperature. Sections III B and

II C treat the deep-donor system. In Sec. III B the steady-state problem is considered as a function of excitation intensity while Sec. II C describes the time-dependent solution.

A. Analysis of Deep-Acceptor System

The rate equations describing minority-carrier recombination in Fig. 1(a) are

$$\dot{n}(t) = G + \frac{N_t^e(t)}{\tau_{tn}} + \frac{N_k^x(t)}{\tau_{kn}} - \frac{n(t)}{\tau_{nt}} - \frac{n(t)}{\tau_{nk}} , \quad (1a)$$

$$\dot{N}_t^e(t) = \frac{n(t)}{\tau_{nt}} - \frac{N_t^e(t)}{\tau_t} - \frac{N_t^e(t)}{\tau_{tn}} , \quad (1b)$$

$$\dot{N}_k^x(t) = \frac{n(t)}{\tau_{nk}} - \frac{N_k^x(t)}{\tau_{kn}} - \frac{N_k^x(t)}{\tau_A} , \quad (1c)$$

where the capture times into the radiative and nonradiative centers are given by τ_{nt} and τ_{nk}, respectively, while the corresponding thermalization times back into the conduction band are represented by τ_{tn} and τ_{kn}. The total decay of electrons out of the radiative center into the valence band, τ_t, includes both radiative and nonradiative mechanisms. The Auger decay at the nonradiative center is equal to τ_A. Saturation of the centers is not provided for in these equations and they are only applicable for low excitation intensities.

Consider first the derivation of an expression for the decay of carriers from the radiative center. The minority carriers n and the bound-exciton population N_k^x are assumed to attain equilibrium rapidly in comparison with the electrons captured by the luminescent center N_t^e,

$$\frac{1}{\tau_{nt}} + \frac{1}{\tau_{nk}} , \frac{1}{\tau_A} + \frac{1}{\tau_{kn}} \gg \frac{1}{\tau_t} + \frac{1}{\tau_{tn}} .$$

Hence, $\dot{n}$, $\dot{N}_k^e \approx 0$; furthermore, since luminescent decay is under consideration, the generation rate G is set equal to zero. Combining the simplified equations we obtain

$$\dot{N}_t^e(t) + N_t^e(t)\left(\frac{1}{\tau_t} + \frac{1}{\tau_{tn}[1 + (\tau_{nk}/\tau_{nt})\,(1 + \tau_A/\tau_{kn})]}\right) = 0 . \quad (2)$$

The solution to this equation is

$$N_t^e(t) = N_t^e(0) e^{-t/\tau_D} , \quad (3a)$$

$$\frac{1}{\tau_D} = \frac{1}{\tau_t} + \frac{1}{\tau_{tn}(1 + \tau_n/\tau_{nt})} , \quad (3b)$$

$$\tau_n \equiv \tau_{nk}(1 + \tau_A/\tau_{kn}) . \quad (3c)$$

The parameter τ_n measures the effectiveness of the nonradiative center; if the decay time τ_A is rapid compared to the thermalization time τ_{kn}, then this parameter is simply the capture time τ_{nk}. The form of Eq. (3) is the same as obtained in work on red-[13] and green-[14] emitting[14] GaP where a non-specific nonradiative center with a capture time τ_n has been considered.

Returning to Eqs. (1), we next consider the steady-state situation and solve for the quantum efficiency of the radiative center:

$$\eta = \frac{N_t^e}{\tau_R G} = \frac{\tau_D}{\tau_R} \frac{\tau_n/\tau_{nt}}{1 + \tau_n/\tau_{nt}} , \quad (4)$$

where τ_R is the radiative decay time and the identity given by Eq. (3c) is again utilized.

We restrict the analysis at this point to a specific example; the quantum efficiency is followed as a function of temperature. A shallow bound exciton is considered such that $\tau_{kn} < \tau_A$ and hence

$$\tau_n \approx (\tau_{nk}/\tau_{kn})\tau_A . \quad (5)$$

From detailed balance the capture and thermalization times are related through the electron-capture cross section σ_k:

$$\tau_{nk} = \frac{1}{\sigma_k v_{th} N_A f_{kp}} , \quad (6a)$$

$$\tau_{kn} = \frac{g_e e^{E_{kn}/kT}}{N_c \sigma_k v_{th}} . \quad (6b)$$

In the above, shallow holes are associated with only a fraction f_{kp} of the deep-neutral acceptors and only this fraction can capture electrons. The binding energy of the electron is E_{kn}, the conduction-band density of states is given by N_c and g_e represents the degeneracy factor of the bound-electron state. The fraction f_{kp} can be evaluated through Fermi statistics:

$$f_{kp} = \frac{1}{1 + (1/g_h)\exp[(\varphi - E_{kh})/kT]} , \quad p = N_v e^{-\varphi/kT} . \quad (7)$$

In these expressions g_h is the hole degeneracy factor, N_v is the valence-band density of states, E_{kh} is the hole binding energy, and p is the free hole concentration. Combining Eqs. (5)–(7) and assuming f_{kp} is small ($E_{kh} < \varphi$) we obtain

$$\tau_n \approx \frac{\tau_A N_c N_v}{g_h g_e N_A p} e^{-E_{kx}/kT} , \quad E_{kx} = E_{kh} + E_{kn} . \quad (8)$$

In Fig. 2 curves are presented of efficiency versus temperature, calculated for the GaP(Zn, O) red-emitting system using Eqs. (4) and (8) and the expression

$$\tau_{nt} = 1/N_t \sigma_t v_{th} , \quad (9)$$

where N_t and σ_t are, respectively, the density and electron-capture cross section of the radiative center (a Zn-O nearest-neighbor complex in this example[9,10]). The parameters used here describing

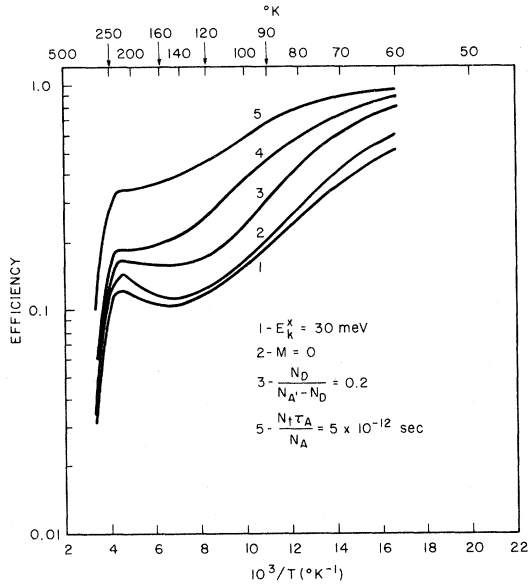

FIG. 2. Theoretical curves of efficiency vs reciprocal temperature for the GaP (Zn, O) system. The radiative center is the Zn-O nearest-neighbor complex and parameter values describing this site were taken from Ref. 13. The nonradiative center is assumed to be a deep-acceptor site as illustrated in Fig. 1(a). Parameter values $N_A - N_D = 2.5 \times 10^{17}$ cm^{-3}, $N_D/(N_A - N_D) = 0.4$, $E_{kx} = 20$ meV, $N_t \tau_A / N_A = 2 \times 10^{-12}$ sec, $\sigma_t = 5 \times 10^{-16} (300/T)^M$ cm^2, $M = 1$ were used on curve 4. The same values were used in the other curves with the exception of a variation in one parameter which is indicated on the figure. A value of $E_A = 60$ meV was used for the zinc acceptor level which determines the hole concentration.

the temperature variation of τ_D/τ_R are found in Ref. 13. The sharp drop in efficiency at ~250 °K stems from thermalization of electrons out of the luminescent center. The interesting feature from the viewpoint of the present discussion is the minimum that occurs in several of the curves. This minimum roughly coincides with the minimum in the ratio τ_n/τ_{nt} described by the expression

$$\frac{dp}{dT}\frac{T^2}{p} - \frac{E_{kx}}{k} - (\tfrac{7}{2} - M) = 0 , \qquad (10)$$

where M is the exponent in the expression $\sigma_t = \sigma_0 \times T^{-M}$. In general a minimum can be expected to exist if the acceptor level determining the hole concentration is greater than the exciton binding energy. The behavior depicted in Fig. 2 has been experimentally observed in GaP(Zn-O) crystals as reported in Ref. 11. The zinc acceptor level is ~60 meV in GaP and excitons bound to neutral acceptors even several hundred meV deep most likely have a lower binding energy.[7]

The results of this section are also pertinent to the case of silicon on a phosphorus site in GaP. Bound-exciton recombination on this site, which is an acceptor about 200 meV deep, has been previously suggested as a possible nonradiative mechanism in GaP.[7] By extrapolation of measurements performed on several shallow acceptors, the authors in Ref. 7 estimated a value of $\tau_A \approx 1$ nsec for silicon. Using this value and values of $N_c = 1.6 \times 10^{19}$ cm^{-3}, $N_v = 2.3 \times 10^{19}$ cm^{-3}, $p = 5 \times 10^{17}$ cm^{-3}, $g_h = g_e = 2$, and $E_{kx} = 25$ meV, we derive the relationship

$$\tau_n \approx 7 \times 10^{10}/N_A \text{ sec}$$

using Eq. (8). This expression was derived for the limit of thermalization time shorter than the Auger recombination time. It might be expected that the opposite limit would render the center more effective. However, the relationship $\tau_A < \tau_{kn}$ places a constraint on the maximum value of the electron-capture cross section, and the above result is also derived in this limit. A relevant minority-carrier lifetime in GaP (Zn, O) is somewhat under 200 nsec, which implies $N_A > 4 \times 10^{17}$ cm^{-3}. Evidence has been reported[15] of silicon acceptor concentrations of 3×10^{16} cm^{-3}, but higher concentrations would be unusual; silicon prefers the gallium donor site,[16] and the silicon acceptor does not appear to be a major recombination center in GaP (Zn, O).

B. Deep-Donor Analysis—Steady State

The deep-donor system illustrated in Fig. 1(b) differs from the acceptor case examined in Sec. II A in that two minority-carrier electrons are captured by the nonradiative center, the first electron bound in a deep level and the second in a shallower level; and nonlinearities are expected even at low intensities where saturation effects are not important. The equations describing the relatively complex recombination in this system are given in the Appendix.

Equation (A5) in the Appendix expresses the relationship between the steady-state electron concentration on the radiative center N_t^e, and the minority-carrier concentration n:

$$\frac{N_t^e}{N_t} = \frac{n/n_t}{1 + n/n_t} ,$$

$$n_t = 1/\sigma_t v_{th} \tau_t' , \qquad (11)$$

$$1/\tau_t' = 1/\tau_t + 1/\tau_{tn} .$$

The behavior of the deep-donor-electron concentration on the nonradiative center is of particular interest for diagnostic purposes and an expression analogous to (11) may be derived for this state from Eqs. (A3) and (A4):

$$\frac{N_D^e}{N_D} = \frac{n/n_D}{1+n/n_D\{1+(\tau_1/\tau_{2n}-1)[n/n_D+(\tau_1/\tau_{2n})(\sigma_D/\sigma_k)(1+\tau_{2n}/\tau_{kn}+\tau_{2n}/\tau_{2d})]^{-1}\}}\ , \quad n_D = 1/\sigma_D v_{th}\tau_1 . \tag{12}$$

The time constants τ_{2n} and τ_{2D} represent the two modes of decay of a donor center which has captured two electrons. The decay time τ_{2n} represents a final state in which one electron is ejected into the conduction band, while the decay time τ_{2D} represents a final state in which an electron is in the donor-deep-electron state.

The functional dependence of the normalized electron concentration N_D^e/N_D on the normalized minority-carrier concentration n/n_D is plotted in Figs. 3(a) and 3(b) for different values of the two parameters τ_1/τ_{2n} and $(\sigma_D/\sigma_k)(1+\tau_{2n}/\tau_{kn}+\tau_{2n}/\tau_{2D})$. Experimentally, the generation rate G is varied as opposed to the minority-carrier concentration, and a solution of Eq. (A6) is required if the various electron concentrations are to be specified over all excitation intensities. One such solution is illustrated in Fig. 4. There are several points of interest. At low excitation levels the shallow-electron cencentration N_k^e increases quadratically with increasing excitation, since the concentration of centers N_D^e that can trap shallow electrons increases linearly with generation rate. This behavior continues until two-electron recombination processes dominate at which point the increase of the deep-electron concentration N_D^e becomes sublinear. The radiative-center electron concentration N_t^e, in contrast to the electron concentrations on the nonradiative center, displays a linear dependence on generation rate until the center saturates. The explanation for the quasilinear behavior lies with the ejection of one of the trapped minority carriers from the nonradiative center into the conduction band upon recombination of the bound exciton. (The time constant $\tau_{2D} \to \infty$ in this example.) This effect tends to cancel out the nonlinearity introduced by the capture of two minority carriers. By varying parameter values the effects enumerated above may be modified, but in general they may be taken as representative of the system's behavior.

In the above example the minority-carrier concentration goes to infinity at a finite generation rate. The filling of all available centers and the lack of diffusion and surfaces in our model accounts for this behavior.

A useful expression that is easily derived from the steady-state version of Eqs. (A1)–(A4) is

$$G = N_k^e\left(\frac{1}{\tau_{2D}}+\frac{1}{\tau_{2n}}\right)+\frac{N_D^e-N_k^e}{\tau_1}+\frac{N_t^e}{\tau_t} . \tag{13}$$

The expression is a statement of particle conservation; the generation rate is balanced by recombination through three electron states. The dashed straight line in Fig. 4, the sum of the three normalized particle concentrations, illustrates this principle.

C. Deep-Donor Analysis—Time-Dependent Solution

Pursuit of the manifestations of bound-exciton recombination at neutral donors is continued in this section with the focus on the decay time of the donor deep-electron population. A complete solution is complex and the discussion here is limited to a particular example where the deep-donor-electron decay time is much slower than other times of interest. The appropriate assumptions and solution are given in the Appendix. A related problem has been treated by Cuthbert[17] with emphasis upon the decay of the minority-carrier concentration.

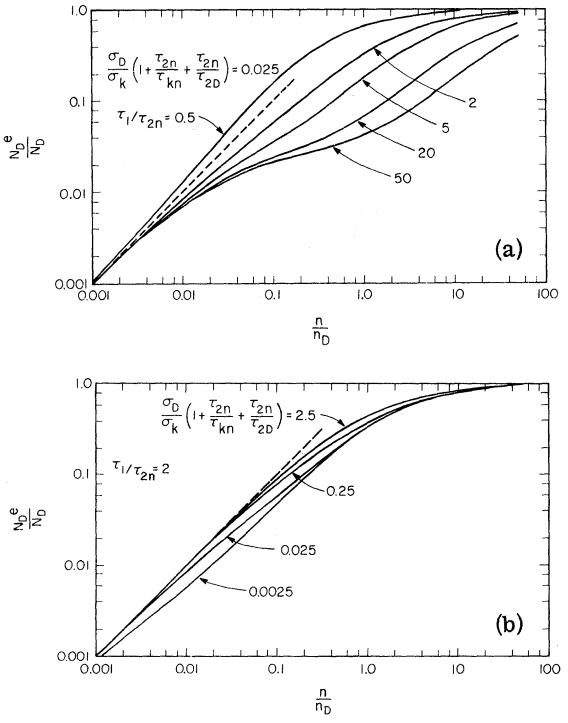

FIG. 3. (a) Normalized deep-donor-electron concentration N_D^e/N_D vs the normalized electron minority concentration n/n_D, as given by Eq. (12). The parameter $(\sigma_D/\sigma_k)(1+\tau_{2n}/\tau_{kn}+\tau_{2n}/\tau_{2D})$ is fixed at a value of 0.025 and the parameter τ_1/τ_{2n} is varied. (b) The same as (a) except that τ_1/τ_{2n} is fixed at a value of two and the parameter $(\sigma_D/\sigma_k)(1+\tau_{2n}/\tau_{kn}+\tau_{2n}/\tau_{2D})$ is varied. Excitation-intensity data in Ref. 11 on the oxygen-donor infrared band in GaP (Zn, O) has a functional dependence closely described by the curve $\tau_1/\tau_{2n}=2$ and $(\sigma_D/\sigma_k)(1+\tau_{2n}/\tau_{kn}+\tau_{2n}/\tau_{2D})=0.025$.

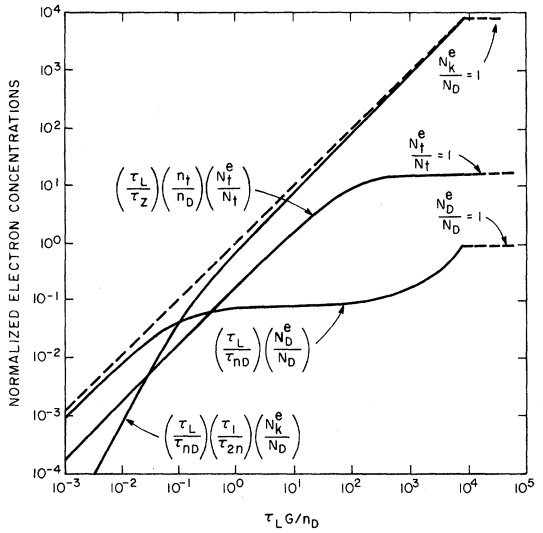

FIG. 4. Plot of three normalized electron concentrations as a function of the normalized generation rate for a system with a radiative center in competition with a two-electron deep-donor center. Parameter values are $\tau_z/\tau_{nD}=5$, $n_t/n_D=100$, $\sigma_k/\sigma_D=10$, $\tau_{2n}/\tau_{kn}=0.1$, $\tau_1/\tau_{2n}=10^4$, and $\tau_{2D}\to\infty$.

A few observations are made here on the basis of Eq. (A7) and a sample solution in Fig. 5. We first make the observation that when deep-donor-electron thermalization is negligible the decay time of N_D^e is given simply by τ_1. This solution is valid for times, following cessation of excitation, greater than the minority-carrier lifetime, the radiative-center decay time, and the Auger decay time. We know, however, from inspection of Fig. 4 that unless very high excitation intensities are utilized the second-electron population is small compared to the deep-donor-electron population (the basis of the approximation $N_k^e \ll N_d^e$ used in the Appendix) and large perturbations from this source are not expected on a short time scale either. There are two terms that depend upon deep-donor-electron thermalization. The first term disappears when $\tau_z \equiv \tau_{nt}(1+\tau_t/\tau_{tn})\to\infty$, which indicates that thermalized electrons are recaptured by the deep-donor level. The second term depends quadratically on N_D^e and represents the loss of thermalized electrons through two-electron recombination. It is this term that leads to the initial fast decay time in Fig. 5 when the deep-donor-electron concentration is high. Because of the quadratic dependence upon N_D^e, the fast component disappears at low initial values of the deep-donor-electron concentration.

III. DISCUSSION AND CONCLUSIONS

The identification of nonradiative centers in semiconductor material presents a formidable problem. In this paper we have considered a likely "killer" mechanism, bound-exciton recombination at neutral donors and acceptors via an intrinsic Auger process, and have presented general sets of equations describing such centers in competition with a radiative site. Two situations were studied, one in which one minority carrier is bound by the nonradiative center and a second case where two of the three bound particles are minority carriers. A number of parameters entered into the calculations and only a few specific examples were examined.

The following results were obtained. The efficiency of the radiative center can go through a minimum as a function of temperature when the bound exciton on the nonradiative site is shallow (where, by shallow, we mean that the thermalization time of the minority carrier associated in the exciton is faster than the Auger-recombination time). Silicon on an acceptor site in GaP has been suspect[7] as a possible important nonradiative center, but on the basis of the analysis given here this possibility is considered unlikely. For the case in which two minority carriers are captured by the nonradiative center several interesting effects emerge. With increasing excitation intensity, the deep-level concentration goes through two inflection points which are easily detectable if a radiative band is associated with this level. Several of the system's parameters can be evaluated on the basis of quantitative saturation measurements. While the two bound-minority-carrier populations as-

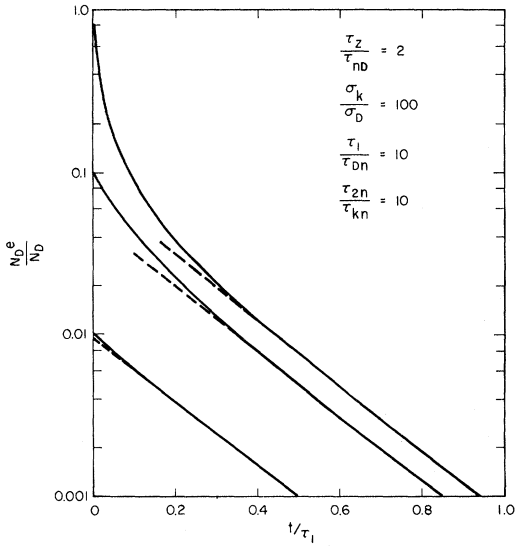

FIG. 5. Plot of the decay of the normalized deep-donor-electron concentration N_D^e/N_D for different initial values. The fast component is due to two-electron processes involving both the deep and shallow electrons. The solution for the upper curve is qualitative, since the assumption $N_k^e \ll N_D^e$ is not valid at time $t=0$.

sociated with the nonradiative center exhibit pronounced nonlinear behavior with increasing excitation intensity, the population of minority carriers captured by the radiative center obeys a nearly linear dependence on generation rate until this center saturates. A time-dependent solution was also obtained for the deep-level population. At elevated temperatures where thermalization of the deep level becomes important, intensity-dependent effects occur.

In an accompanying paper[11] experimental evidence is presented for the deep-donor oxygen in p-type GaP(Zn, O), which is interpreted in accord with two-electron recombination at this center. Data are also given of radiative efficiency versus temperature which can be described by the curves of Fig. 2 of this paper.

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APPENDIX

The equations describing recombination in the deep-donor system illustrated in Fig. 1(b) are

$$\dot{n} = G + \frac{N_k^e}{\tau_{kn}} + \frac{N_k^e}{\tau_{2n}} + \frac{N_D^e - N_k^e}{\tau_{Dn}} + \frac{N_t^e}{\tau_{tn}} - n\left[\frac{1}{\tau_{nt}}\left(1 - \frac{N_t^e}{N_t}\right) + \frac{1}{\tau_{nD}}\left(1 - \frac{N_D^e}{N_D}\right) + (N_D^e - N_k^e)\sigma_k v_{\mathrm{th}}\right], \quad \text{(A1)}$$

$$\dot{N}_t^e = \frac{n}{\tau_{nt}}\left(1 - \frac{N_t^e}{N_t}\right) - N_t^e\left(\frac{1}{\tau_{tn}} + \frac{1}{\tau_t}\right), \quad \text{(A2)}$$

$$\dot{N}_D^e = \frac{n}{\tau_{nD}}\left(1 - \frac{N_D^e}{N_D}\right) - \frac{N_D^e - N_k^e}{\tau_1} - \frac{N_D^e - N_k^e}{\tau_{Dn}} - \frac{N_k^e}{\tau_{2n}}, \quad \text{(A3)}$$

$$\dot{N}_k^e = n(N_D^e - N_k^e)\sigma_k v_{\mathrm{th}} - N_k^e\left(\frac{1}{\tau_{kn}} + \frac{1}{\tau_{2n}} + \frac{1}{\tau_{2D}}\right). \quad \text{(A4)}$$

We consider the steady-state problem first and Eqs. (A1)–(A4) reduce to algebraic expressions. The thermalization of deep donor electrons is neglected in this portion of the analysis. From Eq. (A2) the concentration of electrons on radiative centers in terms of the minority-carrier concentration is

$$\frac{N_t^e}{N_t} = \frac{n/n_t}{1 + n/n_t}, \quad \text{(A5)}$$

where

$$n_t = 1/v_{\mathrm{th}}\sigma_t\tau_t', \qquad 1/\tau_t' = 1/\tau_t + 1/\tau_{tn}.$$

In an analogous manner Eqs. (A3) and (A4) yield expressions for N_D^e and N_k^e in terms of the minority-carrier concentration n and the problem reduces to solving for n in terms of the generation rate G. The appropriate equation as derived from Eqs. (A1)–(A4) is

$$\frac{G\tau_L}{n_t} = \left(\frac{n/n_t}{1 + n/n_t}\right)\frac{\tau_L}{\tau_{nt}(1 + \tau_t/\tau_{tn})} + \frac{(\tau_L/\tau_{nD})(n/n_t)}{1 + (n/n_D)\{1 + (\tau_1/\tau_{2n} - 1)[n/n_D + (\tau_1/\tau_{2n})(\sigma_D/\sigma_k)(1 + \tau_{2n}/\tau_{kn} + \tau_{2n}/\tau_{2D})]^{-1}\}} \times\left(1 + \frac{n/n_D(\tau_1/\tau_{2D} + \tau_1/\tau_{2n} - 1)}{(\sigma_D/\sigma_k)(\tau_1/\tau_{kn} + \tau_1/\tau_{2n} + \tau_1/\tau_{2D}) + n/n_D}\right), \quad \text{(A6)}$$

where

$$\frac{1}{\tau_L} = \frac{1}{\tau_{nD}} + \frac{1}{\tau_{nt}(1 + \tau_t/\tau_{tn})},$$

$$\tau_{nD} = 1/\sigma_D v_{\mathrm{th}} N_D,$$

$$\tau_{nt} = 1/\sigma_t v_{\mathrm{th}} N_t,$$

$$n_D = 1/\sigma_D v_{\mathrm{th}}\tau_1.$$

The time-dependent solution is complex and we consider only one limiting case in which the decay of the deep-donor electron is followed. Equations (A1)–(A4) are utilized with the following assumptions: Saturation of the radiative center is neglected; the minority-carrier concentration n, the exciton electron concentration N_k^e, and the radiative-center electron population N_t^e are all considered to attain equilibrium in times short compared to the equilibrium time of the deep-donor electrons N_D^e, and hence, $\dot{n}$, $\dot{N}_k^e$, and $\dot{N}_t^e$ are set equal to zero. Also, the approximation $N_k^e \ll N_D^e$ is used. The thermalization term from the deep-donor level is retained in this example, while the terms involving τ_{2D} are dropped. Combining the simplified forms of Eqs. (A1)–(A4) we obtain

$$\dot{N}_D^e + N_D^e\left[\frac{1}{\tau_1} + \frac{1}{\tau_{Dn}[1 + (\tau_z/\tau_{nD})(1 - N_D^e/N_D)]} + N_D^e\left(\frac{\sigma_k v_{\mathrm{th}}}{\tau_{Dn}[1/\tau_z + (1/\tau_{nD})(1 - N_D^e/N_D)](1 + \tau_{2n}/\tau_{kn})}\right)\right] = 0, \quad \text{(A7)}$$

$$\tau_z \equiv \tau_{nt}(1+\tau_t/\tau_{tn})\,.$$

The solution to this equation is

$$\frac{t}{\tau_1} = \frac{1+\tau_z/\tau_{nD}}{1+\tau_1/\tau_{Dn}+\tau_z/\tau_{nD}} \ln\left(\frac{N_D^i}{N_D^e}\, g(N_D^e)\right) + \frac{(1+\tau_{2n}/\tau_{kn})\ln[\,g(N_D^e)\,]}{(\tau_1/\tau_{Dn})(\sigma_k/\sigma_D)-(1+\tau_{2n}/\tau_{kn})}\,,$$

$$g(N_D^e) = \frac{1+\tau_1/\tau_{Dn}+\tau_z/\tau_{nD}+(N_D^e/N_D)[(\tau_1/\tau_{Dn})(\sigma_k/\sigma_D)(\tau_z/\tau_{nD})(1+\tau_{2n}/\tau_{kn})^{-1}-\tau_z/\tau_{nD}]}{1+\tau_1/\tau_{Dn}+\tau_z/\tau_{nD}+(N_D^i/N_D)[(\tau_1/\tau_{Dn})(\sigma_k/\sigma_D)(\tau_z/\tau_{nD})(1+\tau_{2n}/\tau_{kn})^{-1}-\tau_z/\tau_{nD}]}\,. \tag{A8}$$

In the above, N_D^i is the initial value of N_D^e. This expression gives the normalized time t/τ_1 in terms of N_D^e; a numerical solution yields N_D^e as a function of time.

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