PHYSICAL REVIEW B VOLUME 48, NUMBER 20 15 NOVEMBER 1993-II

Transient characteristics of isoelectronic bound excitons at hole-attractive defects in silicon: The C(0.79 eV), P(0.767 eV), and H(0.926 eV) lines

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(Received 5 May 1993)

The decay kinetics of isoelectronic bound excitons at hole-attractive defects in silicon is studied by means of time-resolved photoluminescence. From these measurements it is found that their radiative decay generally follows a multiexponential relationship due to fully unthermalized excited singlet ($S=0$) and triplet ($S=1$) states. In the case of the C(0.79 eV) line the intrinsic transient is described by two exponentials whereas in cases of the P(0.767 eV) and H(0.926 eV) lines a triexponential decay is found. From the temperature dependence of the time constants and amplitudes the energetic splittings of the singlet and triplet levels, the relevant singlet-to-triplet transfer times, as well as the radiative decay times of the singlet levels are determined. In all cases consistent results are found only if nearly equal initial excitation densities for the singlet state and for each of the three triplet substates are assumed. In the case of the P line thermalization of the triplet substates around 14 K is observed. In the case of the C line the intrinsic transition is superimposed by nonradiative, sample-dependent, excitation losses which are explained in terms of excited electron tunneling to surrounding defects which also obscures the third exponential.

I. INTRODUCTION

The concept of isoelectronic bound excitons (IBE's) was introduced by Hopfield, Thomas, and Lynch[1] to explain the photoluminescence (PL) properties of substitutional oxygen in ZnTe. From that time on many other deep impurity related PL properties in semiconductors could be successfully attributed to such defect excitations, especially for the indirect materials GaP and Si.[2] In this model an isolectronic defect can act, depending on the nature of the local defect potential, either as an electron trap or as a hole trap. Once the primary particle is captured by the short-range defect potential the second particle with opposite sign is attracted by the long-range Coulomb potential in effective-mass (EMT) -like states, so forming what is called an IBE. Photoluminescence then results from the recombination of the EMT-like particle with the tightly bound one.

In this paper detailed studies on the radiative decay of IBE's at hole-attractive defects in Si are presented, namely the C(0.79 eV) line, the P(0.767 eV) line, and the H(0.926 eV) line. The first of it is, apart from the G(0.97 eV) line, the most prominent luminescent center in electron irradiated, Czochralski-grown Si and was studied in great detail in the past. From electron paramagnetic resonance,[3–5] infrared (IR) absorption,[6] and isotope shifts in PL measurements[7] the microscopic structure of this defect is believed now to consist of a C-Si pair on a substitutional lattice site trapped as a second-nearest neighbor by the interstitial O atom.[5] In the case of the P line the experimental data are not quite as detailed, but based on the close similarities in the PL spectrum, isotope shifts, and from the growth kinetics a microscopic picture for this defect was suggested also, consisting of the same C-Si core but now with two O atoms, sharing one Si vacancy in the neighborhood.[7] No microscopic picture for the H line has been given up to now, but from PL studies[8,9] the presence of C and O in the defect has been proved, too. Furthermore, as shown in the same studies, the growth of the H defect takes place parallel to the growth of the P defect.

The IBE-like electronic structure of these excitons could directly be proved by PL excitation spectroscopy, revealing the EMT series for the photoexcited electron as was done in case of the C and P lines. The hole binding energy E_h could be determined from these measurements to $E_h=341$ meV (Ref. 10) (C line) and $E_h=368$ meV (Ref. 11) (P line). The same structure is assumed for the H line in view of the characteristic PL spectra for this kind of defect. The results of our time-resolved measurements further support this interpretation and E_h is expected to be about 205 meV.

From Zeeman measurements it is known that for both the C and P lines the luminescence does not split for magnetic fields up to 5.2 T,[12] and it is therefore concluded to be a singlet-to-singlet transition. In this case the orbital momentum l_h of the hole must be quenched, due to the low symmetry of the defect, leaving a pure two particle spin singlet-triplet (ST) system. However, no luminescence from the triplet states has been reported, so the quenching of l_h must be nearly perfect since only pure triplet radiation is electric dipole forbidden. From quite general arguments (first Hund's rule) it can be shown that the triplet state is always lying lower in energy than the singlet state (ST splitting about 1 meV), ignoring correlation effects (order of μeV) and this is what is observed experimentally for all ST bound excitons in Si or GaP.[2]

In spite of their common occurrence, there are only few experimental data about the intrinsic kinetic properties of IBE's in Si studied here in comparison to IBE's in GaP.[13] For near-band-edge-related IBE's, however, single exponential decays are found and the radiative life-

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time of both the triplet state as well the singlet state is deduced from the temperature dependence of the decay time constant.[14–16] The occurrence of the triplet luminescence indicates that the electronic levels are not purely spinlike but instead have a finite amount of hole angular momentum ($l_h = 1$), so generally the electronic two-particle levels are determined in that case by *jj* coupling. No results are reported, however, for the deeper bound IBE's considered here, showing no triplet luminescence. Only in case of the C line were time-resolved PL measurements done, but without a detailed analysis of its temperature dependence, leading to less verified or only vague interpretations.[10,17]

II. THE RATE EQUATIONS FOR THE DECAY KINETICS OF A SINGLET-TRIPLET PAIR

The time development of the excited density of states n_S and n_T of the singlet-triplet pair after pulsed excitation can be described by the following simple set of coupled rate equations (indices S and T are used for the singlet and triplet states, respectively):

$$\begin{aligned} dn_S/dt &= -W_{\mathrm{rad},S}n_S - W_{ST}n_S + W_{TS}n_t \ , \\ dn_T/dt &= -W_{\mathrm{rad},T}n_S + W_{ST}n_S - W_{TS}n_t \ , \end{aligned} \tag{1}$$

wherein n_S and n_T denote the density of excited singlet and triplet states, $W_{\mathrm{rad},S}$ and $W_{\mathrm{rad},T}$ are the radiative decay probabilities of these states, and W_{ST} and W_{TS} are the phonon-induced electronic transition probabilities from the singlet to the triplet state and vice versa. By writing down only two equations it is assumed that the triplet substates reach thermal equilibrium in times shorter than the individual transition times in the rate equation. The relation between the ST transition probabilities W_{ST} and W_{TS}, which are a measure of how fast thermal equilibrium is reached for the ST pair, is given by the argument of detailed balance:

$$W_{TS} = \frac{g_S}{g_T} W_{ST} e^{-\Delta E_{ST}/kT} = f W_{ST} \ , \tag{2}$$

wherein $g_S = 1$ and $g_T = 3$ are the degeneracy factors for the singlet and triplet states, respectively, ΔE_{ST} is the energetic splitting of the two states (the energetic separation of the three triplet sublevels are assumed to be of order μeV, whereas ΔE_{ST} is about 1 meV), and f is the Boltzmann factor, as an apparent abbreviation. Since in all cases no triplet luminescence is observed, $W_{\mathrm{rad},T}$, the radiative transition probability of the triplet state, will be neglected in the following.

In cases where the ST thermalization coefficients W_{TS} and W_{ST} are large in comparison to the radiative coefficients $W_{\mathrm{rad},S}$ and $W_{\mathrm{rad},T}$, full thermalization is maintained during the recombination and the decay of the singlet level will be a single exponential. The general solution, however, consists of a superposition of two exponentials, reflecting the two independent time constants in the rate equations:

$$n_S(t) = n_{S,1}e^{-\lambda_1 t} + n_{S,2}e^{-\lambda_2 t} \ . \tag{3}$$

The amplitudes $n_{S,1}$ and $n_{S,2}$ of these two exponentials will be determined by both the initial population densities $n_S(0)$ and $n_T(0)$ of the singlet and triplet states and the different transition probabilities in the rate equations. In cases where the experimentally observed time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ are quite different, as found in the experiments, the reciprocal time constants λ_1 and λ_2 in the solution [Eq. (3)] can be approximated as follows:

$$\begin{aligned} \lambda_1 &\simeq W_{\mathrm{rad},S} + (1+f)W_{ST} \ , \\ \lambda_2 &\simeq \frac{f W_{ST} W_{\mathrm{rad},S}}{W_{\mathrm{rad},S} + (1+f)W_{ST}} \end{aligned} \tag{4}$$

whereas the amplitudes $n_{S,1}$ and $n_{S,2}$ are given by

$$\begin{aligned} n_{S,1} &= \frac{(W_{ST} + W_{\mathrm{rad},S} + \lambda_2) - f W_{ST} n_T(0)}{\lambda_1} \ , \\ n_{S,2} &= \frac{f W_{ST}[n_S(0) + n_T(0)]}{\lambda_1} \ . \end{aligned} \tag{5}$$

Equation (4) gives the connection between the experimentally observed time constants and the intrinsic kinetic properties of the ST system, namely the ST transfer probability W_{ST}, and the radiative transition probability of the singlet level $W_{\mathrm{rad},S}$. The luminescence intensity I is proportional to the excited singlet density $n_S(t)$ so the relative amplitudes A_1 and A_2 found in the experiment are proportional to $n_{S,1}$ and $n_{S,2}$ of Eq. (3) too. Because the Boltzmann factor f ($f < 0.1$) is small in all cases considered, λ_1 can be taken to be constant in view of Eq. (4) whereas λ_2 is thermally activated with energy ΔE_{ST}, for practical purposes. The same is true for the relative amplitudes A_1 and A_2 in view of Eq. (5). In temperature dependent measurements Eq. (5) supplies an independent test for the energy difference of the ST pair by considering $A_2(T)$, which is also obtainable according Eq. (4) from $\lambda_2(T)$.

III. EXPERIMENT

The measurements were done on Czochralski-grown partially C enriched Si samples (values of the concentrations: $[\mathrm{O}] \simeq 6\times10^{17}$ cm^{-3}, [C] up to $\simeq 4\times10^{17}$ cm^{-3}) that were electron irradiated at room temperature (samples showing strong C line luminescence) or at 8 K (samples showing strong P and H line luminescence). The values of the dose and energy of the irradiation are 1×10^{18} cm^{-3} and 2.25 MeV, respectively.[7] In order to get the maximum luminescence intensity the samples were annealed afterwards at 200 °C and for 2 h in case of the C line and at 450 °C and for several hours in case of the P and H lines.

The excitation of luminescence was performed with a Nd:YAG laser (where YAG denotes yttrium aluminum garnet) operating at 1.064 μm in Q-switch operation (pulse width < 150 ns). The samples are mounted in a He cryostat with the possibility of varying the temperature from 2 K up to room temperature. The PL signal was dispersed by a 3/4-m Spex monochromator, detected with a fast Ge photodiode, and recorded with a real-time transient averager. The time resolution of the whole setup was below 200 ns.

IV. EXPERIMENTAL RESULTS

In the following the results of our time-resolved PL measurements are given with emphasis on the C and P lines. For these lines detailed temperature-dependent measurements are presented. In the case of the H line only the decay at one temperature is given. Yet, for all examples the intrinsic transition probabilities and the ST energetic separations are deduced.

A. The C(0.79 eV) line

In Fig. 1 the decay of the C line at 3 K is shown. At this low temperature only a single exponential decay is observable. A fit yields a time constant of 2.3 μs. At elevated temperature a second, much slower decay arises which shows no exponential behavior in the first part but has an exponential part for times large enough. The thermally activated behavior of the second decay is shown in Fig. 2 for the three temperatures 8, 16, and 24 K. Due to the activated second decay the first one can only be fitted unambiguously below 12 K. From these fits the conclusion is drawn that within the experimental error both the amplitude and the time constant of the first decay remain constant, in contrast to the second decay.

In Figs. 3 and 4 the temperature dependence of time constant τ_2 and of the relative amplitude A_2 of the second decay are shown in an Arrhenius plot. The time constant is taken from the exponential part whereas the amplitude is taken as the onset of the nonexponential part just at the end of the first decay. This procedure will be justified in the section below. For temperatures below 20 K the temperature dependence is determined by the intrinsic properties of the ST system, and a fit according to Eqs. (4) and (5) for τ_2 and A_2 is shown. Both are thermally activated with an activation energy of about 3.2 meV. This value lies within the expected range for ST bound excitons in Si (about 1 meV), and according to Eqs. (4) and (5) this energy is taken as the ST energetic separation ΔE_{ST}.

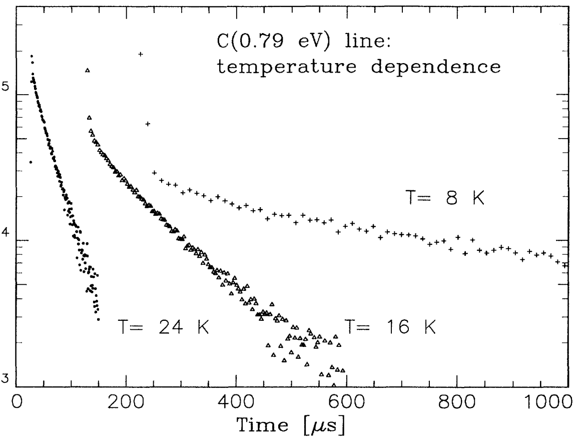

FIG. 2. C line: Temperature dependence of the second part of the decay kinetic. The origins of the time scale are shifted arbitrarily. The first exponential decay is not fully resolved on this larger time scale.

Above 20 K thermalization of the EMT-like electron with the conduction band quenches the time constant τ_2 as well as the relative amplitude A_2. The value for the activation energy is expected to be about 38.8 meV according to the EMT series of the excited electron. But while for the second decay a time constant can be unambiguously determined for temperatures between 8 and 24 K, the data for τ_2 are less reliable for temperatures outside this range because nonexponentialities, not linked to the intrinsic properties, are dominating.

In principle it should be possible with reference to Eq. (4) to calculate from the known values of τ_1 and τ_2 the intrinsic transition probabilities for the C line. But due the smallness of the Boltzmann factor f ($f < 0.1$) in comparison to unity the two transition probabilities $W_{\mathrm{rad},S}$ and

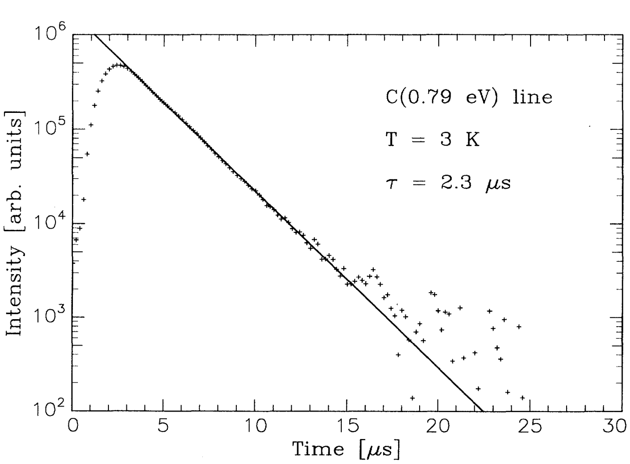

FIG. 1. The low-temperature decay kinetic of the C line. The decay can be fitted by only one exponential.

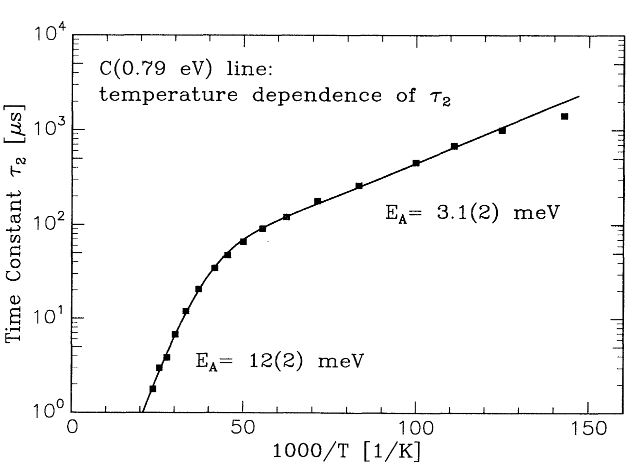

FIG. 3. C line: Temperature dependence of the second time constant τ_2.

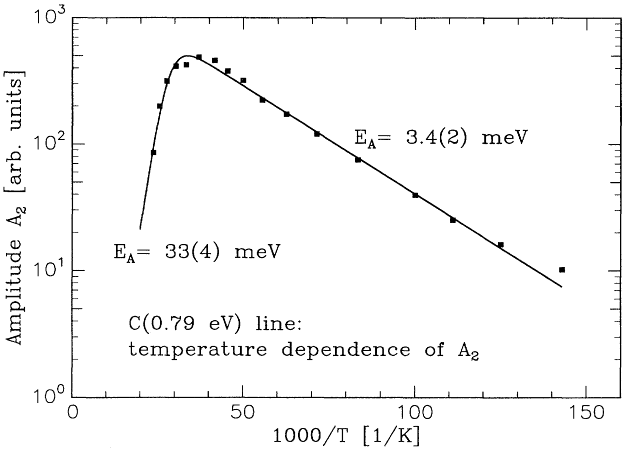

FIG. 4. C line: Temperature dependence of the amplitude of the second decay.

W_{ST} in question enter nearly symmetrically in Eq. (4), so one cannot really distinguish between them. This point can be clarified only if one considers the amplitudes for each decay, too. But to do this it is crucial to know the initial occupation probabilities $n_S(0)$ and $n_T(0)$ of the singlet and triplet levels. For ST bound excitons with finite ST transition times and δ-like excitation it is reasonable to assume that all levels are initially equally populated. From the observation that the intensity ratio of the two separate decays $I_1/I_2 \simeq 1/10$ (with $I_2 = \tau_2 A_2$ and the amplitude A_2 as defined above) and with the assumption of equal population it is clear that the ST transition is faster than the radiative decay time of the singlet level. For if the opposite is true the intensity ratio is expected to be nearly $\frac{1}{3}$. With this observation one can extract the radiative lifetime from Eq. (4), but only if the ratio of degeneracy is other than 3, since for this value both equations of Eq. (4) cannot be fulfilled simultaneously. This means that the three triplet sublevels have to be assumed to be nonthermalized!

As will be shown explicitly in the case of the P and H lines, considered below, the ST interaction is dominated indeed by only one of the triplet sublevels so the degeneracy factor should be set equal to unity. With these assumptions the radiative lifetime $\tau_{\mathrm{rad},S} = W_{\mathrm{rad},S}^{-1}$ of the singlet state will be found to be $\tau_{\mathrm{rad},S} = 14(2)$ μs [graphically it can be obtained from Fig. 3 by extrapolating $\tau_2(T)$ for $T \to \infty$]. The ST transfer time $\tau_{ST} = W_{ST}^{-1}$ is determined now from the relation

$$\frac{1}{\tau_1} = \frac{1}{\tau_{\mathrm{rad},S}} + \frac{1}{\tau_{ST}} \tag{6}$$

from which the value $\tau_{ST} = 2.8$ μs is obtained. With this time constant and assuming equal initial population for both the singlet and the triplet sublevel the intensity ratio I_1/I_2 is expected to be 1/12, in close agreement with the experimentally observed one. This proves the self-consistency of the assumptions made leading to the radiative decay time, namely equal initial population and the ratio of the degeneracy factors equal to one.

The value for the radiative decay time is considerably less than the one used in determining the defect concentration from absorption measurements. Fairly good agreement in the values for the C defect concentrations were obtained by using either IR absorption of the C(3) local mode at 865 cm^{-1} or using the C(0.79 eV) absorption if $\tau_{\mathrm{rad},S} = 100$ μs[6] is used. In the Dexter formula,[18] giving the connection between defect concentration and defect absorption, the so-called Lorentz correction for the effective electric field $\varepsilon_{\mathrm{eff}}$ at the defect was used:

$$\frac{\varepsilon}{\varepsilon_{\mathrm{eff}}} \simeq \frac{n^2+2}{n} = 4.75 \ , \tag{7}$$

with $n = 3.5$ the Si refractive index. But this correction should be generally applicable for localized states only. In cases of delocalized EMT-like electrons, as it is true for the C line, a value close to unity is expected. With the data of Davies *et al.*[6] and $\tau_{\mathrm{rad},S} = 14$ μs, the value for $\varepsilon/\varepsilon_{\mathrm{eff}}$ amounts to 1.3, i.e., close to the one determined for shallow donors in Si.[19] With the corrected values for $\tau_{\mathrm{rad},S}$ and $\varepsilon/\varepsilon_{\mathrm{eff}}$ the observed correlation is not affected since the corrections nearly cancel out.

Electron tunneling

In order to understand the origin of the nonexponentialities which dominate the decay of the C line at low temperatures ($T < 8$ K) but also the absence of any luminescence due to the remaining two triplet sublevels, the following experimental observations are helpful: With increasing temperature the decay gets closer to a biexponential form expected from the ST model with an unthermalized ST pair; at the same time the luminescence intensity increases by a factor of 2–4, depending on the sample; and also at the same time, the amplitude and time constant of the first decay remain constant, i.e., its luminescence intensity remains unchanged. From these observations it can be unambiguously concluded that the nonexponential part has its origin in a deexcitation of the defect and justifies us in taking the onset of the nonexponential part as the true value for A_2. The only way for such a process is to allow for an interaction with defects other than the C defect. With respect to the strong localization of the hole it is assumed that this interaction consists in electron hopping, well known from electron conduction in amorphous or compensated semiconductors at low temperatures. A simple analytical approach is given by the commonly used formula, describing hopping conduction in semiconductors,[20]

$$W_{ij} = W_0 e^{-2R_{ij}/a_B - (\Delta E/kT)} \ , \tag{8}$$

where the jump probability W_{ij} is given as a function of defect separation R_{ij}, the term in ΔE accounts for a possible thermal activation of electron hopping, the constant W_0 accounts for the strength of the transition, and a_B is a measure for the extent of the more delocalized state involved in the transition and should be of the order of the Bohr radius of that state. In case of electron tunneling, no thermal activation is expected, so the last term of the exponent in Eq. (8) will be ignored.

In order to describe the time development in the presence of electron hopping the rate equations to be solved take on the form (index X is used for the surrounding defects)

$$\frac{dn_{S,T}}{dt}=F(n_{S,T},W_{ST},W_{\mathrm{rad},S})-W_{SX}(t)n_{S,T} , \tag{9}$$

in which F stands for the original rate equations [Eq. (1)] and W_{SX} denotes the time-dependent hopping coefficient (dimension $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$). In writing Eq. (9) it was assumed that the losses are independent of spin ($W_{SX}=W_{TX}$). The solution is now given by

$$n_S(t)=(A_1e^{-\lambda_1 t}+A_2e^{-\lambda_2 t})\exp\left[-\int_0^t W_{SX}(t')dt'\right] . \tag{10}$$

The correct expression for W_{SX} is adopted from the description of the kinetic of donor-acceptor pair luminescence, going from the discrete defect distribution R_{ij} to the continuous one r:[21]

$$W_{SX}(t)=4\pi n_X\int_0^\infty W(r)\exp[-W(r)t]r^2dr \tag{11}$$

with

$$W(r)=W_0e^{-2r/a_B} . \tag{12}$$

To describe the nonexponentiality only the first two terms of a Taylor series in W_0t need to be considered, so an approximate analytical expression is obtained for W_{SX}:

$$W_{SX}(t)=\pi n_X a_B^3 W_0(1-\tfrac{1}{8}W_0t) . \tag{13}$$

In Fig. 5 a fit based on this approximation is shown. As can be seen, the time dependence of the kinetic is described reasonably well by the model. It should be stressed that the nonexponentiality is fitted by only two parameters, namely W_0 and $p_1=n_Da_B^3$, where n_D denotes either the concentration of excited C defects itself or the concentration of surrounding trapping levels depending on which concentration dominates. The value of W_0 is about 0.4 s^{-1} and considerably lower than the one obtained typically in the analysis of tunneling processes (order 10^{12} s^{-1}; see, e.g., Mariette *et al.*[22]). It is not clear up to now if this is a failure of the model considered here (as an alternative approach excitation transfer involving both electron and hole of the excited C defect via a nearly resonant dipole-dipole interaction with surrounding defects can be assumed, but this is not believed to be effective in this case due to the triplet character of the initial states) or if this is due to a Coulomb barrier originated by charge separation during the tunneling process. The value for p_1 can be used to estimate the concentration of one species of the defects involved in the transition, if the Bohr radius is known. Since the excited electron of the C defect is known to be EMT-like a_B can be approximated roughly by $a_B\simeq 50$ Å, and from this n_D can be determined to be about 4×10^{17} cm^{-3}, a value which is somewhat greater than the one expected for the C defect itself.[6] From electron spin echo excitation experiments it is known that there exists an efficient excitation transfer mechanism from the C defect to the so-called A center [$(V-O)_S$ defect],[23] which is known to have an acceptor level at E_C- 170 meV.[24] A transfer process is also reported for the shallow donor electron of phosphorus in the presence of the A center.[25] Though the A center is able to cause nonexponentialities, the values for W_0 and p_1 have to be interpreted as effective ones, because in general different kinds of defects can contribute to the tunneling probability.

B. The P(0.767 eV) line

In principle, for the P line, a kinetic similar to that of the C line (studied before) is expected in view of the similar electronic structure. This is indeed the case, but with some additional features. The decay at 12 K for the P line is displayed in Fig. 6. It can be seen that the decay can be fitted by a triexponential function. The first one with a time constant of 1.9 μs is analogous to that one of the C line (2.3 μs). But the subsequent decay can be fitted

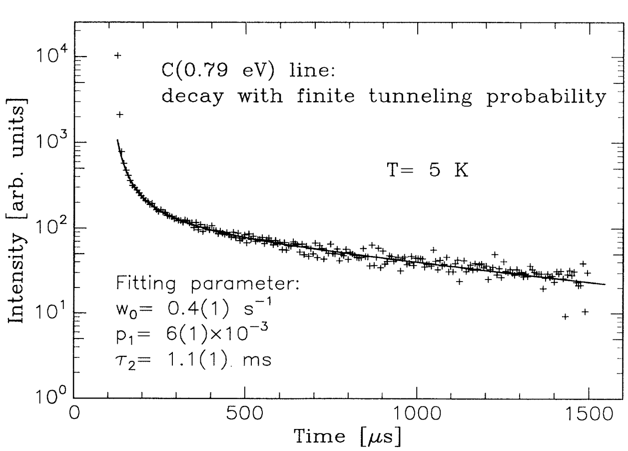

FIG. 5. C line: Fit for the decay kinetic with a finite tunneling probability of the excited electron.

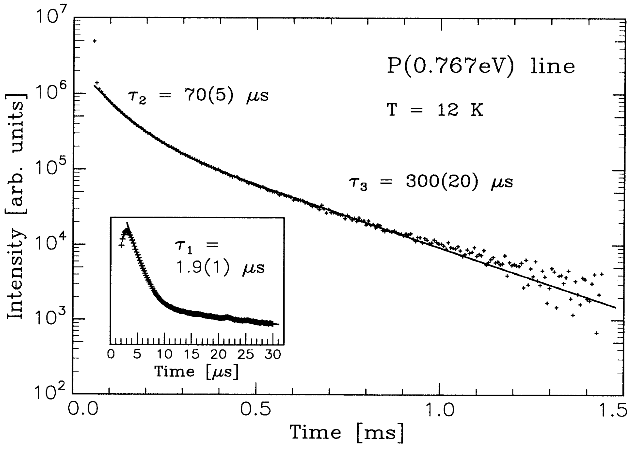

FIG. 6. P line: Decay kinetic of the P line at 12 K. The first faster decay is shown as an inset for the first 30 μs after excitation.

over the whole time domain by a biexponential decay law (Fig. 6). In contrast, in the case of the C line the simultaneously present A center causes nonexponentialities and the second slower decay reveals only one exponential. In the case of the P line, however, and also for the H line, considered in the following, the A center is already annealed out [annealing of the A center takes place around 300 °C (Ref. 26) whereas the growth temperature for the P line is about 450 °C], or if still present to some degree, it is already occupied by an electron, since the Fermi level has moved toward the conduction band due to formation of thermal donors at these annealing temperatures (indeed, for some samples the decay of the P line is lowered and strongly nonexponential for temperatures above 20 K, indicating that there is some delayed excitation due to electron capture from surrounding defects, such as the thermal donors). Therefore nonexponential decays due to excited electron hopping are not expected to be effective in case of the P line.

The occurrence of three exponentials in the decay explicitly shows that there are at least three different unthermalized excited states involved in the transition. Therefore the kinetic of the P line should be described by at least three coupled rate equations, one for the singlet state and two for the triplet state. Due to the quite different time regimes in which each transition takes place, they can be viewed as nearly decoupled, leaving actually only two coupled rate equations of the usual form [Eq. (1)]. In this spirit the first and second decays are ascribed to the dominating ST interaction in analogy to the C line, with one triplet level only, whereas the third exponential is ascribed to the remaining two triplet levels (to be definite, T_0 is assumed to the first case, T_+ and T_- in the second case). All three triplet substates are assumed to be interacting only via the singlet level as long as three exponentials are present. By considering the amplitudes and time constants the approximate relation $I_1:I_2:I_3=1:3.5:7$ is found. So most of the total luminescence is actually due to the third decay.

In Figs. 7 and 8 the temperature dependence of the time constants and the amplitudes of the second and third exponentials are displayed. As already observed for the C line, the slower decay, consisting of two exponentials, is thermally activated. The activation energy, indicating the ST pair separation, is determined from the temperature dependence of $\tau_2(T)$ of Fig. 7 to $\Delta E_{ST}=2.7$ meV. Again, by comparing the intensity ratio I_1/I_2 it is evident that the ST transfer rate dominates the radiative decay rate and the radiative decay time of the singlet level is found from extrapolation of $\tau_2(T)$ for $T\rightarrow\infty$ to be $\tau_{\mathrm{rad},S}=5$ μs, assuming that the ratio of degeneracy is unity again. The ST transfer time τ_{ST} amounts according to Eq. (6) to $\tau_{ST}=3$ μs. With these transition rates, deduced from the time constants only, the ratio I_1/I_2, with the other two triplet states neglected, is expected to be 1:4.3, i.e., close to the experimental one (1:3.5). Again, equal initial population densities of the states are assumed.

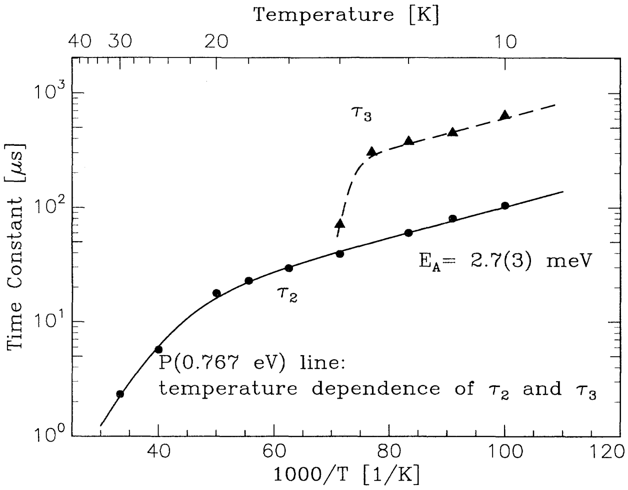

FIG. 7. P line: Temperature dependence of the time constants τ_2 and τ_3 of the second and third exponential. Due to thermalization τ_3 drops rapidly above 14 K.

As can also be seen from Figs. 7 and 8, the third decay has the same activated character as the second decay, ensuring that this transition is an intrinsic one. But this third transition is only present for temperatures below 14 K. The reason for its disappearance follows from Figs. 7 and 8 too. At the same temperature (around 14 K) where the decay time τ_3 drops rapidly, indicating a reduction of I_3, the amplitude A_2 of the second decay rises up. This behavior is expected if one assumes that the triplet sublevels thermalize at this temperature, leaving a biexponential decay kinetic. The ST transition time for each of the two remaining triplet sublevels can be extracted again from Fig. 7 if τ_3 is extrapolated for $T\rightarrow\infty$ and amounts to about 30 μs or if the two are taken together to one degenerate triplet sublevel to 15 μs.

C. The H(0.926 eV) line

The third example for a radiative transition arising from the recombination of an IBE at a hole-attractive de-

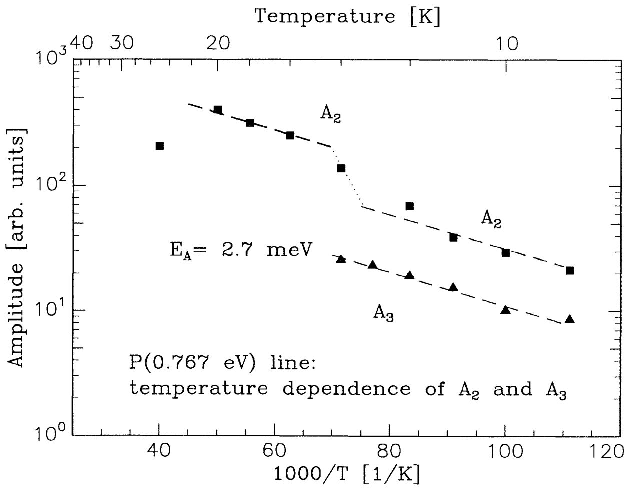

FIG. 8. P line: Temperature dependence of the relative amplitudes A_2 and A_3 of the second and third exponential. For temperatures above 14 K the amplitude A_3 diminishes.

fect in Si considered here is the case of the H line. Assuming the EMT-like electron bound with about 35 meV the hole binding energy for this defect is at about 205 meV and therefore only about one-half of that for the C and P lines. The decay kinetic of the H line is displayed in Fig. 9.

As already observed in case of the P line, the kinetic is triexponential again. Applying the model from the P line with unthermalized triplet sublevels, the following transition probabilities and also the ST energy can be deduced from this single measurement. In the case of the H line the first decay with time constant 2.0 μs is totally determined by the dominating ST transition time. This can be seen either by considering the intensity ratio I_1/I_2, as was done in for the C and P line, or from the nearly equal intensities of the second and third decay (see Fig. 9). If equal population is assumed again, this equality is just what is expected, because in this case the occupation density of the T_0 state gets twice of each of the remaining two. The radiative lifetime can again be estimated from the relation for the intensity ratio

$$\frac{I_1}{I_2}=\frac{n_S\dfrac{W_{\mathrm{rad},S}}{W_{\mathrm{rad},S}+W_{ST}}}{n_T(m=0)+n_S\dfrac{W_{ST}}{W_{ST}+W_{\mathrm{rad},S}}}\simeq\frac{W_{\mathrm{rad},S}}{W_{ST}}\ ,$$

assuming again equal initial excitation densities and with $W_{\mathrm{rad},S} \ll W_{ST}$. For $I_1/I_2 \simeq 1/8$ and with $\tau_1 \simeq W_{ST}^{-1} = 2.0$ μs the radiative decay time is obtained to be $\tau_{\mathrm{rad},S} = W_{\mathrm{rad},S}^{-1} \simeq 18$ μs. Given the radiative decay time and with the value for $\tau_2 = W_{\mathrm{rad},S}e^{-\Delta E_{ST}/kT}$ [according to Eq. (4) and $g_S = g_T = 1$] at 10 K, the ST energetic separation can be determined to be $\Delta E_{ST} = 1.2$ meV. This value is quite close to that one found for the Li-related ST bound excitons at 1.045 eV and 1.082 eV—the so-called Q and S systems[14] ($\Delta E_{ST} = 1.07$ meV and 1.0 meV, respectively).

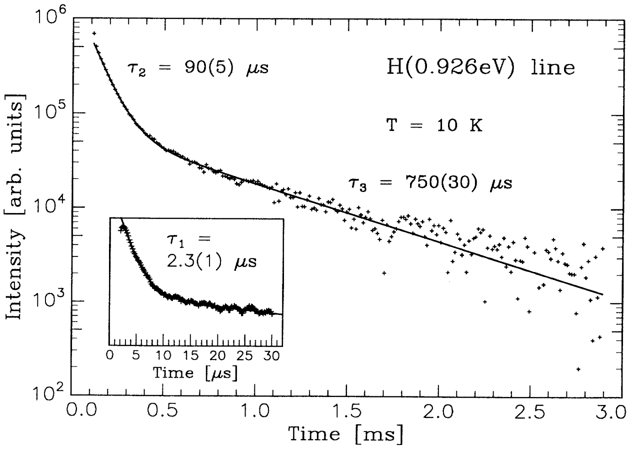

FIG. 9. H line: Decay kinetic of the H line at 10 K. The first faster decay is shown as an inset for the first 30 μs after excitation.

V. DISCUSSION

The decay kinetics of the isoelectronic bound excitons at hole-attractive defects in Si exhibits, in general, as was shown for the C, P, and H lines, a multiexponential behavior. Each single exponential is determined by the intrinsic kinetic properties of the excited electron-hole system. From the experiments three different transition probabilities can be identified: (i) the dominating ST transition ($S \rightarrow T_0$), (ii) the radiative lifetime τ_{rad} of the singlet state, and (iii) the less effective ST transitions $S \rightarrow T_-$ and $S \rightarrow T_+$. Within the experimental resolution the last two levels can be summarized in one doubly degenerate triplet sublevel.

In the time-resolved PL studies presented, the decay is found to be biexponential in the case of the C line and triexponential in the case of the P and H lines. The intrinsic time constants deduced thereof are summarized for convenience in Table I. In principle the decay for the C line should also be triexponential since the ST transition is dominated by only one triplet substate too. The absence of the third exponential is probably due to the electron tunneling mechanism as it was found to be effective in that case, so obscuring the radiative decay due to the second and third triplet sublevels. Slower decays are found, however, for temperatures above 24 K; an unambiguous identification, however, is not possible due to its sample dependence.

As already mentioned in the beginning, the hole orbital momentum l_h has to be assumed to be quenched totally in order to explain the pure singlet-to-singlet-character of the zero phonon lines and also the total absence of any triplet luminescence. As a consequence the spin-lattice relaxation time, which is mediated by the spin-orbit coupling, is also quenched. Therefore much greater ST transition times result in comparison with excitons which have retained some admixture of the hole orbital momentum or to that one with total angular momentum $J=1$ and $J=2$, i.e., with no orbital quenching at all. In the last case ST transition times about 15 ps are reported for the IBE in GaP:N (Ref. 27) whereas in the opposite extreme the spin-lattice relaxation time at low temperatures for shallow donors is of the order of minutes.[28] It is difficult to observe any trends from three data in Table I, but the following is quite reasonable: with higher zero phonon transition energy, i.e., lower hole binding energy, the ST transition time is reduced. This is reasonable due to the fact that the degree of orbital momentum quenching is dependent on the strength of the local defect potential.

TABLE I. ST energy splittings and intrinsic transition times for the IBE considered, as deduced from the time constants found in experiment (estimated errors in the last digit are given in parentheses). Blank spaces denote undetermined values.

	P(0.767 eV)	C(0.79 eV)	H(0.926)
ΔE_{ST} (meV)	2.7(3)	3.2(2)	1.2(5)
$\tau_{\mathrm{rad},S}$ (μs)	5(2)	14(2)	18(4)
$\tau(S \rightarrow T_0)$ (μs)	3(1)	2.8(5)	2.0(2)
$\tau(S \rightarrow T_+, T_-)$ (μs)	30(5)		

The already mentioned IBE's of the Q and S systems at 1.045 and 1.082 eV decay monoexponentially,[14] indicating full thermalization of the levels during the recombination. The same is true for the Be-correlated IBE's at 1.117 and 1.078 eV.[15] Unthermalized triplet states are observed, however, in PL for the 1.911 eV IBE-like bound exciton in GaP,[13] where it is found that the triplet state decays nearly biexponentially, confirming that there are two different kinds of triplet substates with respect to singlet admixture. For the same system nearly equal population rates are found in microwave-induced delayed phosphorescence experiments but different radiative decay rates,[29] also confirming the experimental findings for the C, P, and H lines. In general, however, the IBE's in GaP are found to decay single exponentially for the $S \rightarrow T$ transition, and $T \rightarrow S$ transition times are much smaller than the radiative transition times of both the singlet and triplet state. The mixing of the singlet and triplet states by spin-orbit coupling seems to be more effective in these cases than in case of Si, as is also obvious from the fact that for IBE's in GaP the triplet luminescence is always present.

VI. SUMMARY

Time-resolved PL measurements on the radiative decay of IBE's at hole-attractive defects in Si are presented. It is found in all cases that the intrinsic radiative decay follows, generally, a multiexponential decay law. This is in marked contrast to the known single decay of the shallower, band-edge-related bound excitons in Si, whose decay consists of a single exponential. The reason for this more complex kinetic is shown to have its origin in fully unthermalized excited singlet and triplet states. From the fact that the orbital angular momentum of the hole is totally quenched, the electronic states have to be considered to be purely spinlike. As a consequence the spin-lattice coupling for these IBE's is reduced too.

Especially a biexponential kinetic is observed in the case of the C line and a triexponential kinetic in the case of the P and H lines. The time constants are found to be linked first to the dominating ST transition (about 2 μs) with only one of the three triplet substates, second to the radiative decay (14, 5, and 18 μs for the C, P, and H lines, respectively), and third to the less effective ST transitions of the two remaining triplet sublevels, which can be considered within the experimental resolution as one doubly degenerate state. In order to get consistent results, nearly equal initial excitation densities of each state, independent of its spin, have to be assumed. From the temperature dependence of the decay kinetic the ST splitting is deduced for the C and P lines. Thermalization of the triplet substates is observed for the P line at about 14 K. In the case of the C line strong nonexponential decays are observed, which are interpreted in terms of excitation losses due to excited electron tunneling, which process also obscures the third exponential in this case.

ACKNOWLEDGMENTS

The authors wish to thank K. Thonke, A. Dörnen, and W. Kürner for the samples and also for many helpful and stimulating discussions. We also acknowledge M. Pilkuhn for his steady encouragement.

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