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Time-resolved recombination dynamics of photoionized hydrogenlike impurities

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The dynamics of recombination of photoionized shallow donors and free electrons is investigated on a nanosecond time scale by monitoring the photoconductive decay of high-purity n-type InP ($\mu > 10^5\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$) after pulsed far-infrared excitation. The effects of several parameters (temperature, electric fields, doping concentration, and excitation intensity) on the recombination process have been investigated, and models are proposed to explain the observed phenomena, taking into account excited bound impurity states, impact ionization, and Auger processes.

I. INTRODUCTION

The shallow donor in many III-V semiconductors is known to be a good analog of the hydrogen atom. This is particularly true for GaAs and InP, where the agreement obtained between experimental determinations of energy levels and predictions by hydrogenic theory is very good.[1,2] Very little is still known about the dynamical aspects of this system, such as impurity lifetimes and recombination rates, although these quantities may play an important role in many optical and transport measurements, and may determine performance and properties of (opto-) electronic devices. In this paper, a time-resolved experimental study is presented of the recombination of photoionized shallow donors in n-type InP. In particular we have tried to establish the effects of parameters as temperature, electric field, impurity, and free-electron concentration on the recombination process. By a careful analysis of these effects one can extract detailed information on the mechanisms that play an important role in the process.

Recombination occurs through capture of free electrons in bound states (usually highly excited ones), follows by a cascade down to the impurity ground state by several possible mechanisms. The dominant process in this energy relaxation is phonon emission.[3] Other channels might be photon emission or Auger-type processes, in which two free electrons interact at an ionized impurity, with one recombining to the center whilse the other moves away with excess energy (see, e.g., Ref. 4). The relative importance of these mechanisms is not fully determined: The cross section for the radiative recombination process has been shown to be too small to account for experimental results.[3] Electrical pulse experiments in Ge (Ref. 5) and Si (Ref. 6) indicate that the Auger process might already be important at moderate carrier concentrations. However, donors in these materials, in contrast to the case for InP, do not behave in a very hydrogenlike fashion which makes comparison with theory difficult. Furthermore, in both earlier experiments[5,6] very large electric fields were used for generation and probing of the recombining electron population and it is therefore doubtful if it was in equilibrium. The evidence for Auger recombination from such measurements has also been disputed elsewhere.[7] It has been suggested earlier that Auger processes may also be important in high-purity InP.[8] Here we will present further, quantitative support for this suggestion.

The technique used here to study the recombination is monitoring the photoconductive decay after pulsed far-infrared (FIR) optical excitation. This has some advantages over the methods employed so far by other workers: Using photon energies just above the ionization energy of the impurities makes it possible to create a relatively cold electron gas which is something that cannot be achieved with electrical or short-wavelength excitation, where hot electron effects introduce additional complications. In contrast to saturation measurements, one does not have to rely on models to deduce a lifetime, as one measures directly and time-resolved the free-carrier concentration.

This paper is organized as follows: In Sec. II a theoretical background is presented, which gives the temporal behavior of the free-electron-ionized donor system under several conditions. Section III gives the experimental details on the measurement technique used and the properties of the samples. In Sec. IV the measured dependences of the recombination process on temperature, electric field, free-carrier concentration, and impurity concentration are given and discussed. In the last part of Sec. IV, evidence for Auger processes is presented and further support for the simple analytic theory presented in Sec. II is given,

II. THEORETICAL BACKGROUND

The dynamical properties of a free-electron-ionized impurity system are most easily described with a rate-equation approach. We will first consider as an introduction the case where the impurity is considered to have only one bound state. The generally accepted expression is for n-type material at low temperatures[9]

$$\frac{dn}{dt}=A_T(N_D-N_A-n)+A_In(N_D-N_A-n)+A_O(N_D-N_A-n)-B_Tn(N_A+n)-B_In^2(N_A+n)-B_On(N_A+n)\ , \tag{1}$$

where n is the free-carrier concentration, N_D is the donor concentration, and N_A is the acceptor concentration. The first three terms on the right-hand side represent free-carrier generation due to thermal (T), impact ionization (I), and optical (O) processes, respectively, with the corresponding transition-rate parameters. The last three terms describe the free-electron-ionized donor recombination due to phonon emission, Auger processes and photon emission, respectively.

To a first approximation, the optical rates are much too small to explain experimental observations[3] and, at very low temperatures and electric fields, thermal and impact ionization are very unlikely processes. Furthermore, it is often assumed[9] that at impurity concentrations, where one still expects hydrogenlike behavior of the individual donor atoms ($N_D \leq 10^{15}$ cm^{-3} for GaAs and InP), the Auger process does not noticeably affect the recombination. (Later it will be clear that these assumptions are not always valid.) Equation (1) is now reduced to

$$\frac{dn}{dt}=-B_Tn(N_A+n)\ . \tag{2}$$

If one considers the recombination of a photocreated free-electron-ionized donor system, with initial electron concentration of n_0, one finds from Eq. (2)

$$n(t)=\frac{N_A}{(1+N_A/n_0)e^{B_TN_At}-1}\ . \tag{3}$$

For the case $n_0 \ll N_A$ only, this can be approximated by

$$n(t)\simeq n_0e^{-B_TN_At}\ . \tag{4}$$

Thus by monitoring the decay of the free-electron concentration one can find B_TN_A. This can be done by measuring the conductivity as a function of time, under the assumption that the electron mobility does not change much during the decay process. The validity of this assumption is not self-evident, as the major scattering mechanism at low temperatures is ionized impurity scattering (for an extensive review on this subject, see Ref. 10). It could therefore be argued that when a large fraction of the donors is photoionized, the electron drift mobility will be lower due to the larger concentration of scattering centers. However, the photocreated electron gas will strongly screen all ionized impurities thereby enhancing the mobility. Using the Brooks-Herring formalism,[11] which takes both of these effects into account, it is found that the calculated mobility values for the samples used in this study (see Sec. III) are only very weakly dependent on the degree of photoionization of the donors. Furthermore, the experimental conditions ensure that the electron gas is in approximate thermal equilibrium with the lattice at the beginning of the measured photosignal decay: Electrons are injected a few meV above the conduction-band edge, and establish an effective electron temperature T_e within a few picoseconds,[12] which approaches the lattice temperature within a cool-down period of 10–20 ns after injection.[13] Since the choice of the pulse width (50 ns) and the observed decay times imply that the impurity population remains ionized for a longer period than the cool-down time, the electron population is in near equilibrium with the lattice prior to recombination. There are, therefore, no changes due to the dependence of the mobility on T_e, and it seems justified to ascribe any change in the conductivity during the recombination process entirely to a change in carrier concentration.

In the treatment presented up to now, the presence of many bound states for each impurity atom has not been taken into account. Rather, the interactions of free electrons with these states have been lumped into one parameter. It has, however, been shown that the higher bound state can strongly affect the dynamical behavior of an impurity system.[14] Equation (1) therefore has to be modified in order to incorporate these states

$$\frac{dn}{dt}=\sum_i A_{Ti}N_{Di}+\sum_i A_{Ii}nN_{Di}+\sum_i A_{Oi}N_{Di}-\sum_i B_{Ti}n(N_A+n)-\sum_i B_{Ii}n^2(N_A+n)-\sum_i B_{Oi}n(N_A+n)\ , \tag{5}$$

where the summation runs over all bound states and N_{Di} represents the population of the ith bound donor state. Some simplification can be obtained by noting that the photon and phonon term are analogous in appearance and that the phonon processes have a much higher probability than the corresponding photon processes[3] which may therefore be neglected. A further simplification can be made by noting that, although the hydrogen atom has infinitely many bound states, only a very small number of these can be considered as bound in the case of a hydrogenlike impurity in a semiconductor. It can be argued that due to wave function overlap, only states with principal quantum number up to 3 can be considered as localized for n-InP with impurity concentrations of about 2×10^{14} cm^{-3}. This is consistent with experiments using Fourier-transform spectroscopy,[2] where the highest transition observed on comparable material is 1s-3p.

In order to solve Eq. (5), one needs also to know how the electrons are transferred between the bound states. The dominant processes here are the ones involving absorption or emission of longitudinal acoustical phonons.[15] One can write down a set of rate equations for the populations of these bound states and solve them consistently with Eq. (5). Although this can be easily done numerically, there are too many unknown parameters in these equations to make a meaningful comparison with experimental results possible. Therefore, two different approximative approaches were taken, an analytical one and a numerical one, as described below.

Considering first the analytic approach, it turns out to be possible to find a meaningful solution making the following approximations:

(1) The dominant free-carrier recombination process is under phonon emission.

(2) The dominant free-carrier generation process during decay is impact ionization.

(3) The transitions between bound states do not strongly affect the free-carrier concentration.

The first two solutions will hold at low temperatures and low electric fields. This is not necessarily the case for the third one but we will return to this later. The entire problem has now been reduced to finding the solution of the following differential equation:

$$\frac{dn}{dt}=\alpha(E,t)n(N_D-N_A-n)-B_Tn(N_A+n)\ , \tag{6}$$

where

$$B_T\equiv\sum_{i=1}^{M}B_{Ti}\ ,$$

$$f_i\equiv\frac{N_{Di}}{N_D-N_A-n}\ ,$$

$$\alpha(E,t)\equiv\sum_{i=1}^{M}A_{Ii}f_i(E,t)\ ,$$

and M is the number of states that can be considered as bound. The fractional bound-state occupation f_i will, in general, be a function of time t and electric field E. However, as the decay sets in, the populations of all bound states will start to increase at the expense of the free-carrier concentration, so the fractional occupation of each bound level (f_i) will not change much. It seems therefore permissible to assume that $\alpha(E,t)$ does not change significantly during the free-carrier decay. Further support for this assumption will be presented below. Equation (6) is then readily solvable for an electron concentration starting at n_0:

$$n(t)=\frac{B}{(1+A)e^{t/\tau}-1}\ , \tag{7}$$

where

$$A=\frac{B_TN_A-\alpha(N_D-N_A)}{n_0(B_T+\alpha)}\ , \tag{8a}$$

$$B=\frac{B_TN_A-\alpha(N_D-N_A)}{B_T+\alpha}\ , \tag{8b}$$

$$\tau^{-1}=B_TN_A-\alpha(N_D-N_A)\ . \tag{8c}$$

We thus recover the same nonexponential temporal behavior as under neglect of impact ionization or the presence of many bound states [cf. Eq. (3)]. Both these effects are, however, expected to show up both in the values one finds for the decay time τ and in its dependence on electric field and boundary conditions. In Sec. IV the predictions of this simple analytic model will be compared with experiments.

Unfortunately, the analytical procedure outlined above cannot be simply used to model the population of bound states or the effect of Auger processes. The approach adopted for those cases was to solve a slightly simplified set of rate equations for the conduction-band and bound-state populations numerically. The assumption made here is that the transitions of electrons into or out of donor atoms happen only at the highest bound level. The justification for this is that the interaction of a bound state with the conduction band drops off as a high power or as an exponential of the separation between them, for phonon[15] and Auger[4] processes, respectively. A further reduction of the complexity is obtained by noting that among the bound states with a given principal quantum number, the s states (zero angular momentum) interact most strongly with each other and with the conduction band.[15] Therefore only these states are retained in the analysis, which reduces the set of equations to be solved to

$$\begin{aligned}\frac{dn}{dt}&=A_TN_{3s}+A_InN_{3s}-B_Tn(N_A+n)\\&\quad-B_In^2(N_A+n)\ ,\\\frac{dN_{3s}}{dt}&=-\frac{dn}{dt}+W_{1s\to2s}N_{1s}+W_{2s\to3s}N_{2s}\\&\quad-(W_{3s\to1s}+W_{3s\to2s})N_{3s}\ ,\\\frac{dN_{2s}}{dt}&=W_{1s\to2s}N_{1s}+W_{3s\to2s}N_{3s}\\&\quad-(W_{2s\to3s}+W_{2s\to1s})N_{2s}\ ,\\\frac{dN_{1s}}{dt}&=W_{2s\to1s}N_{2s}+W_{3s\to1s}N_{3s}\\&\quad-(W_{1s\to2s}+W_{1s\to3s})N_{1s}\ .\end{aligned} \tag{9}$$

The transition rates $W_{i\to j}$ between the bound states under phonon emission or phonon absorption can be easily calculated following Brown and Rodriguez (Ref. 15). A final reduction of the number of unknown parameters in Eq. (9) can be obtained from the principle of detailed balance.[16] This principle states that for a system in thermodynamic equilibrium the rates of a given process and of its reverse balance each other exactly. This results in

$$A_TN_{3s}=B_Tn(N_A+n) \tag{10}$$

and

$$A_InN_{3s}=B_In^2(N_A+n)\ . \tag{11}$$

With the approximations made above, the number of undetermined parameters in the rate equations has been limited to two (e.g., B_I and B_T). As the two processes they represent are of different order in the carrier concentration, it might be hoped to find them from a comparison with experimental results. This will be pursued in the last part of Sec. IV.

III. EXPERIMENTAL DETAILS

As was argued above, it is possible to determine the recombination of a free-electron gas resulting from the photoionization of shallow impurities by simply monitoring the conductivity. The samples studied here in this way consisted of unintentionally doped epitaxial n-InP, grown by chloride vapor phase deposition[17] and metal-organic chemical vapor deposition.[18] Their properties, as determined from galvanomagnetic measurements[19] and luminescence experiments[20] are shown in Table I. Care was taken that the bias electric field inside the epilayer was homogeneous. It was checked by varying the separation between the contacts that the contact resistance did not contribute significantly to the total sample resistance even under intense FIR irradiation. Therefore the two-terminal conductance of such a sample is proportional to the electron concentration.

The FIR radiation used in this experiment was generated with the pulse-switched laser system described elsewhere (Ref. 21). The wavelength used in the present work was 90.9 μm with an intensity on the sample of 2×10^2 W cm^{-2}, implying that a very high degree of photoionization can be obtained. A transmission switch was used which enables the FIR pulses to be switched off within 1 ns after approximately 50-ns pulse duration. This guaranteed that a large fraction of the electrons that were photoinjected into the conduction band had cooled down to lattice temperature before the actual decay was studied.

To the experimentally observed decay a curve of the form of Eq. (7) was fitted by the method of least squares. The uncertainty in the values obtained in this way for τ, due to noise, small baseline shifts, etc., was about 5%.

IV. RESULTS AND DISCUSSION

Figure 1 shows a typical decay obtained for sample 1 with a curve fitted according to Eq. (7). For comparison, a simple exponential curve, as in Eq. (4) giving the closest fit to the experimental data is also included and it is clear that this fails to describe the result within the experimental uncertainty. The nonexponential shape of the data curve is a direct consequence of the fact that n_0 can become larger than N_A under the condition of intense FIR illumination realized here. The concentration of recombination centers (i.e., ionized donors) may in consequence vary significantly during the decay; this concentration would be essentially constant if n_0 was much smaller than N_A and would be approximately equal to N_A.

TABLE I. Sample properties.

Sample	μ (77 K) (m^2/V s)	N_D (10^{14} cm^{-3})	N_A (10^{14} cm^{-3})
1	12.3	3.1	1.9
2	11.4	4.2	2.0
3	13.3	3.9	0.2
4	9.2	9.4	0.8
5	7.6	9.7	6.0
6	10.4	4.4	3.6

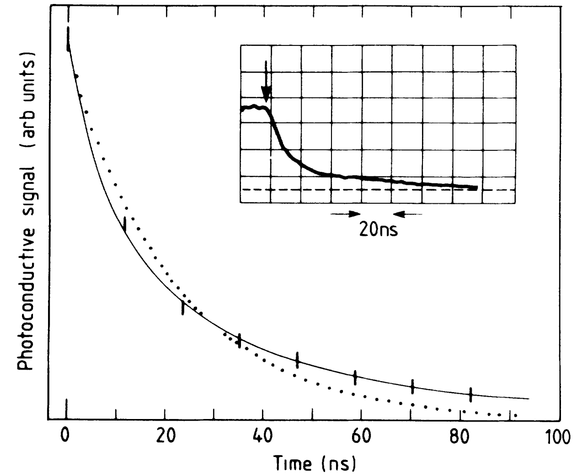

FIG. 1. Photoconducive signal after termination of the laser pulse ($t=0$) for sample 1 at temperature (T) of 4.2 K and bias electric field 1.2 V/cm. Dotted line, best exponential fit; solid line, see text. Inset shows the actual signal; $t=0$ is indicated with an arrow.

Furthermore the good fit indicates the validity of the assumptions that led to Eq. (7). The value obtained for τ will, according to this simple analytic model, be dependent on N_D, N_A, E, T, and n_0 in a very intricate way. The effects of these parameters will be discussed below. The effect of a magnetic field on the decay process is much more complicated and will be discussed elsewhere.[22]

A. Temperature dependence

Figure 2 shows the observed temperature dependence of τ for sample 1. The solid line is a fit to a simple power law, with an exponent 1.7 ± 0.1. This is in good agree-

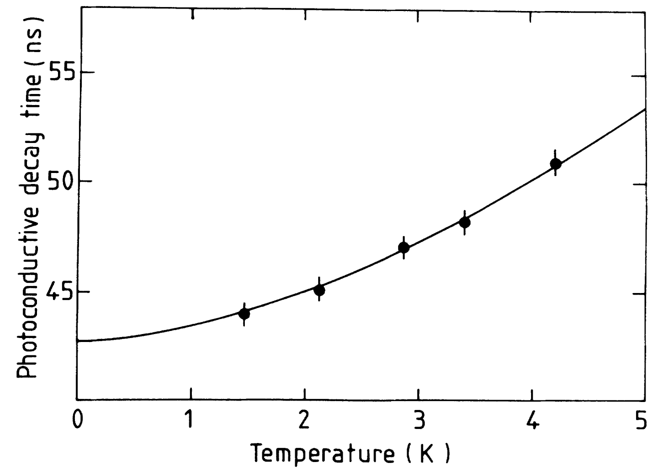

FIG. 2. Temperature dependence of the photoconducive decay time for sample 1 at a bias electric field of 0.8 V cm^{-1}. The solid line is a simple power-law fit to the data points and corresponds to an exponent of 1.7 ± 0.1.

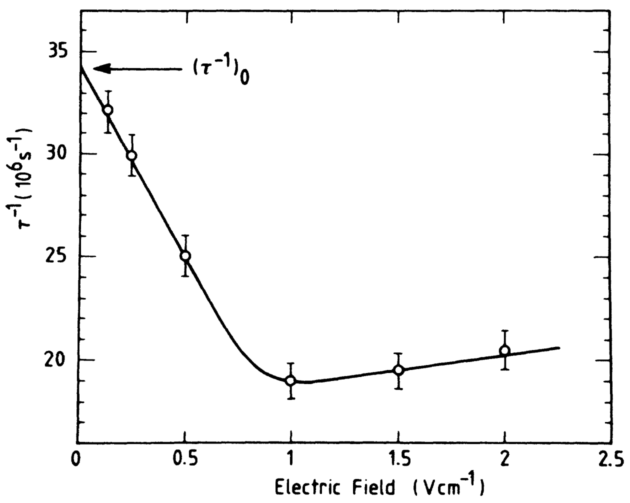

FIG. 3. τ^{-1} obtained from a series of fits of the photoconductive decay for sample 1 as a function of bias electric field at full laser power at $T=2$ K. A linear dependence for the data at the lowest bias fields is indicated.

ment with the results obtained for shallow donors[5] and shallow acceptors[7] in germanium and with theoretical estimates by Brown and Rodriguez,[15] which illustrates the universal character of hydrogenlike impurities in semiconductors. In the aforementioned calculations, the major contribution to the temperature dependence of the total recombination cross section, was found to originate from the temperature dependence of B_T. Such a conclusion cannot be reached from the present measurements, as the temperature dependence of α in Eq. (8) or the neglected thermal ionization terms [A_{Ti}, see Eq. (5)] may also cause the observed dependence.

B. Electric-field dependence

Figure 3 shows the variation of τ^{-1} with bias electric field obtained from a series of fits for sample 1. Similar behavior was also observed at slightly higher temperature for all the samples investigated as shown in Fig. 4. The general features are that τ^{-1} decreases linearly with increasing electric field up to a certain field (typically 0.5 V/cm) above which the dependence levels off or even reverses sign.

This behavior can be qualitatively understood from Eq. (8) in the following way: At the low electric fields used here, the average thermal kinetic energy of the free electrons still exceeds the extra average kinetic-energy gain from the electric field, even at liquid-helium temperature. Therefore only very few electrons will be accelerated by the field to velocities significantly above the average thermal velocity. As $B_T(T,E)$ depends on T and E only through the velocities of the electrons participating in the recombination process, its value will only be slightly lowered by the electric field. Although $A_{Ii}(T,E)$ depends in the same fashion on T and E, there is a minimum electron velocity needed to ionize a bound state, so that the few electrons that are accelerated above the average thermal velocity may increase A_{Ii} significantly. One might, therefore, expect that the dominant electric field dependence of τ at low temperatures and electric fields occurs through A_{Ii}. Calculations indicate that the impact ionization coefficient increases more or less linearly with electric field.[23] Little can be said about the electric-field dependence of the $f_i(E,T)$, but is seems unlikely that major redistributions between the bound state populations will result for low electric fields as compared to the zero-field case. Therefore α will be approximately linear in E, and τ^{-1} will decrease linearly with increasing electric field, as observed experimentally. Furthermore, it follows that

$$\frac{1}{N_A}\frac{\partial \tau^{-1}}{\partial E}=\frac{\partial B_T}{\partial E}-\frac{N_D-N_A}{N_A}\frac{\partial}{\partial E}\sum_i A_{Ii}f_i$$
$$\simeq -c_1-c_2(N_D/N_A-1)\,, \qquad (12)$$

where c_1 and c_2 are positive constants only dependent on material properties. Figure 5 does indeed show this functional relation, in support of the correctness of the simple model that led to Eqs. (7) and (8).

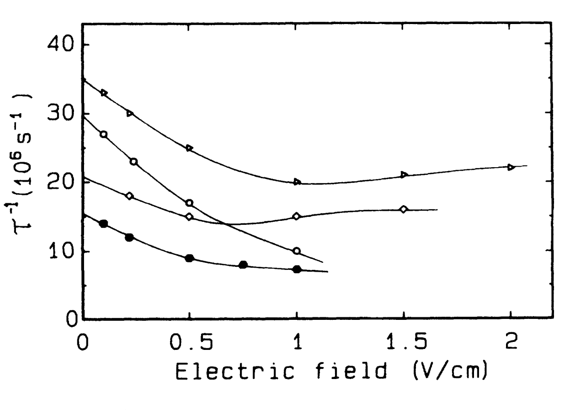

FIG. 4. τ^{-1} as a function of bias electric field for several samples at full laser power at $T=4.2$ K. A linear dependence for the data at the lowest bias fields is indicated. ▽, sample 1; ○, sample 2; ◇, sample 6; ●; sample 4.

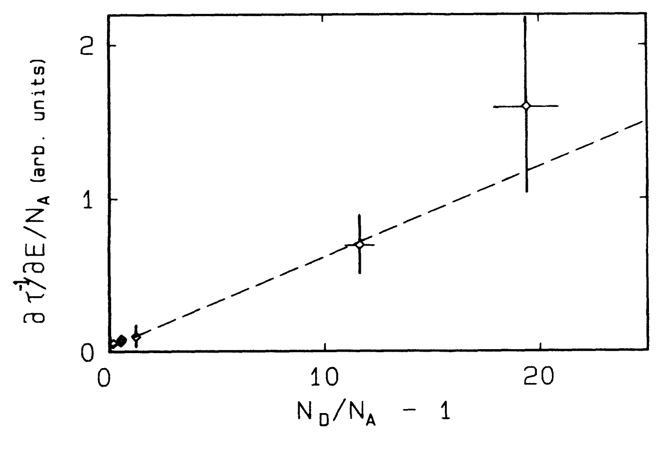

FIG. 5. Electric-field dependence of τ^{-1}/N_A at low fields vs (N_D/N_A-1). A linear dependence, as predicted by Eq. (12), is indicated.

The experimentally observed breakdown of the linear behavior of τ^{-1} at higher fields can have several causes. It is possible that the assumptions made to derive the simplified differential equation (6) are no longer valid in this field range, e.g., because transitions between bound states due to impact excitation start to occur, as been observed elsewhere,[14] or that α is no longer constant during the decay. It should, however, be noted that the (nontrivial) temporal behavior of the decay curve [Eq. (7)] is observed with high accuracy up to fields of 1 V/cm, where τ no longer obeys Eq. (8). This behavior therefore remains to be explained.

C. Excitation dependence

Figure 6 shows the variation of τ^{-1} with FIR intensity for sample 1 at a bias of 0.5 V/cm. As there is no FIR radiation present during the actual decay, its effects on the time constant must occur through the boundary conditions of the process, i.e., the distribution of the electrons over the conduction band and the bound states at the onset of the decay. Evidently, the initial population of excited bound states will decrease with decreasing FIR intensity and therefore also impact and thermal ionization will decrease, making the decay effectively faster. If one neglects the thermal ionization, Eq. (8c) is expected to apply for τ^{-1}. As the impact ionization coefficients A_{Ii} increase with increasing principal quantum number (i.e., shallower state), one finds that τ^{-1} will be larger if more impurity atoms are in the ground state and less are in the excited states. Continuing this argument, one would expect that as long as the bias electric field is below the value for ground-state impact ionization ($A_{I1} \simeq 0$), the limit of zero FIR intensity ($f_i = \delta_{i,1}$) will yield a value of τ^{-1} close to that determined at zero bias for any FIR intensity. Comparison of Figs. 3 and 6 shows that these two limits do indeed yield the same value for τ for sample 1, which is the purest one investigated. Any difference in the two values should come out of the electric-field dependence of B_T (which was above argued to be small), out of thermal ionization effects (which are also expected to be very small at the low temperatures used), or out of the presence of built-in electric fields due to the presence of ionized impurities. The good agreement obtained shows that all these effects are negligible for this sample. The intensity dependence for the other sample investigated has been found to be similar. They all show a significant decrease in τ with decreasing FIR intensity. Table II summarizes the limiting values of τ obtained. However, it shows that the two limits do not coincide for the other, less pure samples. As the values for τ have been obtained at the same bias electric field and temperature as for sample 1, the difference between the two limiting values for τ has to stem from built-in electric fields. We will elaborate on this below.

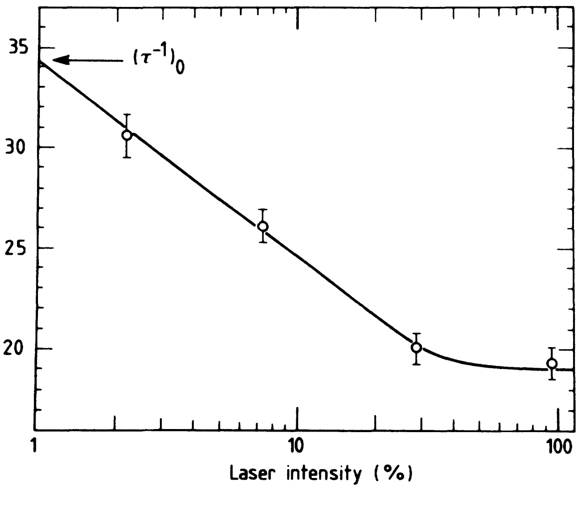

FIG. 6. τ^{-1} obtained from a series of fits of the photoconductive decay for sample 1 as a function of incident FIR intensity at $T = 2$ K and a bias electric field of 1.0 V/cm. The line is meant to guide the eye.

D. Doping dependence

In writing down a rate equation such as (1), it is implicitly assumed that the presence of other impurities does not affect the recombination probability of an electron with a given ionized donor. This will indeed be correct for very-low-impurity concentrations, where the average interimpurity spacing is much larger than the (excited state) Bohr radius. However, for the III-V semiconductors GaAs or InP, this condition is barely fulfilled for the purest material available. For sample 1 one finds an average interimpurity spacing of $\langle r \rangle_I = (3/4\pi N_I)^{1/3} = 84$ nm whereas the expectation value for the radius of a 2*s* electronic state in InP is[24] $\langle r \rangle_{2s} = 3/2 a_B 2^2 = 48$ nm. The presence of impurities will affect the recombination in several ways. They will scatter free electrons and thereby reduce the diffusion coefficient; in addition, charged impurities introduce strong and rapidly varying electric fields in the material (Ref. 25 and references therein). These fields will cause Stark shifts of the bound-state levels and will facilitate thermal ionization (the Poole-Frenkel effect, see, e.g., Refs. 26 and 27). They may even cause field emission from a neutral donor (Ref. 28 and references therein).

Field-assisted thermal ionization will effectively increase the A_{Ti}. This is given for a constant electric field E by[26]

TABLE II. Observed decay rates, extrapolated to zero intensity and zero elastic field.

Sample	τ^{-1} ($E = 0$) (10^6 s^{-1})	τ^{-1} ($I = 0$) (10^6 s^{-1})
1	27	27
2	30	40
3	4	22
4	16	23
5	37	
6	22	94

$$\frac{A_{Ti}(E)}{A_{Ti}(0)} = \left[\frac{kT}{\beta}\right]^2 \left[1+\left[\frac{\beta}{kT}-1\right]\exp\frac{\beta}{kT}\right]+\frac{1}{2}\,, \tag{13}$$

where β is given by $\beta=(e^3E/\pi\epsilon)^{1/2}$. With an electric field of 10 V/cm at 4.2 K this gives a factor of 3 increase in the thermal ionization, and this factor increases rapidly with electric field.

The classical condition for field emission is[28]

$$E > \frac{E_{nlm}}{e\langle r\rangle_{nlm}} = \frac{2E_{\mathrm{Ryd}}}{ea_B n^2[3n^2-l(l+1)]} \tag{14}$$

which for an electronic 3*s* state in InP yields a threshold of 75 V/cm. This may seem high compared to the bias electric field, but such fields have a finite probability to be present.[29] Furthermore, in a quantum-mechanical treatment, there is already a finite probability for emission at much lower fields. The ultimate effect on the photoconductive decay time is then determined by the capture into excited bound states as compared to all ionization mechanisms, including field emission. This is demonstrated by Fig. 7, where $\tau^{-1}(E=0)/N_A$ is shown as a function of N_A. Without the notion of a built-in electric field, the simple analytic theory outlined above states that $\tau^{-1}(E=0)/N_A=B_T$ [Eq. (8)] and is, therefore, a constant. The experimentally observed sharp drop of τ^{-1}/N_A at acceptor concentrations above 1×10^{14} cm^{-3} implies, therefore, an increase in ionization probability or a decreasing recombination probability due to some mechanism not included in this model. The built-in electric field, and therefore the field-emission probability and the field-assisted thermal ionization, are proportional to N_A (Ref. 28) so the drop in Fig. 6 could be explained by this mechanism. A drop in recombination probability could be ascribed to a decrease in diffusion coefficient due to ionized impurity scattering, which ensures that an electron will encounter less ionized donors per unit time. However, the observed drift mobility at 77 K, which is also proportional to the diffusion coefficient, does not show a correlation with the values for τ^{-1}/N_A. This second possibility has thus to be considered as unlikely. The drop of τ^{-1}/N_A is, therefore, tentatively attributed to built-in electric field effects due to the presence of ionized impurities. A more affirmative statement cannot be made as no detailed theories on these effects for hydrogenlike impurities in rapidly spatially varying electric fields are available. The only related work known to the present authors concerns itself with activated emission out of donors in silicon under externally applied electric fields (Ref. 30) which indeed shows strongly reduced lifetimes, especially for the excited states.

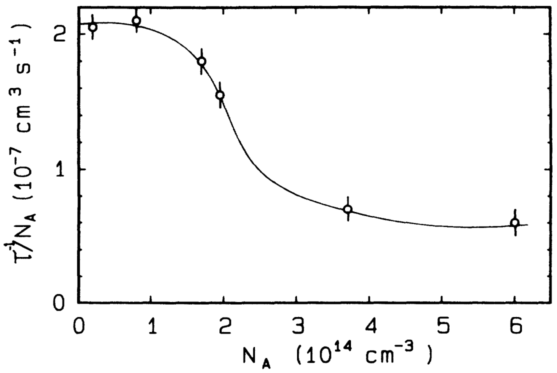

FIG. 7. τ^{-1}/N_A, extrapolated to zero electric field, as a function of N_A. The solid line is meant to guide the eye.

A further phenomenon dependent on the doping concentration that may affect the recombination rate is screening. Both the free electrons and those bound to impurities will redistribute themselves in space under the influence of a Coulomb potential, thereby reducing the effect of such a potential far away. Estimates of the screening length for the simplest possible case, a single-ionization energy impurity system,[31] yield values of the order of the Bohr radius for the samples investigated in this work. These values show only a slight dependence on the ionization fraction of the donors, and are, therefore, constant during the decay. The present experimental regime is a rather awkward intermediate one in which screening cannot be completely neglected, neither can the impurities be considered as noninteracting since the average spacing is also of the order of the Bohr radius. The more realistic case of an impurity system with many energy levels for which the higher ones are partly populated, as is relevant to the present case, has not been considered in the literature. However, the good agreement between the experimental observations and the simple theory outlined above, suggests that screening effects are not very important.

E. Numerical solution

In all the experimental results described up to now, the temporal behavior of the photoconductive decay could be accurately described by an expression of the form given by Eq. (7). However, for the samples with the lowest acceptor concentration, which exhibit a long photoconductive decay time (samples 3 and 4) under high-excitation-intensity conditions, this was no longer the case. Figure 8(a) shows a result obtained for sample 3, with $\simeq 100$ W cm^{-2} incident FIR power. These data cannot be fitted by an expression of the form of Eq. (7). The best attempt to do this is shown in the figure (curve *A*). The simple behavior is recovered at lower excitation intensity [Fig. 8(b)]. In order to explain the faster initial decay noted under high-intensity conditions (and therefore large initial free electron concentrations) Auger recombination is considered. The simple model used so far could be extended to incorporate this effect, but further severe approximations would have to be made to obtain an analytic solution. Therefore it was preferred to solve an approximative set of rate equations [Eqs. (9)] numerically as described in Sec. II. The phonon recombination B_T was deduced from low-intensity measurements on the same sample. With a value of $B_I \simeq 4\times10^{21}$ cm^{6}s^{-1}, good agreement between theory and experiment is obtained; Figure 9 shows the numerical solution for the conduction-band population [curve $N_c(1)$]. The agree-

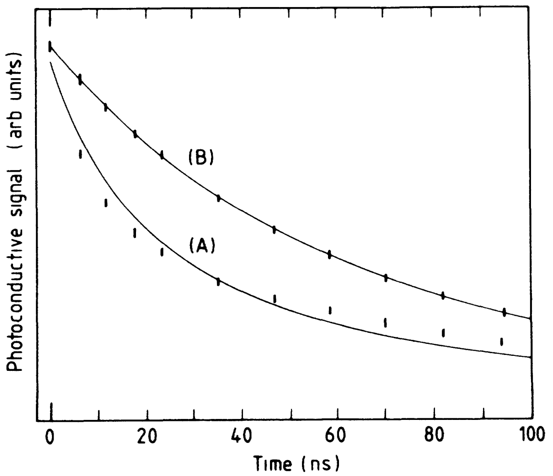

FIG. 8. Normalized photoconductive signal after $t=0$ for sample 3 at $T=3$ K, and bias electric field of 1.0 V/cm. Fits to data at (A) 100% and (B) 7.5% laser intensity.

ment with the experimental data (∇) is clearly much better than for the best-fitting curve according to Eq. (7) [Curve $N_c(2)$], which in addition has very unrealistic parameters. The value for B_I is consistent with theoretical estimates[4] for a hydrogenic level of $\simeq$1-meV binding energy that is believed to be the dominant trapping level for the samples studied here. We therefore conclude that our observations are due to Auger processes. The reason these are visible in such high-purity material lies in the possibility to create a cold, high-density electron gas with pulsed FIR excitation and to study the resulting temporal behavior with high accuracy. Also shown in Fig. 9 are the populations of the bound states involved in the recombination deduced from the solution of Eqs. (9). Clear population inversion is found that can last tens to hundreds of nanoseconds. As only s states are incorporated in the analysis, between which no optical transitions are allowed,[23] no statements on the realizability of optically pumped FIR laser action can be made. Now that the population of the bound state during the decay is known, it is possible to calculate the α that we have previously assumed to be constant during the decay in order to find an analytic solution. In order to do so, one has to make an assumption on the binding energy dependence of the ionization coefficient A_{Ii}. Calculations show[23] that this dependence is linear. α calculated in this way is shown in Fig. 9, and the assumption of its constantness, made to derive Eqs. (7) and (8), is shown to be correct.

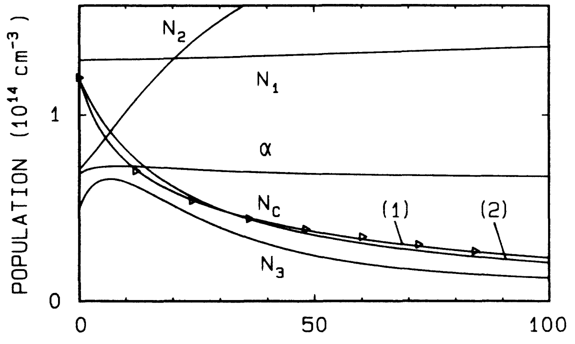

FIG. 9. Experimentally observed PC decay for sample 3 at $T=4$ K and bias electric field 1.0 V/cm (∇). Shown are the bound-state populations N_1, N_2, and N_3 and the conduction-band population N_c for (1) best fit using numerical solution of rate equations, with parameters $B_I=3.5\times10^{-21}$ cm^{6}s^{-1}, $B_T=2\times10^{-7}$ cm^{3}s^{-1}, $N_c(0)=1.2\times10^{14}$ cm^{-3}, $N_1=1.3\times10^{14}$ cm^{-3}, $N_2=0.7\times10^{14}$ cm^{-3}, and $N_3=0.5\times10^{14}$ cm^{-3}. (2) Best fit to simple analytical solution, with $\tau=7$ μs.

Finally, with the numerical model it is also possible to check the assumption that transitions between bound states do not strongly affect the free-carrier concentration. This assumption was made without *a priori* justification in order to be able to find an analytic solution to the problem. We empirically find that the only intraimpurity rate that affects the free-carrier concentration at all is $W_{3s\rightarrow2s}$, which has a value of about 5.5×10^7 s^{-1}. This means that the removal of electrons out of the 3s state is faster than their entering, especially for the samples with $N_A<10^{14}$ cm^{-3}. Therefore the removal of electrons out of the conduction band is dominated by their capture in the highest bound state. Together with the constantness of α, justified above, this gives support to the correctness of the analytic model under conditions that Auger processes can be neglected. In view of the experimental support of the simple model outlined in Sec. II, one can state that measurements of the recombination decay time can provide a method for determination of both N_D and N_A, once B_T is known. This could be especially useful for material of high purity where galvanomagnetic measurements are cumbersome.

V. SUMMARY AND CONCLUSION

We have studied the recombination of free electrons with ionized hydrogenlike donors in InP as a function of temperature, electric field, boundary conditions, and doping concentration. Clear deviations of straightforward exponential decay are observed. Extending the well-known rate equations to incorporation of the higher bound states makes it possible to understand most of the observed phenomena and a simple analytic formulation including impact ionization is proposed to describe these. A numerical approach that also included Auger processes was necessary to explain the observed temporal behavior of the recombination at large free-electron concentrations. From this approach additional support for some of the assumptions in the simple model is also obtained.

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