

Mid-infrared spectroscopy of the Er-related donor state in Si/Si:Er³⁺ nanolayers

I. Izeddin^{a,*}, M.A.J. Klik^a, N.Q. Vinh^b, M.S. Bresler^c, T. Gregorkiewicz^a

^a Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

^b FOM Institute for Plasma Physics “Rijnhuizen”, P.O. Box 1207, NL-3430BE Nieuwegein, The Netherlands

^c A.F. Ioffe Physico-Technical Institute of RAS, 26 Politekhnicheskaya, 194921 St. Petersburg, Russia

Abstract

We present experimental evidence on the donor level related to optical properties of the Er³⁺ ion in crystalline silicon. Using two-color spectroscopy with a free-electron laser we provide a direct link between the identified level in the bandgap and the optical properties of Er³⁺. The investigation is performed in sublimation MBE-grown Si/Si:Er multilayer structure, which allows us to take advantage of the preferential formation of a single Er-related center. Quenching of the Er-related 1.5 μm photoluminescence, due to ionization of the donor state with energy $E_D \approx 225$ meV, is demonstrated. A microscopic model of the PL quenching mechanism as Auger type energy transfer between excited Er³⁺ ions and free carriers optically ionized from the Er-related donor states is put forward.

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1. Introduction

The low optical activity of Er³⁺ in Si is generally pointed out as one of the prominent reasons for the low photoluminescence (PL) intensity of the Si:Er system. This aspect is also of crucial importance for realization of optical gain in Si:Er. Most studies report that only around one percent of Er³⁺ ions are optically active [1]. This fact has often been related to the requirement for Er to form a level in the bandgap of Si in order to be excitable via the host. The formation of donor levels by Er is a much debated issue. It was shown that oxygen content plays a major role in that process. In particular, the oxygen content has been linked to the percentage of Er-related which can be formed. It was shown that as Er concentration increases, an increasing number of oxygen atoms is required per Er ion to obtain a constant percentage of Er-related donors, and a relation between donor and oxygen concentrations has been proposed [2]. Since the concentration of Er ions is very large compared to other impurity centers, this donor dominates, and is responsible for the n-type conductivity typical for Si:Er. From DLTS measurements [3] and the data on temperature quenching of Er³⁺ PL [4–7], the Er-related donor level is generally believed

to be located between 150 and 266 meV below the conduction band.

In the past experiments on Si:Er [8], we have shown that a large number of holes could be ionized from shallow acceptors under illumination with a free-electron laser (FEL). Subsequently, these holes could re-excite Er³⁺ in a single carrier excitation process. In the current contribution, we investigate the role of electrons in the excitation process. In view of the above summarized information on the Er-related donor centers, considerably larger photon energies are needed to manipulate donor states in Si:Er, placing stringent requirements on the experimental set-up.

2. Experimental approach

In the reported study, we have performed time-resolved two-color spectroscopy on a Si:Er structure comprising 400 alternating Si and Si:Er layers. The thickness of the Si:Er layers is 1.7 nm, and the Si spacer layers have a thickness of 2.3 nm. The sample has been grown at a temperature of 520 °C by a sublimation MBE technique [9] on a Cz–Si substrate. The concentration of Er³⁺ and oxygen in the active layers is 2×10^{18} , and 1.5×10^{19} cm⁻³, respectively [10]. Past research [11,12] has shown that the Er ions in this sample are preferentially incorporated in a single type of optically active center, designated Er-1,

* Corresponding author. Fax: +31 20 5255788.

E-mail address: izeddin@science.uva.nl (I. Izeddin).

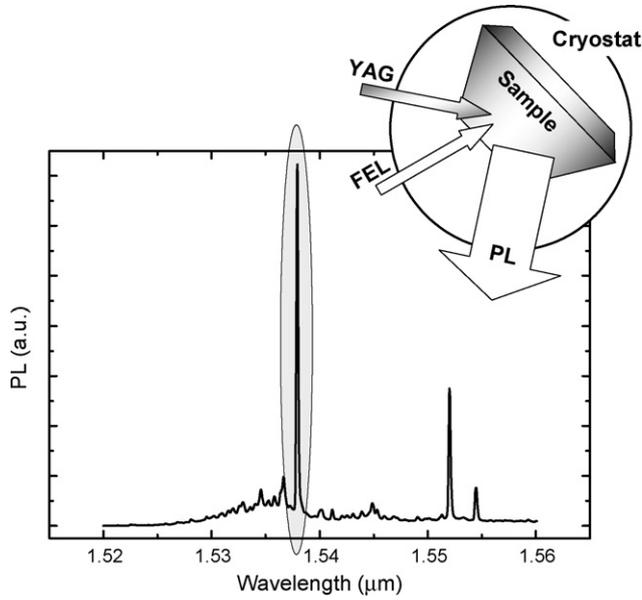


Fig. 1. PL spectrum of the Si:Er structure grown used in the study. In two-color spectroscopy – primary excitation with a Nd:YAG laser, secondary excitation with a FEL, schematics in the inset – intensity of the highlighted PL line has been followed $T=4.2$ K.

whose emission is characterized by the smallest linewidth ever observed for any emission from a semiconductor host. Due to the single center character, this system is particularly suited to investigate the role of the Er-related level in the excitation process. It is expected that a single type of center will create a single level in the bandgap of silicon, thus considerably simplifying the modeling of the complex system of excitation and de-excitation pathways.

In Fig. 1, the idea of the two-color experiment is schematically shown together with PL spectrum of the investigated structure. The two-color spectroscopy measurements were performed at the free-electron laser FELIX facility in Nieuwegein, The Netherlands. The third harmonic of the FEL was used to enable a tunable probe wavelength range between 3.3 and 5 μm . For primary excitation of the system, the second harmonic of a Nd:YAG laser was used (532 nm). The duration of the Nd:YAG pulse is shorter than 100 ps, while the duration of the total FEL pulse is about 5 μs . In the experiment, we monitored changes of PL emitted by the sample upon primary excitation (band-to-band indirect excitation mechanism), as induced by applying the secondary (FEL) beam—see, e.g., [13] for a detailed description of two-color spectroscopy. In the reported study, we have observed reduction of the Er-related PL (monitored at $\lambda \approx 1.5$ μm , due to the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition of Er^{3+} ion) upon application of FEL and then investigated this effect as a function of FEL wavelength, flux, and the delay time between the primary and secondary pulses.

3. Results and discussion

In the experiment, we have observed that the PL intensity from Er^{3+} generated upon primary Nd:YAG excitation is quenched significantly by the secondary probing pulse from

the FEL. In the time domain, we have noticed that the quenching effect: (i) was not observed for FEL pulsed fired before the pump pulse, (ii) had the largest magnitude when the FEL was fired directly after the primary pulse, and (iii) increased nearly linearly with FEL pulse duration [14].

We note that the observation of PL quenching was unexpected, since it has not been seen in our previous two-color experiments performed on the same sample with the FEL operating in the 70–200 meV range. We have therefore investigated in detail the quenching rate of Er PL as function of the FEL wavelength [14]. We have found out that the quenching effect gradually increases for larger quantum energies, with an onset at $E \approx 225$ meV. Consequently, we have identified this energy with a level in the gap, whose ionization (by the FEL) leads to a reduction of the Er excited state population. In view of the earlier remarks, it was natural to associate this level with the postulated Er-related donor center. We note that the observed thermal stability of the quenching effect – which, in contrast to the earlier studies, persists up to at least $T=70$ K – is also consistent with the relatively deeper character of the involved traps.

In order to quantify the observed quenching effect we introduce the quench rate of Er^{3+} PL, denoted by R_{FEL} . In this approach, the effect of the FEL is regarded as an extra decay pathway of excited Er^{3+} , with a constant magnitude during the FEL pulse:

$$R_{\text{FEL}} = \frac{1}{\tau_{\text{FEL}}} = \frac{1}{\tau_{\text{Er+FEL}}} - \frac{1}{\tau_{\text{Er}}}, \quad \text{for } t_{\text{FEL}} \leq t \leq t_{\text{FEL}} + \Delta t_{\text{FEL}}, \quad (1)$$

with τ_{FEL} the effective decay time due to the FEL pulse, and $\tau_{\text{Er+FEL}}$ and τ_{Er} the total (measured) and Er^{3+} PL decay times, respectively, and Δt_{FEL} and t_{FEL} the duration and the timing of the FEL pulse. Taking into account the exponential decay of Er^{3+} PL intensity, we find the following expression for the quench ratio Q of the total number of photons emitted by Er with and without illumination by FEL:

$$\begin{aligned} Q(\Phi_{\text{FEL}}, h\nu_{\text{FEL}}, \Delta t_{\text{FEL}}) &= 1 - \frac{\int_{t_{\text{FEL}}+\Delta t}^{\infty} E_{\text{FEL}}^*(t) dt}{\int_{t_{\text{FEL}}+\Delta t}^{\infty} E_{\text{noFEL}}^*(t) dt} \\ &= 1 - \frac{\int_{t_{\text{FEL}}+\Delta t}^{\infty} E_{\text{noFEL}}^*(0) \exp(-t/\tau_{\text{Er}}) dt}{\int_{t_{\text{FEL}}+\Delta t}^{\infty} E_{\text{noFEL}}^*(0) \exp(-t/\tau_{\text{Er}}) dt} \exp(-R_{\text{FEL}} \Delta t_{\text{FEL}}) \\ &= 1 - \exp(-R_{\text{FEL}} \Delta t_{\text{FEL}}), \end{aligned} \quad (2)$$

where E_{FEL}^* and E_{noFEL}^* corresponds to the amplitude of PL intensity with and without application of FEL, respectively. From here it follows that

$$R_{\text{FEL}} = -\frac{\ln[1 - Q(\Phi_{\text{FEL}}, h\nu_{\text{FEL}}, \Delta t_{\text{FEL}})]}{\Delta t_{\text{FEL}}}. \quad (3)$$

In Fig. 2, the dependence of the quenching rate on the photon flux Φ_{FEL} is illustrated for FEL set to two different wavelengths. As can be seen, the effect saturates at the FEL-induced additional decay rate of $R_{\text{FEL}} = 8 \times 10^4 \text{ s}^{-1}$; this corresponds to the situation when approximately 35% of the original PL intensity

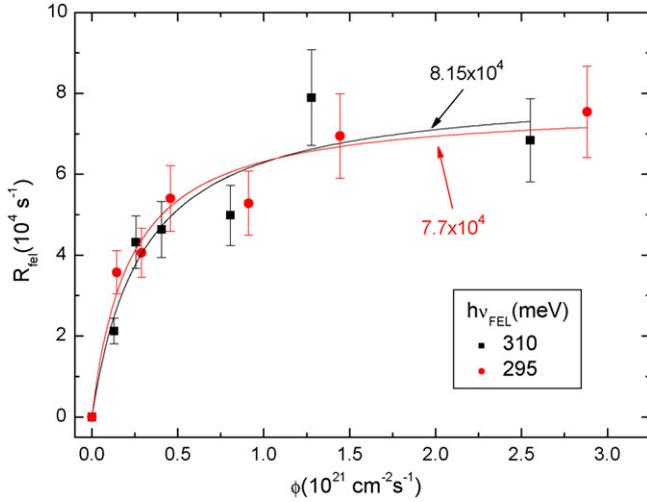


Fig. 2. FEL flux dependence of the quench of Er^{3+} PL at 0.8 eV for various settings of the FEL photon energy. Values indicate the saturation rates as obtained from the fitting to Eq. (9) $T = 4.2$ K.

remains at the end of FEL pulse. From the saturated character, one has to conclude that direct optical energy back-transfer, as was shown for InP:Yb [15], cannot be the cause of the observed PL quenching. In the case of optical back-transfer, the Er^{3+} ion de-excites with an electron-hole pair being formed on the Er-related level. In such a process, however, it should be possible to fully quench the signal, as the quenching effect depends only on the number of excited Er^{3+} ions and the flux. Therefore, the effective decay rate during activation of the FEL is not limited, making it possible to fully quench the signal at high flux, in contrast to the observed saturation.

4. Microscopic model

The microscopic model that explains the observed effects is shown in Fig. 3. We propose that during illumination with the FEL, electrons are ionized from the donor level located at $E_D \approx 225$ meV and brought into the conduction band:

$$\frac{dn}{dt} = C_1 \Phi (N_d^{\text{tot}} - N_d^+ - n) - C_c (N_d^+ + n) n = 0 \quad (5)$$

with N_d^{tot} the total concentration of donors in the system, of which N_d^+ do not have an electron under equilibrium (relaxed) conditions at zero temperature. Some of the donors can be compensated, for example, by acceptors present in the system, increasing the value of N_d^+ . Coefficient C_c denotes the capture coefficient of an electron at the donor level, and C_1 is the cross section for ionization of a filled donor upon application of the FEL beam. Obviously, the parameters C_c and C_1 depend on the specific photon energy to which the FEL beam is tuned. The equation assumes that equilibrium is present during the pulse. The proof that this is indeed the case is given by the experimental observation that the quench saturates with increasing photon flux of the FEL, while no saturation upon an increase of pulse length is observed. Assuming equilibrium, from Eq. (5) we get to the following expression for electron concentration during the

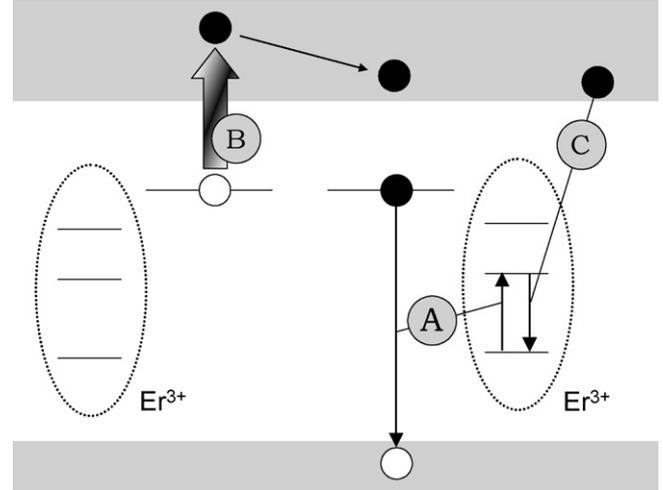


Fig. 3. Microscopic model of quenching of Er^{3+} PL at 0.8 eV observed upon illumination with a FEL. (A) Electron-hole recombination provides the energy needed to excite the Er^{3+} ion to the $^4I_{13/2}$ state. (B) Electrons from the Er-related donor level are ionized by the intense mid-infrared radiation from the FEL. (C) The induced population of electrons in the conduction band reduces the number of excited Er^{3+} ions in an Auger quenching process.

FEL pulse:

$$n(\Phi) = \frac{1}{2} \left[- \left(\frac{C_1}{C_c} \Phi + N_d^+ \right) + \sqrt{\left(\frac{C_1}{C_c} \Phi + N_d^+ \right)^2 + 4 \frac{C_1}{C_c} \Phi (N_d^{\text{tot}} - N_d^+)} \right] \quad (6)$$

As can be expected, for very high flux, this concentration reaches the value $N_d^{\text{tot}} - N_d^+$, which is equal to the total number of donors that have an electron. These free-electrons reduce the excited state population of Er^{3+} by Auger quenching

$$\begin{aligned} \frac{dE_{\text{FEL}}^*}{dt} &= - \frac{E_{\text{FEL}}^*}{\tau_{\text{Er}}} - C_A n(\Phi, t) E_{\text{FEL}}^* \rightarrow E_{\text{FEL}}^* \\ &= E_{\text{FEL}}^*(t=0) \exp\left(\frac{-t}{\tau_{\text{Er}}}\right) \exp\left(-C_A \int_0^t n(\Phi, t) dt\right). \end{aligned} \quad (7)$$

From here we find

$$Q(\Phi_{\text{FEL}}, h\nu, \Delta t_{\text{FEL}}) = 1 - \exp\left(-C_A \int_0^t n(\Phi, t) dt\right), \quad (8)$$

and

$$R_{\text{FEL}} \Delta t_{\text{FEL}} = C_A \int_0^t n(\Phi, t) dt \approx C_A n_{\text{eff}}(\Phi) \Delta t_{\text{FEL}}, \quad (9)$$

where the last step constitutes an approximation of the time-dependent electron concentration by its effective value $n_{\text{eff}}(\Phi)$ for the duration Δt_{FEL} of the FEL pulse. We can see that for our model, the effective quench rate R_{FEL} has approximately a linear dependence on the electron concentration $n_{\text{eff}}(\Phi)$. Therefore, the flux dependencies shown in Fig. 2 can be fitted with the obtained dependence, multiplied with the Auger coefficient C_A

as illustrated by solid lines. We can see that the fits accurately describe the data. The saturation values are also indicated in the figure with arrows, from which it can be concluded that the Er^{3+} quenching by the $5 \mu\text{s}$ illumination with the FEL beam is limited to an effective rate of $R_{\text{FEL}} = 7.7 \div 8.15 \times 10^4 \text{ s}^{-1}$. Following the assumed model, that means that when all the electrons on the donor levels are ionized, the generated population of electron quenches the signal with an effective decay time constant of approximately $12 \mu\text{s}$. Although the exact number of donors with an electron that can be brought to the band is not known, an estimate can be given by fixing the value of the Auger coefficient to $C_A \approx 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, a value often quoted in the literature [16] for free-electron Auger quenching of excited Er^{3+} in Si. With this value, the calculated maximum effective decay rate translates into an electron concentration of approximately $1.6 \times 10^{17} \text{ cm}^{-3}$. This value is similar to the concentration of Er^{3+} ions, which is $2 \times 10^{18} \text{ cm}^{-3}$.

As mentioned in the introduction, it has been shown that oxygen content plays a major role in the ability of an Er ion to form a donor, and a relation between donor and oxygen concentrations has been proposed [2]. From this follows that with an oxygen content of $1.5 \times 10^{19} \text{ cm}^{-3}$, as in the sample under study here, about $4 \times 10^{17} \text{ cm}^{-3}$ Er donors can be formed. This concentration is very close to the number of electrons estimated in our model from the reported PL quenching. Together with the FEL photon energy dependence, this provides a very strong argument that the electrons are indeed originating from the Er-related level formed in the bandgap of Si, because no other impurity in the lattice is present in such a large concentration. Further evidence whether the donor level identified here is also responsible for the indirect excitation of Er^{3+} ions in this material will have to come from excitation spectroscopy [14].

5. Conclusions

We have observed quenching of PL from excited Er^{3+} ions by illumination with mid-infrared radiation in the photon energy range of 240–390 meV. In order to explain the

microscopic mechanism of this effect, it is proposed that this radiation efficiently ionizes the donor level associated with Er in Si. The electrons that are brought to the conduction band in this way quench the excited state PL from Er in a free-electron Auger quenching process. The number of Er-related donor levels was calculated from optical data. Our experiments suggest that the system under investigation is in fact “self-limiting”, with the electrons that are used to quench the Er^{3+} excited state PL possibly originate from the Er-related donor itself.

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