

Donor-State-Enabling Er-Related Luminescence in Silicon: Direct Identification and Resonant Excitation

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We conclusively establish a direct link between formation of an Er-related donor gap state and the 1.5 μm emission of Er in Si. The experiment is performed on Si/Si:Er nanolayers where a single type of Er optical center dominates. We show that the Er emission can be resonantly induced by direct pumping into the bound exciton state of the identified donor. Using two-color spectroscopy with a free-electron laser we determine the ionization energy of the donor-state-enabling Er excitation as $E_D \approx 218$ meV. We demonstrate quenching of the Er-related emission upon ionization of the donor.

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Doping with Er is possibly the most investigated way for improving photonic properties of crystalline silicon (*c*-Si). Nevertheless, low level of optical activity of Er^{3+} and thermal quenching of emission intensity have not been resolved. Moreover, the physical basis of these limitations is not fully understood. This justifies further research in fundamental aspects of energy transfer mechanisms governing excitation and deexcitation processes of Er^{3+} ions embedded in a *c*-Si matrix. The proposed formation of a gap state mediating energy flow between extended effective-mass-like shallow levels of the host and localized 4*f*-electron states of Er^{3+} is of profound importance. Thus far only indirect evidence in support of the Er-related donor level has been derived from thermal quenching of Er luminescence [1] and deep-level transient spectroscopy measurements [2,3], where ionization energy E_D values between 150 and 250 meV have been reported. These measurements, however, are not able to discriminate between optically active and nonactive fractions of Er dopants. Consequently, the often postulated link between formation of a donor level and optical activity of Er^{3+} is not supported by these experiments, that reflect properties of the majority of Er dopants, which do not take part in light emission. In addition, formation of an Er-related donor level in Si has never been justified by theoretical modeling; this in contrast to Yb^{3+} in InP [4]. Therefore, it is possible that the donor level observed in *c*-Si:Er is induced by Er doping but bears no relation to optical activity of Er^{3+} , i.e., oxygen related thermal donors [5].

As can be concluded from the above, the identification of a gap state mediating the energy transfer to (and from) the Er^{3+} ion, and in this way controlling its optical activity in *c*-Si, remains open. In the present study we resolve this long-standing problem: using complementary information obtained by excitation and two-color spectroscopies, we identify a specific donor state and establish its unambiguous link with the 1.5 μm emission in *c*-Si:Er.

Photoluminescence (PL) excitation spectroscopy (PLE) has been performed at $T = 10$ K under pulsed excitation with an optical parametric oscillator (OPO), tunable in the near-infrared range, close to the band gap of *c*-Si. The two-color measurements were performed at the free-electron laser (FEL) facility FELIX in Nieuwegein, the Netherlands. The third harmonic of the FEL was used to enable a probe wavelength in the spectral range between 150 meV and 485 meV. For primary excitation, the second harmonic of a Nd:YAG laser (532 nm) was applied. The duration of the Nd:YAG pulse was shorter than 100 ps, while the full width at half maximum (FWHM) of the total FEL (macro-)pulse—which is formed by a 1 GHz train of picosecond pulses, and therefore can be effectively considered as a square pulse with picosecond rise and decay slopes [6]—was about 5 μs . The delay time Δt between the primary (Nd:YAG) and secondary (FEL) pulse could be tuned at will. The measurements were taken at $T = 4.2$ K using a gas-flow cryostat. PL spectra were resolved with a TRIAX 320 spectrometer and detected with an InGaAs photomultiplier tube.

The study was conducted on a Si/Si:Er multilayer structure grown by sublimation molecular-beam epitaxy technique, comprising 400 alternating Si and Si:Er layers on a Cz-Si substrate. As discussed before [7], the Er^{3+} ions in this sample form predominantly only a single type of center, whose PL is characterized by homogeneous and ultrasmall linewidth of $\Delta E < 10$ μeV . Low temperature PL spectrum of the investigated sample—see, e.g., [7]—features a series of very sharp lines related to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion, with the main emission at 1538 nm. This system is particularly suitable for the investigation of the Er-related level in the excitation process. It can be expected that a single type of optical center will create a single level in the Si band gap, thus considerably simplifying the experiment.

In Fig. 1, we present a PLE spectrum of the Er-related emission measured in the investigated structure for excitation energy E_X close to the band gap of c -Si. As can be seen, in addition to the usually observed contribution produced by (the onset of) the band-to-band excitation, also a resonant feature, peaking at the energy around $E_X = E_R \approx 1.18$ eV, is clearly visible. We propose to identify this with a different excitation channel appearing in this energy range. Such a hypothesis is directly supported by PL intensity power dependence, shown in the inset, for the two photon energies indicated with arrows. While the data obtained for the higher energy value of $E_X = 1.54$ eV exhibit the saturating behavior characteristic of the band-to-band excitation mode [8], the dependence for $E_X = E_R \approx 1.18$ eV has a strong linear component superimposed on this saturating background. Such a linear dependence is expected for “direct” pumping. For Er in c -Si a resonant excitation could indeed take place via a bound exciton state induced by the long-sought Er-related donor discussed earlier. In that case, the energy E_R required for this resonant pumping would be given by:

$$E_R \approx E_G - E_{\text{FEX}} + E_{\text{LO}} - E_{\text{BE}}, \quad (1)$$

where E_G is the c -Si band-gap energy $E_G = 1.17$ eV, $E_{\text{FEX}} = 15$ meV is the exciton formation energy, E_{LO} is the energy of the lattice phonon—necessary in view of the indirect band gap of c -Si—and E_{BE} is the exciton-donor binding energy. Using the $E_R \approx 1.18$ eV value derived from the PLE spectrum given in Fig. 1, we can estimate the exciton binding energy as $E_{\text{BE}} \approx 30$ meV. Since exciton binding and donor ionization energies of a donor are mutually related [9], this implies that the relevant donor state involved in the postulated resonant excitation of Er is relatively deep, with the ionization energy in the range of 200–300 meV.

Direct identification of this donor state governing the optical activity of Er in c -Si and enabling its excitation has been obtained by two-color spectroscopy in the visible and the midinfrared (MIR) regions. In the past, this powerful

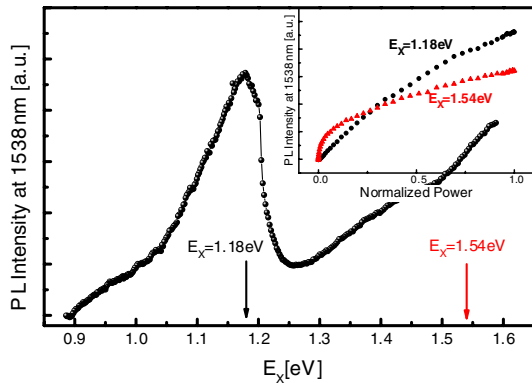


FIG. 1 (color online). PLE spectrum of the $1.5 \mu\text{m}$ Er-related emission. For two excitation wavelengths indicated with arrows, normalized power dependence of PL intensity is given in the inset.

experimental technique [10] has been successfully applied for investigation of excitation mechanisms in rare-earth-doped matrices [11–13], spin relaxation in semiconductors [14], and excited states of atomic clusters [15]. In these experiments one monitors PL of the system emitted after band-to-band excitation with the primary pulse, which is then altered by the secondary MIR beam (FEL). In the current case, we have observed that the Er-related PL is quenched upon application of a FEL pulse with a sufficiently large photon quantum energy. This is illustrated in the inset to Fig. 2, which shows the change of PL transient induced by the MIR pulse. Amplitude of the relative quench remains independent of temperature, up to at least 70 K, thus indicating a deeper character of the levels involved in the process [10,16,17]. Detailed investigations revealed that the magnitude of quenching depends on the timing of FEL with respect to the band-to-band excitation Δt and on the quantum energy $h\nu_{\text{FEL}}$ and the flux ϕ_{FEL} of MIR photons. In order to quantify these effects, we define the quench ratio as

$$Q(\Delta t, h\nu_{\text{FEL}}, \phi_{\text{FEL}}) = \frac{I_{\text{no FEL}} - I_{\text{FEL}}}{I_{\text{no FEL}}} = 1 - \frac{\int_{\Delta t}^{\infty} E_{\text{FEL}}^*(t) dt}{\int_{\Delta t}^{\infty} E_{\text{no FEL}}^*(t) dt}, \quad (2)$$

where I stands for the time-integrated PL intensity, from the moment when the MIR pulse is fired, and E_{FEL}^* and $E_{\text{no FEL}}^*$ are the PL signals observed with and without the FEL pulse, respectively. $Q = 1$ corresponds to the total quench of the PL signal. Figure 2 shows the wavelength dependence of PL quench for several flux values. As can be seen, PL quenching is observed for the MIR photon energy $h\nu_{\text{FEL}} \geq 250$ meV, but not in the region $h\nu_{\text{FEL}} \leq 210$ meV. We conclude that the quenching effect appears once the photon quantum energy exceeds a certain threshold value located between 210 and 250 meV and saturates

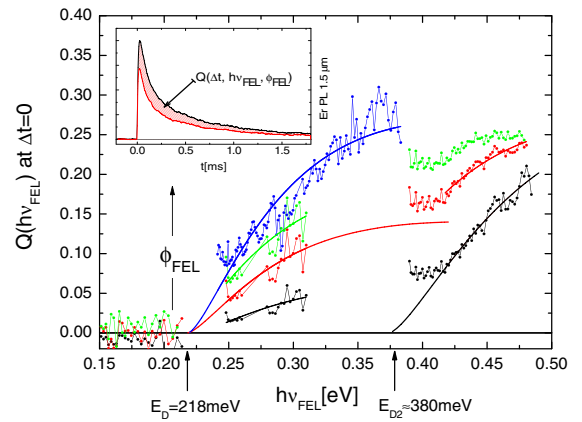


FIG. 2 (color online). FEL wavelength dependence of the induced quenching ratio of Er-related PL at $1.5 \mu\text{m}$, for several flux settings of the FEL. Solid lines correspond to simulations with Eq. (2). In the inset: illustration of the FEL-induced quenching of Er-related PL.

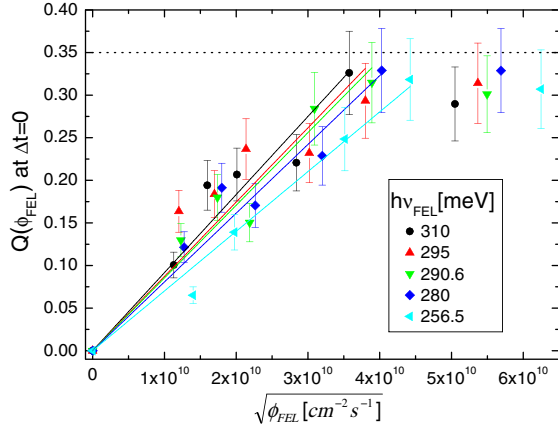


FIG. 3 (color online). Quenching ratio as a function of the square root of the FEL photon flux for $h\nu_{\text{FEL}} = 310, 295, 290.6, 280,$ and 256.5 meV, $T = 4.2$ K, $\Delta t = 0$. Linear dependence is shown for low flux values; the saturation level is indicated with the dotted line at $Q = 0.35$.

at a higher photon flux—see Fig. 3, with the maximum signal reduction of $Q \approx 0.35$.

Figure 4 shows the quench ratio as a function of the time delay Δt . As can be seen, the quenching does not take place when the FEL is fired before the pump, gradually increases as the two pulses overlap ($-8 \mu\text{s} \leq \Delta t \leq 0 \mu\text{s}$), attains maximum for $\Delta t \approx 0 \mu\text{s}$ —see the detailed kinetics in the inset—and then slowly, on the time scale of $\tau_d \approx 300 \mu\text{s}$, reduces towards an equilibrium value of $Q_{\text{eq}} \approx 10\%$. This observation excludes heating as a possible explanation for the reduction of PL, since this has a relaxation time of an order of milliseconds and therefore PL quenching should take place also for FEL pulses applied before the Nd:YAG. We conclude that application of FEL induces an additional, nonradiative deexcitation of Er^{3+} ions. One possible candidate for such a process could be cooperative up-conversion, well known from Er-doped glasses. In this case energy is transferred between two excited Er^{3+} ions. Effectively, this means that one excitation is lost. However, the up-conversion process depends only on the average distance between ions and on the medium and cannot be influenced by photons from the FEL. This rules out up-conversion as a possible mechanism of the FEL-induced PL quenching.

A prominent nonradiative recombination process is the excitation reversal (“back transfer”). It has been identified as the main reason for reduction of Er^{3+} luminescence at elevated temperatures and involves creation of an electron-hole pair at the Er-related level at the expense of Er^{3+} deexcitation. At higher temperatures, the additional energy required for this process is provided by multiphonon absorption. For InP:Yb, it was shown that the “back transfer” can also be induced by intense FEL illumination. In that case, a steplike dependence on photon energy and a linear dependence on photon flux, leading to complete quenching of the emission, have been observed [13]. This is clearly different in the present case, where a pronounced wave-

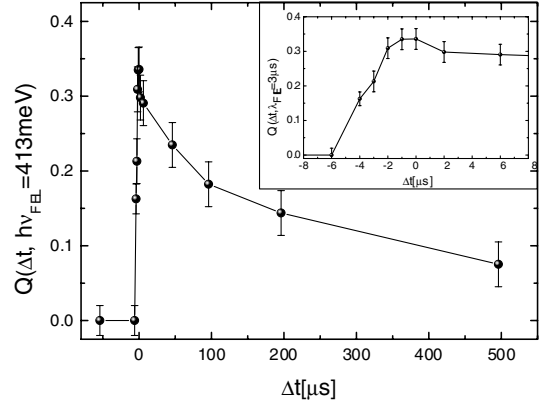


FIG. 4 (color online). Quenching ratio as a function of mutual delay of pump and probe pulses Δt , for $h\nu_{\text{FEL}} = 413$ meV. In the inset: detailed behavior for the region of overlap between the pump and the FEL pulses.

length dependence and also saturation of the quench ratio are measured. We note further that when we assume that the resonant feature of Fig. 1 represents the Er-related BE state, then the minimum activation energy necessary for the back transfer can be estimated as $E_{\text{bt}} \geq E_R - E_{\text{PL}} \approx 1180 - 800 \text{ meV} = 380 \text{ meV}$. In contrast to that, data in Fig. 2 show PL quench already at much smaller energies. Taken together, the evidence at hand argues against identification of the observed PL quenching with the “back transfer”. Also, the aforementioned thermal stability of the observed quenching points against the “back transfer”, as this process should enhance upon temperature increase—to this end, we point out that complete PL quench is indeed observed at higher temperatures.

In the past, also Auger mechanism has been found to hamper PL process of Er in *c*-Si: a carrier in the conduction or valence band can absorb the energy of an excited Er^{3+} ion, leading to PL quenching [18]. Auger quenching can be induced with the FEL by optical ionization of trap states [17]. In that case, the quench rate is proportional to the concentration of carriers liberated by the FEL pulse. Assuming that an equilibrium carrier concentration is maintained during FEL illumination, the PL quenching should increase with the square root of photon flux [8] towards saturation determined by full ionization of relevant traps. As evidenced by Fig. 3, this characteristic square root dependence is indeed observed in the experiment for small photon fluxes. On the other hand, the quench should increase (practically linearly) with the exposure time of excited Er population to free carrier concentration, i.e., with the “effective” duration of the FEL pulse, again in agreement with the experiment—see Fig. 4. We also note that following the full overlap of the two pulses, a small decrease of the quench takes place upon further increase of the delay time. It is plausible to attribute this gradual reduction to decay of (nonequilibrium) population of traps involved in the Auger process. This additionally supports the proposed Auger process rather than the “back transfer”, which should be time independent. Finally, it is only

fair to point out that the energy (back)transfer process in Si:Er is significantly more complex than in direct band-gap materials; therefore, we cannot rule out that it indeed contributes to the observed quenching.

Since for the fixed duration of the FEL pulse, the Auger effect should saturate at a level determined by trap concentration, then the quenching saturation level can be used to estimate this concentration. Taking the maximum quench to be 35% of the original signal—Fig. 3—and the FEL pulse FWHM as 5 μ s, and using the frequently quoted value of the Auger coefficient for free electrons of $C_A \approx 10^{-13}$ – 10^{-12} cm³ s⁻¹ [18], we arrive at a trap concentration of 10^{17} – 10^{18} cm⁻³. This concentration is much higher than the donor or acceptor doping level of the matrix and can only be compared to the concentration of Er-related donors found in an oxygen-rich material [19].

Following our microscopic interpretation of the quenching mechanism, its wavelength dependence should reflect photoionization spectrum of traps releasing carriers taking part in the Auger energy transfer. It has been shown [20] that the ionization cross section for traps can be described by:

$$\sigma(h\nu) \propto \frac{(h\nu - E_D)^{3/2}}{h\nu^{3+2\gamma}}, \quad (3)$$

with $h\nu$ and E_D corresponding to the quantum energy of the ionizing radiation and the ionization energy of the trap, respectively. The parameter γ depends on the specific form of the binding potential, being $\gamma = 0$ for δ -like potentials and $\gamma = 1$ for Coulomb potentials. Since $Q \propto \sigma(h\nu)$ then we can fit the data in Fig. 2 with Eq. (3). In this way we find the thermal ionization energy of the involved level as $E_D = 218 \pm 15$ meV. Note that only the low FEL flux data are used for fitting in order to minimize saturation effects. The best fit has been obtained for a localized potential, with $\gamma \approx 0$. We recall that $E_D \approx 218$ meV is similar to the trap level found in Si:Er by deep-level transient spectroscopy [3]. Therefore, it appears plausible that the FEL ionizes electrons from the donor level associated with Er³⁺, the same as identified earlier from the PLE data. Further, it appears that in the high photon energy range, another deeper trap, with ionization energy in 350–450 meV range, contributes to the free carrier density.

We conclude that the results obtained in two-color and excitation spectroscopies explicitly demonstrate that optical activity of Er in *c*-Si is related with a gap state. Taking advantage of the preferential formation of a single optically active Er-related center in sublimation molecular-beam-epitaxy-technique-grown Si/Si:Er multilayer structures, we determine the ionization energy of this state as $E_D \approx 218$ meV. We prove that this level provides indeed the gateway for Er³⁺ excitation by demonstrating 1.5 μ m emission upon resonant pumping into the bound exciton state of the identified donor. We point out that the relatively large width of the resonant excitation band, exceeding that for bound exciton recombination bands in

Si [21], follows directly from the involved physical mechanism. In the current case, the absorption of a photon by a bound exciton is accompanied by a simultaneous excitation of Er³⁺ ion and a transfer of a donor electron into the conduction band. Therefore, the minimum energy $E_{X\min}$ required for this process is given by the sum of Er excitation (800 meV) and donor ionization (218 meV): $E_{X\min} \approx 1.020$ eV. This corresponds precisely to the onset of the resonant excitation band, as evidenced by Fig. 1, thus supporting the proposed identification.

At the same time, we show that carriers located at the Er-related donor state introduce a channel of effective non-radiative relaxation of excited Er³⁺ ions via Auger process of energy transfer. In this way, new light is shed on the long-standing puzzle concerning the physical origin of the low emission intensity from Er-doped *c*-Si: while formation of the donor state enables Er core excitation, the same donor level opens also an efficient path of nonradiative relaxation. Future research will tell whether these two processes can be separated by careful material engineering. We would also like to point out that the direct “resonant” pumping into the bound exciton state identified here allows for excitation of Er³⁺ while avoiding Auger quenching by free carriers.

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