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Theoretical modeling of thermally activated luminescence quenching processes in Si:Er

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A theoretical description of processes responsible for thermally activated nonradiative relaxation of excited Er^{3+} ions in Si is developed. Microscopic models for the back transfer mechanism of excitation reversal and for Auger energy transfer to free and localized carriers are proposed. Simulations based on physical parameters are made and reasonable agreement with experiment is obtained. At the same time, the proposed theoretical treatment reveals aspects of the Auger deexcitation. In particular, important differences between interaction with free electrons and free holes are concluded. Experimental support for these findings is pointed out.

I. INTRODUCTION

Optical properties of rare-earth ions in semiconductors are the subject of a considerable amount of research due to potential applications in optoelectronics. The major advantage of placing rare-earth ions into a semiconductor matrix is the possibility to excite their intra-4*f* transitions through a carrier-mediated process. In particular, erbium-doped silicon has attracted much attention. There are two main reasons for that. First, the Er^{3+} transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) is in the 1.5 μm range, which coincides with the optical window of glass fibers currently used in telecommunication. Second, this system can be easily integrated with devices manufactured by highly successful standard silicon technology. Furthermore, Si:Er light-emitting structures are attractive in association with potential applications for optical interconnections in future photonic chip technology.

In recent years a great progress has been achieved in understanding of the main processes controlling the excitation of Er^{3+} ions in silicon. There is evidence that Er^{3+}-related optically active centers in silicon form donors with a binding energy of about 150–260 meV and the excitation of erbium ions is a result of an Auger recombination process of the electron bound at the donor and a free hole or bound exciton. The excess energy is taken away by phonons in the former case and by the bound electron in the latter.

In contrast to excitation, microscopic models of nonradiative relaxation are much less understood. It is assumed that thermal quenching of Er emission is caused by two effective de-excitation processes:[1] (*i*) the back transfer process, regenerating electron-hole pairs and (*ii*) collisions with free carriers. Here we present theoretical modeling of these two processes. In addition, the "*localized*" Auger deexcitation process, in which the energy of the Er^{3+} ion is consumed by promoting an electron, initially present at the Er-related donor, to the conduction band, has been investigated as well. Our calculations demonstrate a high efficiency of this process.

II. BACK TRANSFER

Back transfer has been recognized as the most important decay process responsible for quenching erbium lumines-

cence at high temperature.[1,2] This process is schematically shown in Fig. 1: the excited Er^{3+} ion decays nonradiatively by promoting an electron from the valence band to a level of the Er-related donor. This process can be viewed as an exact reversal of excitation. In silicon, the Er^{3+} ion with oxygen atoms in its neighborhood is believed to form a donor center with binding energy ε_D. It is therefore important to take into account the occupation of the donor level—the process can only take place if it is empty. The extra energy required to complete the back transfer process, $\Delta_e = E_g - \varepsilon_D - \Delta_{ff'}$, where E_g is the bandgap energy and $\Delta_{ff'}$ the erbium transition energy, is contributed by phonons. Therefore the back transfer process is thermally activated and multiphonon assisted.

The probability for the back transfer process is given by Fermi's golden rule:

$$W_{bt} = \frac{2\pi}{\hbar} \sum_{\mathbf{k},j} \frac{1}{N_{f'}} \sum_{f,f'} |\langle f,D|\hat{V}_c|f',j,\mathbf{k}\rangle|^2 \sum_N \mathcal{I}(N) \delta(E_g - \varepsilon_D + \varepsilon_\mathbf{k} - \Delta_{ff'} - N\hbar\omega), \tag{1}$$

where j enumerates the valence subbands, $\mathbf{k}$ is the wave vector of electron in the valence band, and $\hbar\omega$ is the energy of the phonons enabling the excitation reversal.
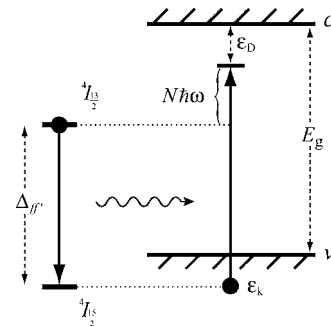

FIG. 1. The scheme of the back transfer process. E_g is the Si band gap energy, ε_D is the binding energy of the donor related with Er^{3+}, $\varepsilon_\mathbf{k}$ is the kinetic energy of the hole created in the back transfer process, and $\Delta_{ff'}$ is the average energy difference between the first excited and ground states of Er^{3+}.

The detailed electron matrix element calculation is presented in Appendix B. (In the preceding Appendix A, the necessary overlap integrals of Bloch amplitudes are evaluated.) The phonon part in Eq. (1) is given by

$$\mathcal{I}(N) = \sum_{N_i} |\langle L_f, N_i - N | L_i, N_i \rangle|^2 F(N_i), \qquad (2)$$

where $F(N_i)$ is the probability for the phonon number to be N_i in the initial (L_i) state and N is the difference in phonon number between final (L_f) and initial states of the vibrational system. In the model of two displaced oscillators with the same frequency the factor $\mathcal{I}(N)$ was calculated in the theory of radiative transitions[3] to be

$$\mathcal{I}(N) = e^{-2S(N_T + 1/2)} e^{-\frac{N}{2}\frac{\hbar\omega}{kT}} I_{-N}[2S\sqrt{N_T(N_T+1)}], \qquad (3)$$

where S is Huang-Rhys factor:

$$S = \frac{\varepsilon_{opt} - \varepsilon_{th}}{\hbar\omega}, \qquad (4)$$

with ε_{opt} and ε_{th} corresponding to the optical and thermal ionization energy, respectively. N_T is the Bose-Einstein factor:

$$N_T = \frac{1}{e^{\hbar\omega/kT} - 1}, \qquad (5)$$

and I_{-N} is the modified Bessel function of order $-N$.

Finally, introducing the radiative lifetime τ_{rad} of the erbium ion in the first excited state $(^4I_{13/2})$[4],

$$\frac{1}{N_{f'}} \sum_{ff'} d_{ff'}^2 = \frac{3}{4} \frac{1}{\sqrt{\varkappa}} \frac{\hbar^4 c^3}{e^2 \Delta_{ff'}^3} \frac{1}{\tau_{rad}} \qquad (6)$$

(where c is the light velocity) we obtain for the back transfer probability:

$$W_{bt} = \frac{1}{\tau_{rad}} b_{bt} P(T), \qquad (7)$$

where

$$b_{bt} = \frac{4}{3} \frac{e^2 c^3 m_h^{3/2} m_e^{1/2}}{\pi^2 \varkappa^{5/2} \hbar} \frac{\sqrt{\varepsilon_D \Delta_e}}{\Delta_{ff'}^3} \left(\frac{\varkappa}{\varkappa_0}\right)^2 |I_{s,v}|^2 \varphi^2(\gamma), \qquad (8)$$

and $P(T)$ is a temperature dependent factor:

$$P(T) = \sum_N e^{-2S(N_T + 1/2)} e^{-N\hbar\omega/kT} I_{-N}[2S\sqrt{N_T(N_T+1)}] \sqrt{\frac{N\hbar\omega}{\Delta_e} - 1}. \qquad (9)$$

In Eq. (8), $m_e = 0.321 \ m_0$ and $m_h = 0.527 \ m_0$ are the density-of-state effective masses for the Si conduction and valence bands, respectively; $|I_{s,v}|^2 = 0.33$ is the overlap integral contribution (see Appendix A); $\varphi(\gamma) = 2.14$ (see Appendix B); $\varkappa$ is the dielectric constant of Si; and $\varkappa_0$ is introduced to take into account short range Coulomb interactions, when the screening effect is decreased.
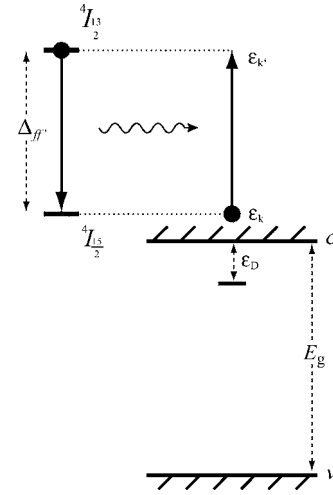

FIG. 2. The scheme of the Auger quenching process by collision with free electrons. $\varepsilon_\mathbf{k}$ and $\varepsilon_{\mathbf{k}'} = \varepsilon_\mathbf{k} + \Delta_{ff'}$ are initial and final kinetic energies of the free electron.

Taking $\varkappa_0 = 1$, we can evaluate the temperature-independent coefficient of the back transfer process as $b_{bt} = 7.8 \times 10^6$.

III. COLLISION WITH FREE CARRIERS

Due to its relatively large activation energy, the back transfer process can only take place at elevated temperatures. At low temperature, erbium luminescence quenching in bulk silicon is considered to be determined by free carrier collisions. This process is schematically illustrated in Fig. 2: energy from an excited Er^{3+} ion is transferred to a free carrier which is being promoted to higher states in the band.

The probability of such an Auger process is given by

$$W_{fe} = \frac{2\pi}{\hbar} \sum_{\mathbf{k},\mathbf{k}'} \sum_i \frac{1}{N_{f'}} \sum_{f,f'} |\langle f, i, \mathbf{k}' | \hat{V}_c | f', i, \mathbf{k} \rangle|^2 f(\varepsilon_\mathbf{k})$$
$$\times \sum_N \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_\mathbf{k} - \Delta_{ff'}). \qquad (10)$$

Here $f(\varepsilon_\mathbf{k})$ represents the distribution function of free carriers with effective mass m_c. The calculation can be done following Ref. 4 and the result is

$$W_{fe} = \frac{1}{\tau_{rad}} \frac{n_c}{n_0}, \qquad (11)$$

where n_c is the concentration of free carriers, and

$$n_0 = \frac{\sqrt{2}}{4\pi} \frac{\varkappa^{5/2} \Delta_{ff'}^{7/2}}{e^2 \hbar^2 c^3 \sqrt{m_c}} \left(\frac{\varkappa_0'}{\varkappa}\right)^2. \qquad (12)$$

As the momentum transferred in this process is of the order of the reversed lattice constant a^{-1},

$$q_0 = \sqrt{2m_c \Delta_{ff'}} / \hbar = 1.4 a^{-1}, \qquad (13)$$

factor $(\varkappa_0' / \varkappa)^2$ was introduced into Eq. (12) to take into account possible reduction of the screening of the Coulomb

interaction. In numerical calculations this factor is assumed to be equal to unit. We can see that in this description the deexcitation process becomes important for concentrations exceeding n_0. For electrons in silicon ($m_c = m_e$), we find $n_0 \approx 1.3 \times 10^{15}$ cm^{-3}. In the case of collisions with free holes the critical concentration is determined by Eq. (12), where the mass m_c is changed for m_h. For collisions with a neutral Er-related center the deexcitation rates for electrons and holes are thus practically the same.

However, if the donor center associated with excited Er^{3+} is positively charged (see earlier remarks on the photoluminescence (PL) excitation mechanisms), one should expect a great difference in efficiency of deexcitation by electrons and holes. The positive charge affects the wave function of free electrons, increasing the probability of electron presence in the vicinity of the erbium ion. As the collisions with free electrons in the deexcitation processes take place at a distance $\sim 1/q_0$, which is smaller than the Bohr radius, the effect of the positive charge can be taken into account by introducing Sommerfield's factor $Z_+(\varepsilon_\mathbf{k})$ for each of the initial and final states of the free electron in Eq. (10):

$$Z_+(\varepsilon_\mathbf{k}) = 2\pi \sqrt{\frac{E_\mathrm{B}}{\varepsilon_\mathbf{k}}} \frac{1}{1 - \exp\left(-2\pi\sqrt{\frac{E_\mathrm{B}}{\varepsilon_\mathbf{k}}}\right)}, \qquad (14)$$

where $E_\mathrm{B} = m_e e^4/(2\varkappa^2\hbar^2)$ is the Bohr energy. The calculation of W_fe leads to an expression similar to Eq. (11), but with n_0 changed to $\tilde{n}_0$:

$$\tilde{n}_0 = \frac{n_0}{Z_+(\Delta_{ff'})\tilde{Z}_+}, \qquad (15)$$

where

$$\tilde{Z}_+ = \frac{\int_0^{+\infty} Z_+(\varepsilon_\mathbf{k}) f(\varepsilon_\mathbf{k}) \sqrt{\varepsilon_\mathbf{k}}\, d\varepsilon_\mathbf{k}}{\int_0^{+\infty} f(\varepsilon_\mathbf{k}) \sqrt{\varepsilon_\mathbf{k}}\, d\varepsilon_\mathbf{k}}. \qquad (16)$$

If free carriers are not degenerated

$$\tilde{Z}_+ \approx 4\sqrt{\pi}\sqrt{\frac{E_\mathrm{B}}{kT}} \qquad (17)$$

and at room temperature $\tilde{n}_0 \approx 0.1\, n_0$, according to Eq. (15).

In the case of collision with free holes the positive charge of the ionized donor produces a repulsive barrier around the erbium ion. So, one should introduce into Eq. (10) Sommerfield's factor $Z_-(\varepsilon_\mathbf{k})$ for each of the initial and final states of the hole:

$$Z_-(\varepsilon_\mathbf{k}) = 2\pi\sqrt{\frac{E_\mathrm{B}}{\varepsilon_\mathbf{k}}}\frac{1}{\exp\left(2\pi\sqrt{\frac{E_\mathrm{B}}{\varepsilon_\mathbf{k}}}\right) - 1}, \qquad (18)$$

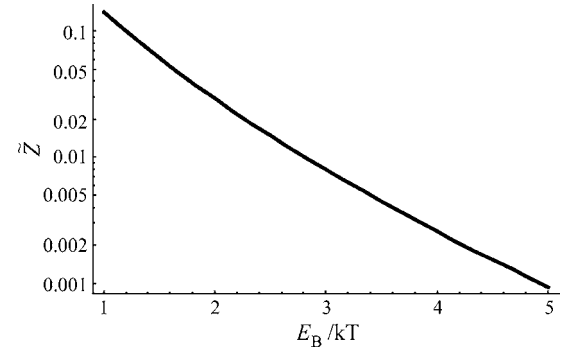where E_B is calculated using effective mass value m_h.

FIG. 3. The temperature dependence of $\tilde{Z}_-$, calculated with $E_B = 55$ meV corresponding to the Bohr energy using the density of states effective mass for holes $m_h = 0.561 m_0$.

$$\tilde{p}_0 = \frac{p_0}{Z_-(\Delta_{ff'})\tilde{Z}_-}, \qquad (19)$$

where $\tilde{Z}_-$ is determined by the formula similar to (16) and for nondegenerate holes

$$\tilde{Z}_- = 2\pi\sqrt{\frac{E_\mathrm{B}}{kT}}\frac{\int_0^{+\infty} \exp\left(-2\pi\sqrt{\frac{E_\mathrm{B}}{kT}\frac{1}{x}}\right)\exp(-x)\,dx}{\int_0^{+\infty}\sqrt{x}\exp(-x)\,dx}. \qquad (20)$$

Temperature dependence of $\tilde{Z}_-$ is shown in Fig. 3. Equation (18) gives $Z_-(\Delta_{ff'}) = 0.49$ and at room temperature $\tilde{p}_0 \approx 100 p_0$ and grows dramatically with temperature decreasing. One finds that the quenching by free holes is practically negligible.

IV. ENERGY TRANSFER ASSISTED BY DONOR IONIZATION

At low temperature, the lifetime of excited Er^{3+} in bulk Si is in the millisecond range, which is enough for an electron to be captured by the related empty donor center. When the donor traps an electron, a very effective (localized) Auger deexcitation process assisted by donor ionization can take place (see Fig. 4). The calculation of the probability for this process is similar to that performed in Sec. III. The difference is in the initial state of the electron only, which is now the donor state with a wave function given by Eq. (B3), rather than a conduction band state as in Eq. (10). The result for the probability W_di is

$$W_\mathrm{di} = \frac{1}{\tau_\mathrm{rad}} b_\mathrm{di}, \qquad (21)$$

where the dimensionless factor is given by

$$b_\mathrm{di} = \frac{2}{3\pi^2}\frac{e^2 c^3 m_e^2}{\varkappa^{5/2}\hbar}\frac{\sqrt{\varepsilon_\mathrm{D}(\Delta_{ff'} - \varepsilon_\mathrm{D})}}{\Delta_{ff'}^3}\varphi^2(\gamma_1), \qquad (22)$$
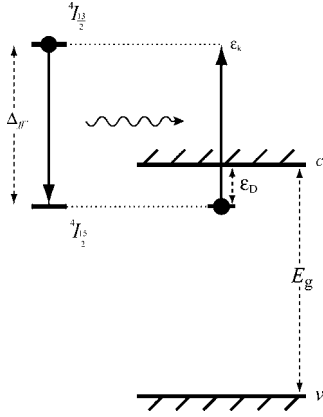
with

FIG. 4. The scheme of the donor ionization assisted quenching process. The energy of the free electron after ionization is given by $\varepsilon_{\mathbf{k}'} = \Delta_{ff'} - \varepsilon_D$.

$$\gamma_1 = \sqrt{\frac{\varepsilon_D}{\Delta_{ff'} - \varepsilon_D}}, \tag{23}$$

and $\varphi(\gamma)$ is given by Eq. (B11). For a donor binding energy $\varepsilon_D = 0.24$ eV, we get $\gamma_1 = 0.65$ and $b_{di} = 2.6 \times 10^4$. Thus, if an electron is captured by the donor associated with an excited erbium ion, the deexcitation should occur immediately.

V. COMPARISON WITH EXPERIMENT

A. Quenching of luminescence at high temperature by back transfer

Experimental data on the back transfer transition rate are generally analyzed assuming an Arrhenius-type temperature dependence

$$W_{\mathrm{bt}} = \nu_0 e^{-\Delta E/kT}, \tag{24}$$

with ΔE the activation energy and ν_0 a preexponential factor.[1,2] In order to confront our calculations with experiments, reasonable estimates for Δ_e, S, ω, and $\varkappa_0$ should be made.

The extra energy required to complete the back transfer process is $\Delta_e = E_g - \varepsilon_D - \Delta_{ff'}$, with the temperature dependence of E_g (in eV) taken from Ref. 5:

$$E_g = 1.170 - \frac{4.73 \times 10^{-4} T^2}{636 + T}. \tag{25}$$

The erbium-donor level in Si is generally believed to be at $\varepsilon_D = 150-260$ meV below the conduction band.[6-10] We take here a value $\varepsilon_D = 240$ meV and $\Delta_{ff'} = 810$ meV. As no phonon replicas have been observed in the PL spectra of Er in Si, we suppose that the electron localized at the Er-related donor is responsible for electron-phonon coupling, which is usually found to be weak for deep defects in Si. It may be expected that $0 < S < 1$ in this case.[11] Moreover, it is not *a priori* clear what the energy of the phonon mode providing the thermal energy should be.

Figure 5 shows a simulation of the temperature dependence of $W_{\mathrm{bt}}\tau_{rad}$, assuming $\varkappa_0 = 1$, with $S = 0.5$ [Fig. 5(a)] and
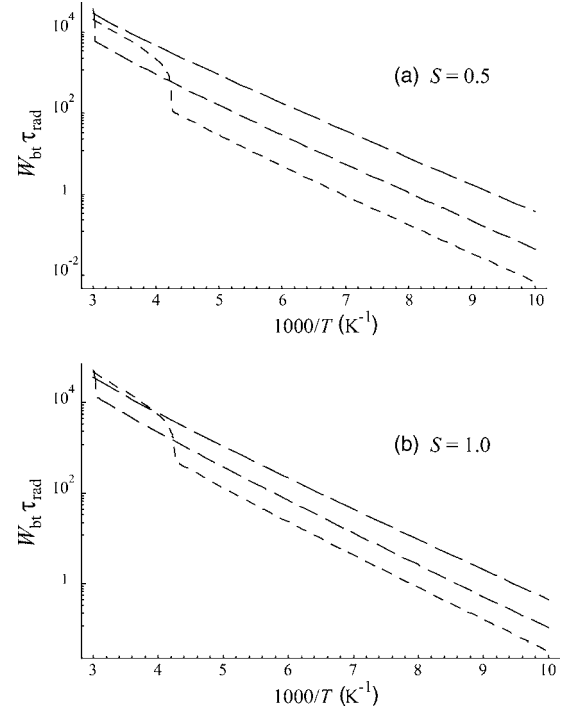

FIG. 5. The temperature dependence of the probability of the back tranfer process: $W_{\mathrm{bt}}\tau_{\mathrm{rad}}$ as a function of $1000/T$ for (a) $S = 0.5$ and (b) $S = 1.0$. Three values of phonon energy $\hbar\omega$ are used: 45, 67, and 125 meV. The longer dash corresponds to higher $\hbar\omega$.

$S = 1$ [Fig. 5(b)] for three phonon energy values $\hbar\omega$:
(*i*) 45 meV, smaller than the optical phonon of Si ("local" phonon mode),
(*ii*) 67 meV, the TO optical phonon of Si,
(*iii*) 125 meV, an oxygen-related local mode in Si, as oxygen is believed to be involved in Er donor formation.
For these phonon energies, the sum in Eq. (9) starts from $N = 3$, 2 and 1, respectively, in the temperature region of interest (100–200 K). The steps in the simulated temperature dependencies reflect changes in the minimum number of phonons required for thermal deexcitation. As can be seen, the simulations show only a small dependence of the back transfer probability on S, but a pronounced dependence on the phonon energy.

Although the temperature dependence of W_{bt}, as given by Eq. (9), is actually more complicated, it may be approximated by an Arrhenius law in a large temperature range. A direct comparison with experiment is obtained by reproducing temperature dependence of W_{bt}, as simulated within the presently developed theoretical description, using Eq. (24), assuming $\varkappa_0 = 1$ and $\tau_{rad} = 2$ ms.[1] The results of such a procedure are summarized in Table I. Here we have taken $\varkappa_0 = 1$ because electron screening is ineffective on the length scale at which the back transfer interaction takes place. We note that the preexponential factor may be reduced up to 144 times by varying, $\varkappa_0$ which may be regarded as a fitting parameter for reproducing experiments. Table I includes also experimental results obtained by Kik *et al.*[2] and Priolo *et al.*[1] We conclude that the theoretical description of the back transfer process as proposed here offers a fair agreement with experiment. On the other hand, this validates the use of

TABLE I. The comparison of best fit values of ΔE and ν_0 for the data in Fig. 5(a) (in temperature range 100–250 K) with literature data using $S = 0.5$. N shows the minimal number of phonons required.

	$\hbar\omega$ (meV)/N	ΔE (meV)	ν_0 (s^{-1})
	45 meV/3	148	8.0×10^7
Calculated	67 meV/2	145	4.0×10^8
	125 meV/1	135	1.0×10^9
Experimental	Ref. 2	135	10^8–10^{10}
	Ref. 1	150	1.0×10^9

the back transfer process as the major physical mechanism responsible for thermally quenching excited Er^{3+} ions embedded in a silicon matrix, as has generally been assumed.

B. Luminescence quenching at low temperatures by Auger processes

Auger interaction between excited Er^{3+} ions and free carriers has been frequently studied in the past. To this end, reduction of lifetime and intensity of Er-related PL appearing upon thermal[1] or optical[12] release of carriers into the band have been investigated. In a dedicated study,[1] Auger coefficients C_A have been determined for both holes and electrons, and a similar value of $C_A \approx 4.4 \times 10^{-13}$ cm^{-3} s^{-1} has been found. This result followed from fitting of the experimentally measured lifetime dependence using the simple relation

$$\tau_{\rm eff}^{-1} = \tau_0^{-1} + C_A n_c, \qquad (26)$$

where τ_0 corresponds to the low temperature luminescence lifetime and $(C_A n_c)^{-1}$ represents the characteristic time constant of deexcitation introduced by the Auger effect, with n_c being the (thermally or optically activated) concentration of free carriers participating in this process.

The current paper offers a microscopic understanding of the physical mechanism responsible for the Auger interaction and reflects on the experimentally determined value of C_A. Taking into account a realistic model of an Er-related optical center and, in particular, accounting for its donor character,[6,13] our calculations predict significant differences between Auger quenching by free electrons and holes. For donor centers, the excitation process leaves the Er-related donor state positively charged. The Coulomb interaction of the charged donor with free carriers enhances the Auger coefficient for electrons [see Eq. (17)] and renders Auger quenching by holes at low temperatures insignificant due to repulsion [see Eq. (20)]. Indeed, in samples with low B concentrations (5×10^{16} cm^{-3}), implanted by erbium, at 15 K an excited $^4I_{13/2}$ state lifetime of $\tau \approx 2$ ms has been found, which very likely represents a unique measurement of the truly radiative lifetime of Er^{3+} in Si. In these samples only little thermal lifetime quenching has been observed for temperatures up to 77 K[1]. Auger quenching by holes may only appear if the excited Er^{3+} ion is associated with a neutral (isoelectronic) center.

In Fig. 6 computer simulations, based on the physical model developed here, are presented. These correspond to
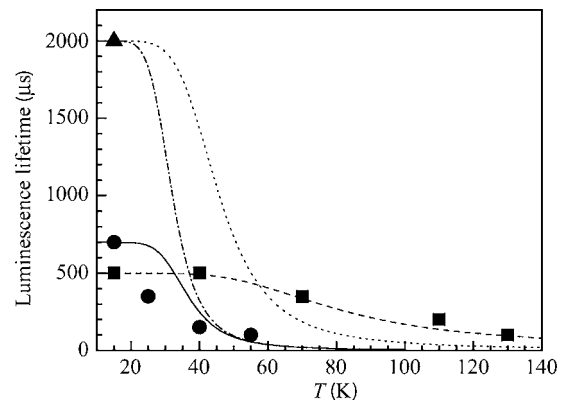

FIG. 6. The temperature dependence of Er^{3+} luminescence lifetime controlled by Auger interaction with free carriers. Symbols represent experimental data points taken from Ref. 1 for (circles) n-type Si (4×10^{16} cm^{-3} P), (rectangles) p-type Si (3×10^{17} cm^{-3} B), and (triangle) radiative lifetime of the Er^{3+} excited state as measured in p-type Si (5×10^{16} cm^{-3} B). Theoretical calculations using Eq. (26) are represented by lines: for quenching by free electrons of excited Er^{3+} involved in positively charged donor centers assuming $\tau_0 = \tau_{\rm rad}$ (dash-dot line), and $\tau_0 = 0.7$ ms (solid line); for quenching by free holes of excited Er^{3+} involved in neutral (isoelectronic) centers assuming $\tau_0 = \tau_{\rm rad}$ (dotted line), and $\tau_0 = 0.5$ ms with $C_{A,h}$ reduced by a factor of 5 (see text) (dashed line).

the expected Auger-process-controlled lifetime [Eq. (26)] of the Er^{3+} excited state in Er-related centers of donor character in (n-type) phosphorous-doped (dash-dotted line) and in neutral (isoelectronic) Er centers in p-type Si implanted with high B concentrations (dotted line). The aforementioned value of 2 ms (Ref. 1) has been taken as the radiative lifetime of Er in Si and we assume that at low temperature $\tau_0 = \tau_{\rm rad}$. From Eqs. (11), (12), and (15) we derive the temperature dependence of the Auger coefficient for electrons as

$$C_{A,e} = 3.8 \times 10^{-12}\left(\frac{300}{T}\right)^{1/2} \text{ cm}^{-3}\text{ s}^{-1}, \qquad (27)$$

and for holes $C_{A,h} = 5.0 \times 10^{-13}$ cm^{-3} s^{-1}. The concentration of free carriers is assumed to be thermally activated:

$$n_{e/h} = \left(\frac{N_{C/V}N_{D/A}}{2}\right)^{1/2} e^{-E_{D/A}/2kT}, \qquad (28)$$

with $N_D = 4 \times 10^{16}$ cm^{-3} and $N_A = 3 \times 10^{17}$ cm^{-3}.

It is important to note that the theoretical model developed here and used for simulations does not involve any free parameters, and is exclusively based on well-known materials characteristics relevant to the investigated system: in particular, an ionization energy of 45 meV has been used for thermal activation of free carrier concentration in both phosphorous- (n-type) and boron- (p-type) doped Si.

For comparison, experimental data points, taken from Ref. 1, are also included in Fig. 6. As mentioned before, this detailed experimental study was devoted to a direct measurement of the Auger coefficient relevant to PL quenching in Si:Er. In what follows, the compassion between simulations and experimental points will be discussed. Somewhat in contrast to what might appear from superficial inspection of Fig.

6, we will argue that the agreement with experimental data is satisfactory.

First, we discuss the situation for Er-related donor centers in *n*-type material. From Fig. 6 (dash-dotted line), we note that in the 40–60 K temperature region, where Auger energy transfer to free carriers dominates, the simulated lifetime reproduces the measurements very well. This is remarkable, since, as mentioned before, this result is obtained without adjusting parameters. The agreement in the lower temperature region is poor. This, however, follows directly from the fact that the Er luminescence lifetime commonly determined at low temperature in *n*-type material is $\tau_0 \approx 0.7$ ms, much shorter than the purely radiative value of $\tau_{rad} = 2$ ms assumed in the model and providing the low temperature calibrating point for all the simulations. The reason for the lifetime shortening observed at low temperatures is not clear. It can certainly not be induced by the Auger effect due to collision with free carriers, as considered here, since no free carriers are available in this temperature range. Clearly a different, and thus far unrecognized, process has to be responsible for this effect. One possibility for such a process would be the capture of mobile electrons in an impurity band by the charged donor associated with excited Er^{3+}, as suggested in Sec. IV. For low mobility carriers, the capture time may be controlled by diffusion. In this case, the capture time at the Coulomb attractive center is given by[11]

$$\tau^{-1} = \frac{4\pi e^2}{\kappa kT} D_n, \qquad (29)$$

with D_n the diffusion coefficient of electrons in the impurity band. As low temperature electron mobility data for these samples are not available, we will not elaborate on this point. For the present purpose of comparison, we can account for this additional lifetime shortening by setting τ_0 in Eq. (26) to the experimentally measured low temperature value. The simulation based on such a procedure is also depicted in Fig. 6 (solid line); in that case the agreement with experiment becomes better.

According to our calculations, excited Er^{3+} involved in a charged donor hardly experiences any quenching by holes. In heavily B-implanted Si formation of Er-B complexes has been postulated; such centers are characterized by a different PL spectrum of Er luminescence and may have neutral character.[1] In that case Auger quenching is possible (see simulation in Fig. 6, dotted line), although the effect is smaller than for donor centers in an *n*-type matrix. Again, the agreement with experiment can be improved by accounting for an unknown mechanism of low-temperature lifetime shortening and taking for τ_0 the experimentally determined value, $\tau_0 = 0.5$ ms, rather than τ_{rad}. The relevant simulation is also depicted in Fig. 6 (dashed line) where we have taken into account that the acceptor concentration is effectively reduced due to the formation of neutral Er-B complexes and that holes can only quench the luminescence of Er ions involved in the latter complexes (reduction of $C_{A,h}$ to about 20%).

Summarizing, we conclude that the proposed microscopic mechanism of Auger energy transfer between excited Er^{3+} ions and free carriers leads to a very satisfactory agreement
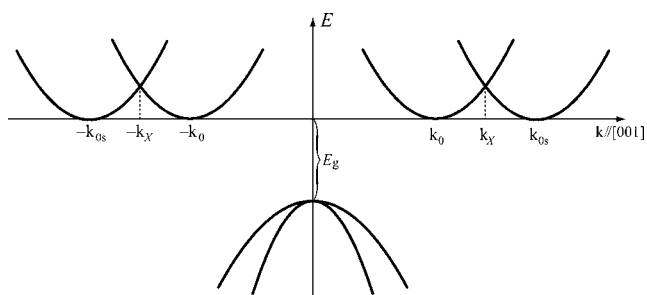

FIG. 7. The scheme of the minima of the conduction band and the maxima of the valence band in Si.

with the available experimental data pertinent to this process.

VI. CONCLUSIONS

The three main Er^{3+} deexcitation processes in bulk silicon—back transfer, collision with free carriers, and Er-related donor ionization—have been modeled theoretically. The relevant transition probabilities have been calculated and a reasonable agreement with available experimental data has been obtained. For Er^{3+} involved in a donor center, the deexcitation rate due to collisions with free electrons was found to be 1000 times higher than that for free holes. High probability has been demonstrated for deexcitation involving ionization of the Er-related donor center. The latter process may be responsible for Er luminescence lifetime shortening at temperatures where no free carriers are available.

APPENDIX A: BLOCH AMPLITUDES OVERLAP INTEGRAL

The conduction band in silicon has a complex structure. It has six minima in the first Brillouin zone, at $\pm \mathbf{k}_{0i}$, where *i* enumerates the valleys in three directions in *k* space: [001], [010], and [100], as shown in Fig. 7 (for [001]). The value of k_0 is 0.85 k_X, where $k_X = 2\pi/a$ is the edge of the Brillouin zone for this direction [*a* is the lattice constant which equals 5.43 Å for Si (Ref. 14)].

As the spin-orbit interaction in silicon is weak, it is neglected in further consideration. In such an approximation the conduction band is doubly degenerate at each of the six *X* points. This is a consequence of the fact that the silicon lattice has two atoms in the elementary unit cell and the origin is chosen at the center of one of them. Consider the band structure around $\mathbf{k}_X = (0,0,1)2\pi/a$. The two-band ap-

proximation allows one to choose the basis wave functions in plane wave approximation:[15]

$$\psi_{c,k_X} = \cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right) + i\sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right),$$
(A1)

$$\psi_{s,k_X} = \cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right) - i\sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right).$$
(A2)

The corresponding two-band Hamiltonian is diagonal when $k_\perp = 0$. The parameters of the Hamiltonian are chosen in such a way that ellipsoidal spectrum of the lower conduction band (c) has a minimum at $k=k_0$ and its effective masses have experimental values ($m_\parallel = 0.916 m_0, m_\perp = 0.19 m_0$). The higher band ($s$) has a minimum at $k_{0s} = k_X + \tilde{k}_0$ which is in the second Brillouin zone ($\tilde{k}_0 = k_X - k_0$).

The normalized Bloch amplitudes corresponding to (A1) and (A2) are

$$u_c = \sqrt{2}\left[\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right) + i\sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\right]$$
$$\times \exp\left(-i\frac{2\pi}{a}z\right),$$
(A3)

$$u_s = \sqrt{2}\left[\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right) - i\sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\right]$$
$$\times \exp\left(-i\frac{2\pi}{a}z\right).$$
(A4)

Therefore the wave functions at the conduction band minima are

$$\psi_{c,\mathbf{k}_0} = e^{ik_0 z} u_{c,k_X},$$
(A5)

$$\psi_{s,\mathbf{k}_0} = e^{ik_{0s} z} u_{s,k_X}.$$
(A6)

The wave functions at the opposite point $-k_X = (0,0,-1)2\pi/a$ can be written using the symmetry properties of silicon lattice, where the inversion I is substituted by the inversion plus translation I':[15]

$$(x,y,z) \rightarrow \left(-x+\frac{a}{4}, -y+\frac{a}{4}, -z+\frac{a}{4}\right).$$
(A7)

Then, one can find the relation between the Bloch amplitudes at the k_X and $-k_X$ points:

$$u_{c,-k_X} = (u_{c,k_X})^*,$$
(A8)

$$u_{s,-k_X} = (u_{s,k_X})^*.$$
(A9)

Spin-orbit interaction is neglected and a spherical approximation for the effective mass is used to consider the valence band. In this approximation we have a threefold degenerate valence band top in the Γ point. In plane wave approximation the Bloch amplitudes for each is given by[15]

$$u_{v,1} = 2\left[\sin\left(\frac{2\pi}{a}z\right)\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\right.$$
$$\left. + \cos\left(\frac{2\pi}{a}z\right)\sin\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\right],$$
(A10)

$$u_{v,2} = 2\left[\sin\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right)\right.$$
$$\left. + \cos\left(\frac{2\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right)\sin\left(\frac{2\pi}{a}z\right)\right],$$
(A11)

$$u_{v,3} = 2\left[\sin\left(\frac{2\pi}{a}y\right)\cos\left(\frac{2\pi}{a}z\right)\cos\left(\frac{2\pi}{a}x\right)\right.$$
$$\left. + \cos\left(\frac{2\pi}{a}y\right)\sin\left(\frac{2\pi}{a}z\right)\sin\left(\frac{2\pi}{a}x\right)\right].$$
(A12)

In the approximation used here, the Bloch amplitudes of both the c subband at $\mathbf{k}_0$ and the s subband at $\mathbf{k}_{0s}$ are determined by their values at the X point [(A5) and (A6)]. One can find, using (A3), (A4), and (A10)–(A12), that the overlap integrals between the Bloch amplitudes of the minimum of the conduction band and the top of the valence band are equal to zero:

$$I_{c,\pm\mathbf{k}_0;v,i} = \frac{1}{V_\Omega}\int_\Omega (u_{c,\pm\mathbf{k}_0})^* u_{v,i} d^3\mathbf{r} = 0.$$
(A13)

For the s band only one overlap integral is nonzero:

$$I_{s,\pm\mathbf{k}_{0s};v,1} = \frac{1}{V_\Omega}\int_\Omega (u_{s,\pm\mathbf{k}_{0s}})^* u_{v,1} d^3\mathbf{r} = \mp i/\sqrt{2}.$$
(A14)

It should be remarked that the calculation produced by the $(\mathbf{k}\cdot\mathbf{p})$ method[16] gives a value for overlap integral in close agreement with this calculation: $|I_{s,v}|^2 = 0.33$. This value will be used in the calculation of deexcitation probability. Similar expressions can be written for valleys in other directions.

APPENDIX B: ELECTRON MATRIX ELEMENT IN THE BACK TRANSFER PROCESS

The matrix element

$$M = \langle f, D|\hat{V}_c|f', \nu_h, \mathbf{k}\rangle$$
(B1)

describes the process of erbium ion deexcitation ($f' \rightarrow f$) which is accompanied by the transition of an electron from valence band (subband ν_i, wave vector $\mathbf{k}$) to donor (D).

The Coulomb interaction is represented in the form of the Fourier series:

$$\hat{V}_c = \frac{4\pi e^2}{V}\sum_{\mathbf{q}} \frac{e^{i\mathbf{q}(\mathbf{r}_1-\mathbf{r}_2)}}{|\varkappa(\omega,q)|q^2},$$
(B2)

where $\varkappa(\omega,q)$ is the dielectric function depending on the wave vector $\mathbf{q}$ (spatial dispersion) and the frequency ω (time dispersion). In the Auger process under consideration those values correspond to the wave vector and energy transferred

due to Coulomb interaction. The transition frequency is determined by the energy $\Delta_{ff'}$ of the Er^{3+} transition: $\omega = \Delta_{ff'}/\hbar$.

We will show below that the characteristic q is about $k_{0s}/2$, corresponding to Coulomb interaction at distances of the order of the lattice constant, where screening is weak. So, some constant $\varkappa_0$, which is smaller than the silicon dielectric constant, should be used in (B2).

All considerations are made in the spherical approximation of effective mass theory. The donor-localized electron is supposed to be in the singlet state with binding energy ε_D. The zero range approximation is used for its wave function, which is also expanded into Fourier series:

$$\psi_D(\mathbf{r}) = \frac{\sqrt{\kappa_D}}{2^{3/2}\pi^{5/2}}\frac{1}{6}\sum_{i=1}^{6}u_{c,\mathbf{k}_{0i}}e^{i\mathbf{k}_{0i}\mathbf{r}}\int d^3\mathbf{k}'\frac{e^{i\mathbf{k}'\mathbf{r}}}{\kappa_D^2+k'^2}, \quad (B3)$$

where $\kappa_D = \sqrt{2m_e\varepsilon_D}/\hbar$, $m_e = (m_\parallel m_\perp m_\perp)^{1/3}$ is the density of states effective mass, and the summation is performed over six valleys having centers at $\mathbf{k}_{0i}$.

The wave function of an electron in the valence band is

$$\psi_{j,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}u_{v,j}e^{i\mathbf{k}\mathbf{r}}, \quad (B4)$$

where j enumerates the subbands.

In (B1), f and f' denote strongly localized wave functions of the erbium ion's f electrons. The transition of the electron from valence band to donor takes place at $\mathbf{r}_1$. The radius vector of the f electron is $\mathbf{r}_2$. The centers of the erbium ion and the related donor are supposed to be at the same point:

$$M = \frac{1}{V^{3/2}}\sqrt{\frac{2\kappa_D}{\pi^3}}\frac{1}{6}\sum_{\mathbf{q}}\frac{e^2}{|\varkappa(\omega,\mathbf{q})|q^2}$$

$$\times\sum_{i=1}^{6}\int\frac{d^3\mathbf{k}'}{\kappa_D^2+k'^2}\int d^3\mathbf{r}_1 u_{c,\mathbf{k}_{0i}}^*(\mathbf{r}_1)u_{v,j}(\mathbf{r}_1)e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{k}_{0i}+\mathbf{q})\mathbf{r}_1}$$

$$\times\int d^3\mathbf{r}'e^{-i\mathbf{q}\mathbf{r}'}f^*(\mathbf{r}')f'(\mathbf{r}'). \quad (B5)$$

The integral over $\mathbf{r}_1$ can be transformed into a sum of integrals over N elementary cells Ω_n, substituting $\mathbf{r}_1$ by the sum of vector $\mathbf{R}_n$, pointing to the nth cell, and vector $\mathbf{r}$ inside the cell:

$$I = \frac{1}{V}\int d^3\mathbf{r}_1 u_{c,\mathbf{k}_{0i}}^*(\mathbf{r}_1)u_{v,j}(\mathbf{r}_1)e^{i(\mathbf{q}-\mathbf{q}_0)\mathbf{r}_1}$$

$$= \frac{1}{N}\sum_{n=1}^{N}e^{i(\mathbf{q}-\mathbf{q}_0)\mathbf{R}_n}\frac{1}{V_\Omega}\int_{\Omega_n}d^3\mathbf{r}\,u_{c,\mathbf{k}_{0i}}^*(\mathbf{r})u_{v,j}(\mathbf{r})e^{i(\mathbf{q}-\mathbf{q}_0)\mathbf{r}},$$

$$(B6)$$

where V_Ω is the volume of the elementary cell ($NV_\Omega = V$), and $\mathbf{q}_0 \equiv \mathbf{k}_{0i} + \mathbf{k}' - \mathbf{k}$.

The sum yields the δ symbol and one can get

$$I = \delta_{\mathbf{q},\mathbf{q}_0+\mathbf{G}}\frac{1}{V_\Omega}\int_\Omega d^3\mathbf{r}\,u_{c,\mathbf{k}_{0i}}^*(\mathbf{r})u_{v,j}(\mathbf{r})e^{i\mathbf{G}\mathbf{r}}, \quad (B7)$$

where $\mathbf{G}$ is a reciprocal lattice vector.

The common practice of calculating such integrals is to put $\mathbf{G}=0$, but in the case of silicon it leads to $I=0$ (see Appendix A). For each valley i a nonzero result can be obtained choosing a vector $\mathbf{G}$ with length $G=4\pi/a$ and directed opposite to $\mathbf{k}_{0i}$. One can check that such selection of $\mathbf{G}$ gives the same effect as if $u_{c,\mathbf{k}_{0i}}$ would be substituted with $u_{s,\mathbf{k}_{0s,i}}$ in (B7) (see Appendix A):

$$I = \delta_{\mathbf{q},\mathbf{q}_0+\mathbf{G}}I_{s,\mathbf{k}_{0s};v,1}. \quad (B8)$$

Further increasing G leads to vanishing results because of the fast oscillating integrand. So the transition vector is

$$\mathbf{q} = \mathbf{q}_0 + \mathbf{G} = -\mathbf{k}_{0s} - \mathbf{k} + \mathbf{k}'. \quad (B9)$$

As $\varepsilon_\mathbf{k}$ in the argument of the δ function in (B5) is limited by the phonon energy, $\mathbf{k}$ can be neglected. The last exponent in (B5) can be expanded and the integration over $\mathbf{r}'$ gives the dipole momentum $d_{ff'}$. The complete matrix element is

$$M = \frac{-i}{3\sqrt{\pi}V^{1/2}}\frac{e^2\sqrt{\kappa_D}}{\varkappa_0}d_{ff'}\varphi(\gamma)\sum_{i=1}^{6}I_{s,\mathbf{k}_{0s};v,1}, \quad (B10)$$

where

$$\varphi(\gamma) = \int_0^{+\infty}\frac{y^2}{\gamma^2+y^2}\left(1 - \frac{1-y^2}{4y}\ln\frac{(1-y)^2}{(1+y)^2}\right)dy,$$

$$(B11)$$

and $\gamma = \kappa_D/k_{0s}$. In this case $\gamma \approx 0.11$ and $\varphi(\gamma) \approx 2.14$ for ε_D.

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[1] F. Priolo, G. Franzò, S. Coffa, and A. Carnera, Phys. Rev. B **57**, 4443 (1998).

[2] P. G. Kik, M. J. A. Dood, and A. Polman, Appl. Phys. Lett. **70**, 1721 (1997).

[3] B. K. Ridley, *Quantum Processes in Semiconductors* (Oxford, Clarendon, 1982).

[4] A. Suchocki and J. M. Langer, Phys. Rev. B **39**, 7905 (1989).

[5] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley InterScience, New York, 1981).

[6] S. Libertino, S. Coffa, G. Franzò, and F. Priolo, J. Appl. Phys. **78**, 3867 (1995).

[7] F. Priolo, G. Franzò, S. Coffa, A. Polman, S. Libertino, R. Barklie, and D. Carey, J. Appl. Phys. **78**, 3874 (1995).

[8] J. Michel, J. L. Benton, R. F. Ferrante, D. C. Jacobson, D. J. Eaglesham, E. A. Fitzgerald, Y.-H. Xie, J. M. Poate, and L. C. Kimerling, J. Appl. Phys. **70**, 2672 (1991).

[9] F. P. Widdershoven and J. P. N. Naus, Mater. Sci. Eng., B **4**, 71 (1989).

[10] M. A. J. Klik, "Energy Transfer Processes in Optically Doped Matrices: a Spectroscopical Approach," Ph.D. thesis, University

of Amsterdam, 2005.

[11] V. N. Abakumov, V. I. Perel, and I. N. Yassievich, *Nonradiative Recombination in Semiconductors* in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1991).

[12] M. Forcales, T. Gregorkiewicz, and M. S. Bresler, Phys. Rev. B **68**, 035213 (2003).

[13] M. Forcales, T. Gregorkiewicz, M. S. Bresler, O. B. Gusev, I. V.

Bradley, and J.-P. R. Wells, Phys. Rev. B **67**, 085303 (2002).

[14] A. Dargys and J. Kundrotas, *Handbook on Physical Properties of Ge, Si, GaAs and InP* (Science and Encyclopedia Publishers, Vilnius, 1994).

[15] P. Y. Yu and Manuel Cardona, *Fundamentals of Semiconductors. Physics and Materials Properties. Third, Revised and Enlarged Edition* (Springer, New York, 2002).

[16] Manuel Cardona and Fred H. Pollak, Phys. Rev. **142**, 530 (1966).