EXCITATION AND DE-EXCITATION OF Yb^{3+} IN InP AND Er^{3+} IN Si: PHOTOLUMINESCENCE AND IMPACT IONIZATION STUDIES

T. GREGORKIEWICZ*, I. TSIMPERIDIS*, C.A.J. AMMERLAAN*, F.P. WIDDERSHOVEN**, AND N.A. SOBOLEV***
*Van der Waals - Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands, tom@phys.uva.nl
** Nederlandse Philips Bedrijven B.V., Prof. Holstlaan 4, NL-5656 AA Eindhoven, The Netherlands
*** Ioffe Physical-Technical Institute, Politechnicheskaya ul. 26, St Petersburg, Russia

ABSTRACT

In the paper the existing information on the optical excitation of the erbium ion in crystalline silicon is critically reviewed. The proposed excitation mechanism is compared to the one which is believed to be responsible for the luminescence of ytterbium in indium phosphide. To this end the influence of constant and microwave electric field on the photoluminescence of both systems is inspected. It is shown that, although both systems show some similarities, their analogy is limited.

The particular role of excitons and electrons in both the excitation as well as the de-excitation mechanism is investigated for the Si:Er system. The results of photoluminescence decay studies (T=4.2 K) are presented. It is argued that a nonradiative energy transfer to conduction electrons is responsible for the limitation of the energy transfer to the Er core and for its nonradiative recombination. Also, a prominent role of excitons in the energy transfer mechanism is confirmed. Finally, the origin of the 873 meV photoluminescence band recently reported in Er-implanted Si is discussed in relation to a possible defect-mediated activation of Er.

INTRODUCTION

Rare Earth Ions in Semiconductors

Rare earth (RE) atoms are characterized by an incompletely filled 4f electron shell. Excited states of this shell give rise to characteristic photoluminescence (PL). Since the 4f shell is well screened from external influence the photoluminescence spectrum shows very little dependence on the host crystal and is very similar to that of a free atom. Because it is due to internal atomic transitions the energy of the PL spectrum is independent of temperature. These characteristic features of their PL make RE's very attractive for practical applications and they stimulated intensive investigations. Most research effort so far has been focused on ytterbium in indium phosphide and erbium in silicon.

The photoluminescence of Yb in InP is relatively best understood. This follows from the fact that the PL spectrum has in this case rather strong intensity and energies which are identical regardless of the sample preparation method or parameters of the matrix; identical spectra have been observed in InP crystals doped during different growth techniques (MOCVD, LPE, high-pressure gradient freeze synthesis), and also in implanted material. The spectrum has been identified with a substitutional Yb^{3+} ion on an In site. However, the precise assignment of individual spectral components to particular transitions between the two lowest manifolds is still not fully resolved [1,2]. It is nevertheless established that the structure of the spectrum is due to the crystal field splitting of the ground and excited states.

In comparison to Yb in InP the understanding of the Si:Er system is still at a lower level. This is somewhat disappointing since the photoluminescence of Er ions implanted in crystalline silicon and related materials (SiO_2, SIPOS, amorphous and porous silicon) is intensively investigated in the prospect of possible applications. This is stimulated by the fact that the sharp, atomic-like emission of Er coincides with the absorption minimum of glass fibers commonly used in telecommunications. The studies on Er-doped silicon form part of a much broader effort aimed at the development of optical devices compatible with the highly successful silicon technology.

Mat. Res. Soc. Symp. Proc. Vol. 422

However, in spite of a continued effort, the intense emission at room temperature has not yet been demonstrated. This is mainly due to the complicated character of energy transfer between the rare-earth ion core and silicon crystal as well as to the forbidden character of the intrashell transition responsible for radiative recombination. In comparison to Yb in InP, the case of Er in Si appears to be more complicated. Although the PL emission always takes place around the 1.6 μm wavelength value the particular spectrum and overall PL efficiency exhibit a clear dependence on the preparation conditions and other defects/dopants simultaneously present in the material. In that situation it has been suggested that Er in Si forms complexes of varying symmetry and atomic composition; each particular complex being characterized by an individual PL spectrum. It has been established that oxygen is especially effective in promoting the Er PL and the formation of Er-O clusters has been postulated.

Excitation and De-excitation Mechanism

As already mentioned before the sharp spectra emitted by RE ions are due to the internal atomic character of involved transitions. This implies that the interaction between the RE core and the host crystal is very weak. As a consequence, the energy transfer between the crystal and RE ion is inefficient. In the case of InP:Yb it is rather generally assumed that the excitation of the core is mediated by a formation of an exciton bound to the RE ion via a local potential. Indeed, various DLTS studies reported on the existence of an Yb-related electron trap, relatively shallow with respect to the conduction band. The core excitation is then accomplished in an Auger process involving the nonradiative recombination of the bound exciton (BE) with a simultaneous energy transfer to an electron localized in the 4f shell, with the energy mismatch of about 100 meV being compensated by phonon emission. In the case of Er in silicon the situation is again more complicated as no states, which could unambiguously be related to Er, have been found in the band gap. Nevertheless, also here evidence for an electron trap has been reported. In contrast to InP:Yb the reported level has a deep character; for the binding energy values as high as 150 meV [3] or 260 meV [4] have been given. Also in this case the postulated energy transfer mechanism involves recombination of an exciton captured at this trap with a simultaneous Auger excitation of a core electron and a phonon-compensated energy difference.

Apart from an indirect, and therefore not very efficient, excitation, the RE PL suffers also from low efficiency. This follows from the fact that the internal 4f transitions are parity-forbidden and become only partially allowed due to crystal-field-induced mixing of the states. Consequently the radiative recombination times should be long. In contrast to that, the experimentally measured low-temperature decay time of Yb PL in InP is only about 10^{-2} ms [5]. For Er PL in Si the decay time at T=4.2 K is approx. 1 ms [6], but decreases quickly for higher temperatures. This effective shortening of the life time is ascribed to an efficient nonradiative de-excitation channel competing with the radiative recombination. As a possible mechanism responsible for this quenching a nonradiative Auger process, involving conduction electrons, has frequently been postulated.

In the studies of RE luminescence in semiconductors various experimental techniques have been used. In this paper we concentrate on the influence of an electric field on the PL spectra of both above discussed systems, and on the decay characteristics of photoluminescence of Er-implanted float zoned silicon (Fz-Si).

PHOTOLUMINESCENCE UNDER APPLICATION OF AN ELECTRIC FIELD

Application of an electric field of moderate amplitude alters the carrier capture rate at impurity centers [7]. The effect is predominantly due to the heating of the electron gas which diminishes the number of low energy electrons at the bottom of the band, which are preferentially being localized by local potentials at impurity/defect sites. The actual magnitude of the lowering of the capture rate is proportional to the effective electron temperature T_e. The heating of the (free) electron gas will take place in a constant (DC) as well as in a microwave electric field. (In the latter case cyclotron resonance might be observed if a magnetic field is simultaneously applied). For stronger electric fields the carrier capture rate will additionally be influenced by another mechanism - the effective lowering of a (Coulombic) potential of a trap due to the so-called *Poole-Frenkel* effect. As a result of both mechanisms, the capture of carriers at shallow traps can be significantly reduced. Such an effect blocks the recombination which proceeds via such traps, effectively enhancing alternative de-excitation paths. For moderate electric fields ($\mathcal{E} \leq 10^2$ V/cm) the increase of the electron temperature usually does not exceed values of approximately 25 K.

Ytterbium in Indium Phosphide

Figure 1 presents a comparison of the behavior of the PL spectrum of Yb-doped InP under the influence of the microwave and DC electric fields.

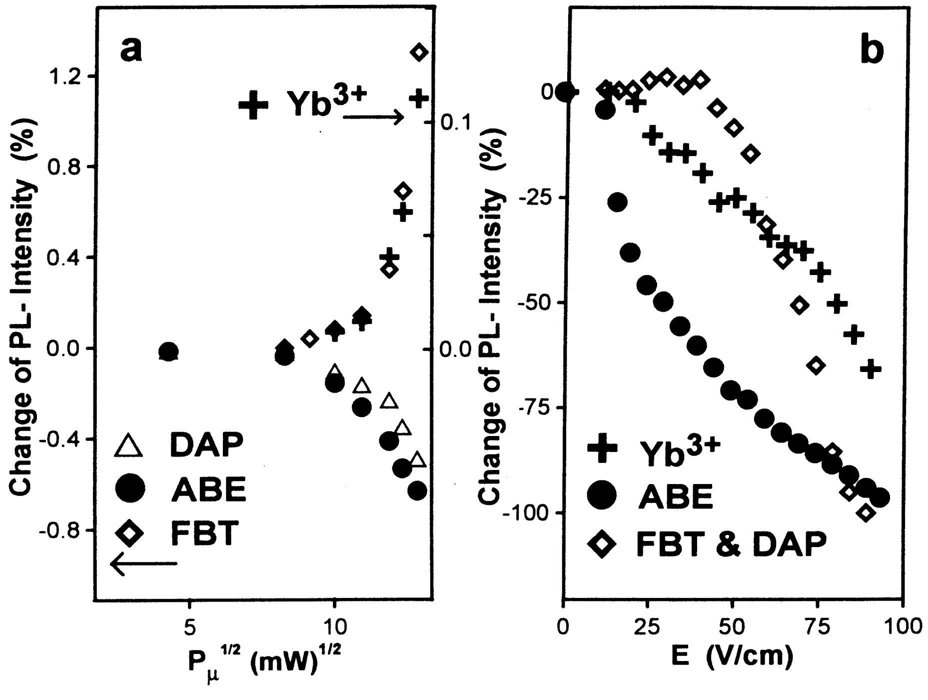

*Figure 1. Relative intensity of PL bands observed in InP:Yb (at LHe temperature) as a function of the microwave (**a**) and the DC (**b**) electric fields. (For the microwave field the square root of the power P_μ is given). The individual behavior for the Yb-related, bound-exciton (ABE), donor-acceptor pair (DAP), and free-to-bound (FTB) recombinations is shown.*

In the experiment the sample was either placed in the microwave cavity (Q band, 35 GHz) with optical access, or metal contacts were made to which the DC voltage could be applied. The measurements were performed at liquid helium (LHe) temperature under an argon laser excitation. Details of the experiment and sample preparation can be found elsewhere [8]. Without the electric field the spectrum was characterized by three PL bands corresponding to bound excitons (ABE), a donor-acceptor pair (DAP) band superimposed with a free-to-bound (FBT) transition to acceptor states, and a characteristic Yb luminescence. As can be concluded from Fig.1a, upon increase of the microwave electric field, (given in the plot as a square root of the microwave power P_μ), the photoluminescence corresponding to band-edge excitons and DAP recombination is quenched. Based on the earlier presented reasoning one can explain it by an increase of the electron temperature which lowers the capture cross section of shallow centers involved in these recombination channels. At the same time the Yb photoluminescence and the FB transition involving acceptor states are enhanced. Such an effect could be an indication that these two recombination channels involve deeper states which are less affected by the microwave heating of the free carriers and are being enhanced at the expense of the shallower ones. In this case there should be a linear correlation between the quenching and the enhancing effects. Careful analysis of the data shows that although the changes are indeed co-linear for small electric field values, they become decoupled as the microwave power increases. Therefore, another mechanism has to be called upon in order to account for the experiment. Such a conclusion is further supported by a similar set of measurements performed on another InP:Yb sample whose PL spectrum consisted of the Yb-related band only. Also in that case the Yb luminescence increased upon application of the microwave field [8]. Since such an increase of Yb-related PL is not accompanied by a simultaneous decrease of any other radiative recombination, the effect must be explained either by a microwave-induced quenching of a nonradiative recombination channel, or by an influence on the Yb PL itself; this could proceed via an increase of the efficiency of the radiative recombination at Yb, or by enhancement of the excitation of Yb core. Although an existence of nonradiative recombination channels, related to shallow levels in the gap of semiconducting host, cannot be excluded, and indeed has been reported for MBE-grown silicon and Si-Ge superlattices [9], it does not appear very likely since i) the effective nonradiative recombination centers usually have midgap levels and, therefore, should be rather insensitive to small variations of the effective electron temperature, and ii) if the microwave-induced quenching of nonradiative recombination was indeed important it should also demonstrate itself in the data depicted in Fig.1, as an increase of all the radiative recombination channels - an effect which is not observed. We conclude therefore that the enhancement of Yb luminescence in the microwave field is independent of other recombination channels available in a particular material and is rather connected to the mechanism of Yb PL itself. In view of the above, a microwave-induced quenching of the nonradiative de-excitation of Yb has been postulated [10].

Fig.1b shows the influence of a DC electric field on the PL spectrum of the same sample for which the effect of the microwave field has been studied. As can be concluded, in this case the behavior of the PL bands is somewhat different. Already a relatively small electric field of approximately 10 V/cm effectively quenches the band-edge exciton PL. This can be explained by an earlier mentioned Poole-Frenkel effect which diminishes the capture cross section for shallow exciton traps. For a somewhat higher value of the electric field, also the Yb band lowers its intensity. At the same time the intensity of the acceptor-related FB transition slightly increases - it can be quenched only for substantial electric fields, most probably as an effect of the free carrier sweeping. The similar behavior of the Yb-related and the band-edge exciton PL bands, as evidenced by the presented DC field dependence of the PL spectrum, is consistent with the excitonic mechanism of Yb photoluminescence. As mentioned in the introduction, the existence of a BE state in the excitation scheme of Yb in InP has been postulated but its actual fingerprint could not be given until now. The current results also show that the local potential, that binds an exciton to an ytterbium ion, is not very deep; it can be influenced by an electric field of approximately 20 V/cm. It remains, however, unaffected by microwave-induced carrier heating.

Er in Silicon

The influence of a microwave field on the photoluminescence of erbium in silicon has been reported in the past [11]. The effect is illustrated in Fig.2, where the spectral dependence of the Er-doped (Czochralski-grown) silicon PL under application of a microwave field is depicted. (For details on sample preparation see Ref.[11]). As can be seen, the microwave field quenches the intensity of the band-edge-exciton-related PL and simultaneously enhances the Er band. While the first effect can again be explained by a reduction of the capture coefficient of shallow exciton traps upon increase of the free carrier temperature, the origin of the enhancement of the Er PL is more difficult to account for. Possible explanations include the decrease of a nonradiative quenching of the excited erbium ions [11] and an increased efficiency of the Er core excitation upon carrier heating [12].

Fig.3 shows the influence of the DC electric field application on the photoluminescence of Er. The effect is in this case remarkably different from that discussed in the preceding paragraph for

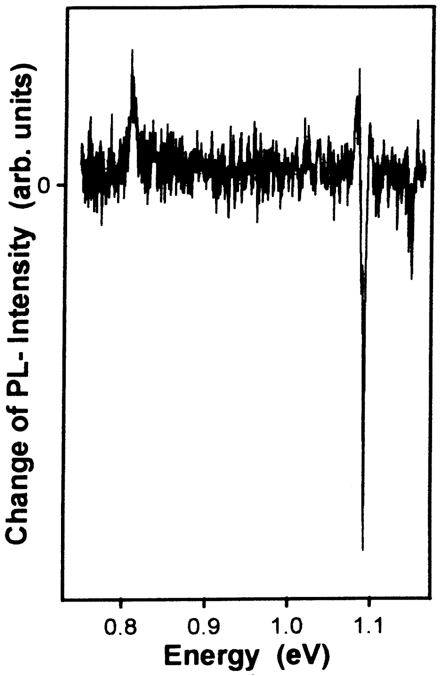

Figure 2. Spectral dependence of the microwave induced changes of the PL spectrum of Er implanted Cz-Si. The microwave power is 200 mW, T=1.8 K.

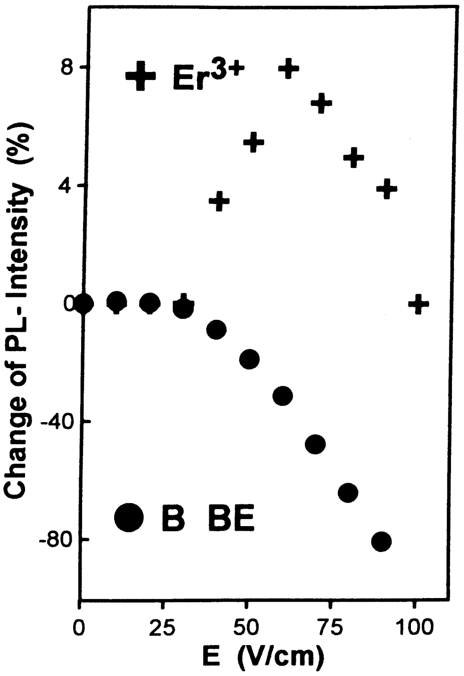

Figure 3. Relative intensity of PL spectrum in Si:Er as a function of DC electric field. The experimental data for the Er-related and boron BE PL bands are given.(Note change of scale)

InP:Yb. While the excitonic PL band is quenched for electric fields $\mathcal{E} > 30$ V/cm, the erbium PL does not follow this behavior; in contrast to the results for Yb in InP the intensity of Er PL band starts to increase its intensity for the same field value. This strongly suggests that both processes are correlated. The observed effect illustrates the importance of deep electron trap in the Er excitation scheme [3]. We can rationalize the observed field dependence of Er PL by assuming that the Poole-Frenkel effect diminishes capture at shallow traps which, in turn, leads to a lower BE recombination rate. Consequently, this effect will increase the free electron concentration and promote their capture by deep traps, and among them also at an Er-related level. The existence of this trap has been postulated from the DLTS measurements [4] and from the temperature dependence of erbium PL intensity. The observed increase of the intensity of Er PL could alternatively be explained by an increase of its radiative efficiency. However, this possibility has been ruled out experimentally by showing that the decay time of Er PL does not change upon the application of the DC electric fields up to 50 V/cm. As will be discussed in the next section, such a result means that the nonradiative recombination of excited Er atoms, (which strongly competes with the radiative de-excitation), cannot be affected by an application of electric fields.

Finally, it should be mentioned that special care must be taken when comparing results obtained for constant electric fields with those for microwave fields. Similarly to the case of the resistivity measurements, one should keep in mind that for highly nonhomogeneous samples both methods can yield very different results: the microwave field will heat carriers available in the more conductive parts of the sample where the DC potential will be negligible. In contrast to that, the DC potential will be effectively applied only to the resistive parts of the material and will be short-circuited for the regions of low resistivity. It can therefore happen that, for a very inhomogeneous material, different parts of the sample will contribute to the PL spectrum measured under application of the DC and microwave electric fields.

MEASUREMENTS OF PHOTOLUMINESCENCE DECAY TIME FOR Er IN Si

Role of Electrons in the Photoluminescence Mechanism

As can be concluded from the electric field measurements presented in the preceding section, electron capture at a relatively deep level plays an important role in the luminescence of Er in Si. In a recent contribution [3] it is argued that the temperature dependence of the electron capture rate at Er-related trap at approximately 150 meV below the bottom of the conduction band (CB) determines thermal quenching of Er photoluminescence for the higher temperature range T > 70 K. For lower temperatures, the thermal dependence of Er PL is reported to be governed by a process with an activation energy of 10-15 meV [13-15], i.e. similar to the dissociation energy of excitons. Also the power dependence of Er PL confirms the prominent role of excitons in the activation of erbium atoms [16].

On the other hand more evidence is being gathered that CB electrons have also a prominent role in limiting the efficiency of Er PL. In a model likely to account for the kinetics of Er photoluminescence the interaction with free electrons in CB limits the energy transfer to the erbium core, and also provides a nonradiative way of de-excitation of Er, alternative to the radiative recombination. The second process shortens the effective life time of the excited state of Er atoms and thus influences a parameter which can be directly measured in an experiment.

In a probable description of the kinetics of Er PL in silicon [17] it is assumed that the 4f-shell is excited by recombination of a bound exciton system which is formed via free excitons generated upon laser illumination. However, the nonradiative energy transfer between an exciton bound at the Er-related trap and the 4f-shell is hampered by an alternative de-excitation route involving an energy transfer to electrons in CB. Also for an excited Er atom (at least) two recombination paths exist; a radiative one giving rise to the characteristic PL band at 1.6 μm, and a nonradiative one based on an Auger mechanism involving again the energy transfer to CB electrons. A relevant set of rate equations comprises then:

$$\frac{d}{dt}n = I\sigma - \alpha n^2 \ , \tag{1}$$

$$\frac{d}{dt}N^{ex} = \alpha n^2 - \frac{N^{ex}}{\tau_{eff}^{ex}} \ , \tag{2}$$

$$\frac{d}{dt}N^* = \frac{N^{ex}}{\tau_{TR}} - \frac{N^*}{\tau_{eff}^{Er}} \ , \tag{3}$$

where Iσ corresponds to the generation rate and is proportional to the laser power density, α is a coefficient describing exciton formation at the expense of free electrons and holes, and N^{ex} and N^* are concentrations of excitons mediating Er excitation and excited Er atoms, respectively. Further, τ_{eff}^{ex} and τ_{eff}^{Er} are effective life times of Er-trapped excitons and excited Er atoms, respectively. In such a scheme equations 1, 2, and 3 describe the time dependence of the concentrations of free carriers, excitons capable of transferring their energy to Er atoms, and excited Er atoms capable of luminescence, respectively. In the process description given by the above equations several simplifications, in respect to the real situation, have been included. The most important here are the assumptions that i) the laser energy absorbed by the crystal is mainly converted into exciton generation, that ii) the energy transfer to erbium is not saturated (i.e. the concentration of excited Er atoms is much smaller than that of the "excitable" ones and therefore does not limit the energy transfer process), and that iii) all the generated (free) excitons can transfer their energy to Er core. The last assumption means that an important step in the excitation scheme - a transformation from free excitons (FE) to Er BE system - is not explicitly included. To a certain extent the fact that not all the generated free excitons will be bound at Er-related traps can be incorporated in the exciton generation constant α, but in this way the influence of the Er atom itself on the capture of an exciton cannot be accounted for. Both effective life times can be seen as superpositions of 2 independent components corresponding to alternative decay mechanisms:

$$\frac{1}{\tau_{eff}^{ex}} = \frac{1}{\tau_{TR}} + \frac{1}{\tau_{A1}} = \frac{1}{\tau_{TR}} + c_{A1}n \ , \tag{4}$$

$$\frac{1}{\tau_{eff}^{Er}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}} = \frac{1}{\tau_R} + c_{A2}n \ , \tag{5}$$

where τ_{TR} is the time constant characteristic for the energy transfer between the BE and Er core, τ_R is the radiative recombination time of excited Er atoms, and $\tau_{A1} = (c_{A1}n)^{-1}$ and $\tau_{NR} = (c_{A2}n)^{-1}$ are the nonradiative recombination time constants describing the Auger energy transfer to CB electrons from Er BE and excited Er core, respectively. The observed Er-related PL intensity will then be proportional to the concentration of the excited erbium atoms N^* and their radiative life time:

$$I_{PL} \propto \frac{N^*}{\tau_R} \ . \tag{6}$$

PL Decay Measurements

Upon a steady excitation level equilibrium concentrations of electrons n_0, excitons $(N^{ex})^0$, and excited erbium atoms $(N^*)^0$ will be reached. These will lead to particular values of both effective life times τ_{eff}^{ex} and τ_{eff}^{Er} and of PL intensity. When the excitation is terminated, the equilibrium concentrations will decay with their kinetics determined by the rate equations (1-3). The fastest decay will be that of excess electrons in the conduction band. When n has been annulled then, following Eq.(2), we can write:

$$\frac{d}{dt}N^{ex} = \alpha n^2 - \frac{N^{ex}}{\tau_{eff}^{ex}} = -\frac{N^{ex}}{\tau_{TR}} \ . \tag{7}$$

As a solution we get an exponential decay of the exciton concentration, with the decay time being now the transfer time τ_{TR}:

$$N^{ex} = (N^{ex})^0 exp(-\frac{t}{\tau_{TR}}) \ . \tag{8}$$

(In view of a very short life time of excess electrons n we have assumed here the equilibrium exciton concentration $(N^{ex})^0$ as the initial value of the decay). The onset of the exponential decay of Er-bound excitons will coincide with the beginning of the decay of boron-bound excitons which could be observed experimentally in the same sample. The exponential decay of the excitons will lead also to the decay of the concentration of excited erbium atoms. Following Eq.(3) this process, which determines the decay of the Er-related PL, can be described by:

$$\frac{d}{dt}N^* = \frac{(N^{ex})^0}{\tau_{TR}} exp\left(-\frac{t}{\tau_{TR}}\right) - \frac{N^*}{\tau_R} \ . \tag{9}$$

The first term gives here an increase of the concentration of the excited Er atoms due to the energy transfer from bound excitons, and the second one corresponds to their radiative decay. (Since the excess electron concentration $n = 0$ the nonradiative decay of Er is no longer possible and $\tau_{eff}^{Er} = \tau_R$). Solving the above equation we get:

$$N^*(t) = \frac{(N^*)^0}{\tau_R - \tau_{TR}} \left\{\tau_R exp\left(-\frac{t}{\tau_R}\right) - \tau_{TR} exp\left(-\frac{t}{\tau_{TR}}\right)\right\} \ . \tag{10}$$

(Here again we have neglected the decrease of N^* during the decay of excess electrons). The photoluminescence decay will then be given as:

$$I_{PL}(t) \propto \frac{1}{\tau_R} N^*(t) = \frac{(N^*)^0}{\tau_R(\tau_R - \tau_{TR})} \left\{ \tau_R exp\left(-\frac{t}{\tau_R}\right) - \tau_{TR} exp\left(-\frac{t}{\tau_{TR}}\right) \right\} \ . \tag{11}$$

The above formula describes the decay of the erbium-related photoluminescence when the excitation source is turned off and when the excess electrons are no longer present in the sample. In terms of an experiment it should describe the decay curve starting from the moment determined by the onset of boron BE luminescence decay. Since the Er radiative recombination time τ_R is of an order of milliseconds and therefore longer than the excitation transfer time τ_{TR}, it will govern the PL decay in its later phase. However, in the initial part also the second exponential term will be important and will lead to a relatively slow change of the Er photoluminescence intensity. This follows from the fact that, although no new Er-bound excitons are being generated, the ones already existing in the crystal continue to excite Er, while their effective life time is considerably increased, since the excess carriers concentration diminished and the energy transfer to CB is no longer possible. Therefore the exponential decay of Er PL will start with some time delay whose magnitude is related to the ratio between the radiative recombination time τ_R and excitation time τ_{TR}. Such an effect has been observed experimentally before [18] and is consistent with the intensity behavior described by Eq.(11).

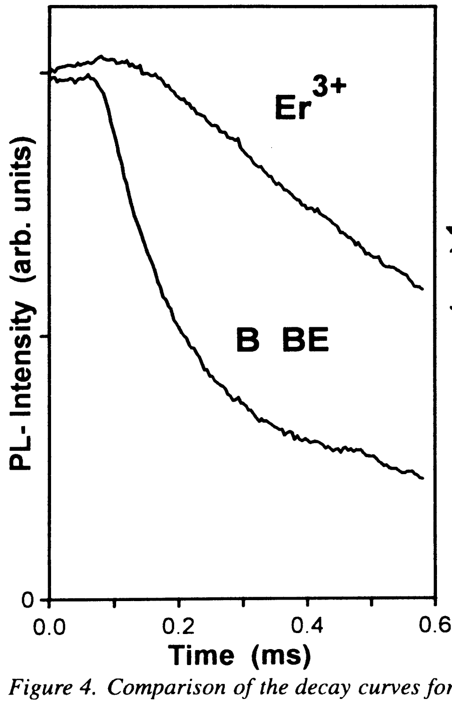

Figure 4. Comparison of the decay curves for Er-related and boron BE PL bands measured in the same sample; for Er $\tau \approx 900\mu s$, T=4.2 K.

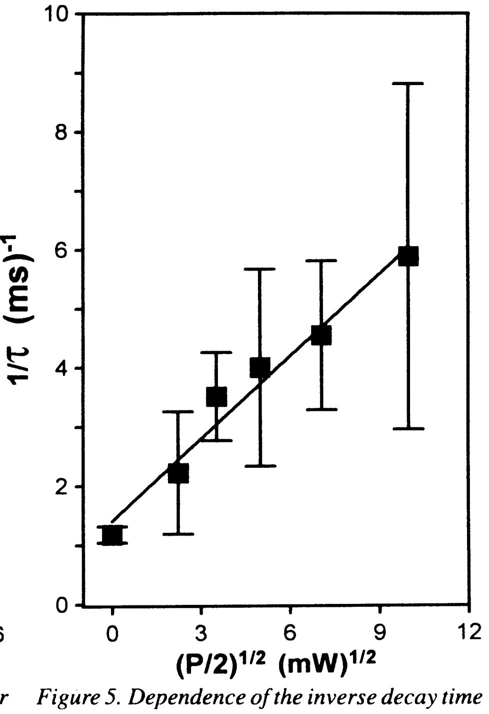

Figure 5. Dependence of the inverse decay time on the square root of the background excitation power for Si:Er. For details see text.

Fig.4 shows the decay of Er and boron BE luminescence as measured under on/off modulated laser power of 100 mW at LHe temperature. The material used for the decay measurements was

Fz-Si, implanted (1100 keV) at a temperature of 500°C to a dose of 10^{14} Er/cm^2 - for details see Ref.[4]. The decay time, as determined from the depicted measurement, is approximately $\tau \approx 900\mu$s. Also a considerable delay in an onset of the Er decay curve, when compared to that of boron BE, can be seen. (In view of an extremely short life time of BE in Si, the depicted decay curve for B BE is illustrative for the response time of the experimental setup; all the measurements performed in this study concern decay constants which are clearly longer than the response time). As discussed before, the magnitude of the delay is related to the excitation transfer time τ_{TR}. Based on the presented measurement its value can be estimated as $\tau_{TR} \approx 50\mu s$. This is an order of magnitude more than the estimation given in Ref.[17]. We should, however, bear in mind that in Ref.[17] an oxygen-rich material was investigated, while the PL decay results presented here have been obtained for float-zone (FZ), oxygen-lean samples, where the energy transfer to Er is known to be more difficult.

In order to investigate the influence of conduction electrons on the mechanism of Er photoluminescence we followed changes of PL decay characteristics in an experiment where the excitation laser beam was modulated to approximately 50% of its intensity, instead of the normally applied on/off chopping. This was accomplished by the use of a chopper blade made of a partially transparent material. In its concept such a measurement is similar to the two-beam experiment described in Ref.[15]. Under conditions of the partially, low-frequency modulated excitation the intensity of the photoluminescence spectrum will alternate between equilibrium values determined by laser power levels corresponding to 100% and 50% of the set value. Fig.5 shows the effective time constant of the intensity decay from the higher to the lower equilibrium levels as a function of the laser power applied during the decay, i.e. 50% of the nominal laser power P. The time constants given in the plot were always determined for the "later" part of the decay curve. According to the earlier presented description, for the partially modulated excitation, the effective decay time τ_{eff}^{Er} will be given by Eq.(5), where the excess carrier concentration n is now a steady, time-independent value corresponding to the equilibrium value for the laser excitation at half power P/2:

$$\frac{1}{\tau_{eff}^{Er}} = \frac{1}{\tau_R} + f\left(\frac{P}{2}\right) . \tag{12}$$

It should be noted that all the measurements depicted in Fig.5 were taken outside the saturation range, i.e. for the region where PL intensity is linearly proportional to excitation power, and which is well described by the rate equations set (1-3). As can be seen from the figure, the experimental data are linear in respect to the square root rather than to the full background excitation power level and could be fitted with the formula:

$$\frac{1}{\tau_{eff}} = A + B\sqrt{\frac{P}{2}} . \tag{13}$$

We conclude therefore that the equilibrium concentration n of the excess carriers is governed by the relaxation mechanism proportional to n^2. Such a result confirms the prominent role of exciton generation in the mechanism of Er luminescence in silicon. At the same time the observed data directly indicate a strong influence of the free carriers concentration n on the effective life time of the excited Er atom. This conclusion is evident when one compares the photoluminescence decay measured under on/off and partially modulated excitation.

In Fig.6 the decay of Er PL upon laser excitation of 25 mW is compared for the standard on/off and the partial modulation. In this case the zero on the time scale corresponds to the onset of the boron BE decay. The upper curve, taken without the background excitation, is characterized by a long delay of approximately $\tau_d \approx 80\mu$s, followed by a slow decay corresponding to the life time $\tau \approx 800\mu$s. The lower curve, which shows the decay under the background illumination corresponding to 12.5 mW, shows practically no delay ($\tau_d < 20\mu$s), and is characterized by an almost 3 times faster decay $\tau \approx 300\mu$s. This dramatic shortening of the effective life time of the excited Er under background illumination confirms the important role of carriers in the de-excitation process and is consistent with the assumed nonradiative quenching of Er PL. As discussed before, a delay in the photoluminescence decay curve is due to the excitons, bound at Er-related trap,

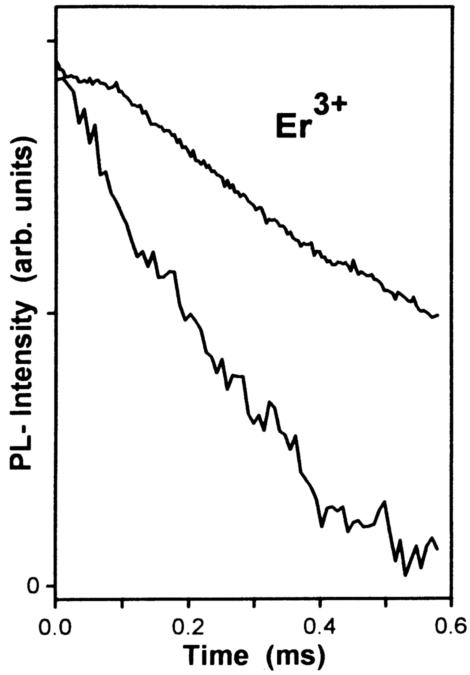

Figure 6. Decay of Er-related PL without - upper curve, $\tau \approx 800\mu s$, and with background excitation - lower curve, $\tau \approx 300\mu s$, T=4.2 K.

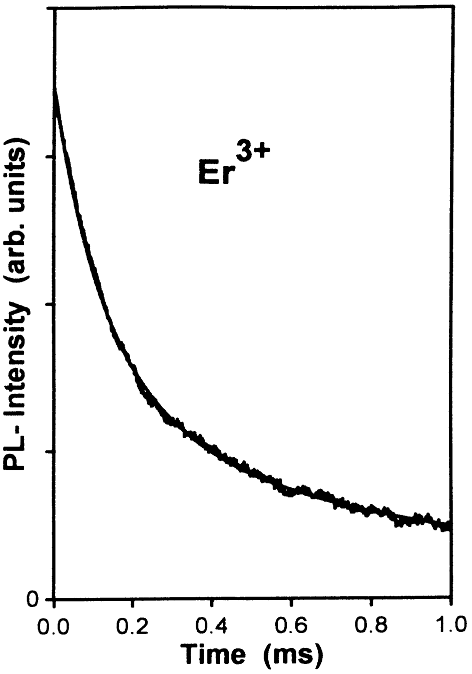

Figure 7. PL decay of Si:Er under 50 mW argon laser excitation, T=4.2 K. For details of the fit - see text.

which continue to excite the Er core when the laser power is reduced, and is therefore linked to the effective life time of these states. The evident reduction of the delay time τ_d shows the involvement of CB electrons in the quenching of the Er-related BE state. In this way the results presented here give an experimental confirmation of the free carrier quenching of the excitonic state intermediating Er luminescence. We can therefore conclude from our experiment that free carriers indeed limit both: the energy transfer to the Er core as well as its subsequent radiative recombination. This conclusion supports therefore the important role of these two processes as assumed in the rate equations Eqs.(1-3).

Fig.7 presents the Er PL decay as measured for an on/off modulated argon laser excitation (nominal power 50 mW). The experimental data can be fitted as a superposition of two exponential curves: a faster one with $\tau_1 \approx 500\ \mu s$ and a slower one with $\tau_2 \approx 2$ms. The coexistence of a fast and a slow components in the Er decay curve was observed before in oxygen-rich material [19] and attributed to two different Er-related centers. Here we report a similar effect also for Er-implanted FZ silicon. The data presented in Fig.7 could be alternatively fitted when we assumed that excited Er atoms could also transfer their energy to another center whose concentration diminished exponentially with time. In this case the PL decay would be described with the pseudo-exponential decay characterized by an effective life time τ_{eff}^{Er} given as:

$$\frac{1}{\tau_{eff}^{Er}} = \frac{1}{\tau_R} + cN_x exp\left(-\frac{t}{\tau_x}\right) , \tag{14}$$

where c is the coupling constant, and N_x and τ_x initial concentration and life time of the deactivator, respectively. Using Eq.(14) a good fit to the experiment could be obtained yielding in that case both time constants of approx. 2 ms. Further studies are necessary to explore which of the alternative descriptions is more adequate.

POSSIBLE DEFECT-RELATED EXCITATION OF Er PL IN Si

We finally turn our attention to the 873 meV band reported recently in Er-implanted Cz-Si annealed briefly at 1100°C temperature [20,11]. We note that, in a sample where the intensity of this band is big - see Fig.8, the width of the PL line appearing in the region of Er luminescence is increased and its maximum is shifted toward higher energies. The positions of both, very strong in this case, PL bands coincide nearly precisely with the D1 and D2 lines reported earlier in silicon annealed under stress and identified with dislocations [21]. The same lines were later detected also in laser-annealed ion-implanted silicon [22]. In this situation an interesting question arises whether the PL bands depicted in Fig.8 are related to Er, as expected from the sample preparation conditions and supported by an appearance of a band, which certainly overlaps with the PL spectrum usually assigned to Er, or to defects, as suggested by a close coincidence of their energies. In an attempt to solve that dilemma we studied the temperature dependence of the intensity of the spectrum and this turned out to be different from the one reported for D-lines [23]. Also the saturation behavior of both lines is puzzling - upon increased excitation power a strong asymmetric broadening on the high energy side develops for both lines. Such a behavior is characteristic for free-to-bound transitions and is difficult to reconcile with the intrashell character of Er luminescence, but also with the reported bound-to-bound character of the D1 line [22]. One cannot, however, exclude that a rapid annealing of heavily (Er) implanted material could result in formation of dislocations in the subsurface Er-rich layer. In such a case the close coincidence of the energy of D1 line with that of the 4f-shell transitions of Er^{3+} could offer a defect-related channel of a near-resonant transfer of energy to and from the Er core. This interesting situation clearly requires further studies. Even more so, since the 873 meV energy of the D2 line again coincides rather perfectly with one of the transitions for the $4f^{12}$ configuration of the Er^{2+} ion.

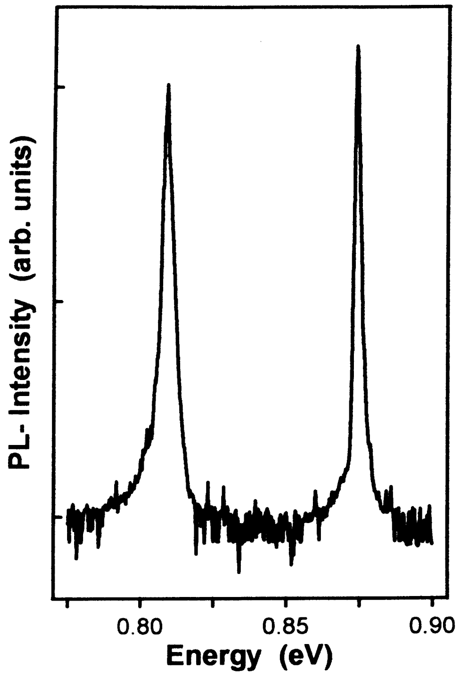

Figure 8. PL spectrum observed in Er implanted Cz-Si, annealed briefly at 1100°C, T=4.2 K.

CONCLUSIONS

By investigating the influence of an electric field on the PL spectrum of Yb in InP we confirmed the excitonic character of its generation and found evidence for dissociation of the Yb BE system. Similar measurements for Si:Er show importance of a deep trap in the excitation scheme. By studying the photoluminescence decay of this system we could give experimental fingerprint of excess carrier-related processes limiting the energy transfer to the Er core and its subsequent radiative recombination.

ACKNOWLEDGMENTS

The authors would like to thank E.O. Parshin and E.I. Shek for their help in preparing the samples. This project was partially sponsored by the Netherlands Foundation for Fundamental Research on Matter [Stichting voor Fundamenteel Onderzoek der Materie (FOM)] and Russian Fund for Fundamental Research (grant 96-02-17901a).

REFERENCES

1. G. Aszodi, J. Weber, Ch. Uihlein, L. Pu-lin, H. Ennen, U. Kaufmann, J. Schneider, and J. Windscheif, Phys. Rev. B**31**, 7767 (1985).
2. I. de Maat–Gersdorf, T. Gregorkiewicz, C.A.J. Ammerlaan, P.C.M. Christianen, and J.C. Maan, proceedings of this symposium.
3. F. Priolo, G. Franzò, S. Coffa, A. Polman, S. Libertino, R. Barklie, and D. Carey, J. Appl. Phys. **78**, 3874 (1995).
4 F.P. Widdershoven and J.P.M. Naus, Mat. Sci. Eng. B**4**, 71 (1989).
5. P.B. Klein, Solid State Commun. **65**, 1097 (1988).
6. G.N. van den Hoven, J.H. Shin, A. Polman, S. Lombardo, and S.V. Campisano, J. Appl. Phys. **78**, 2642 (1995).
7. V.N. Abakumov, V.I. Perel, and I.N. Yassievich in Nonradiative Recombination in Semiconductors, Modern Problems in Condensed Matter Science **33**, edited by V.M. Agranovich and A.A. Maradudin, Elsevier Science Publishers B.V., Amsterdam 1991, pp. 172-188.
8. I. Tsimperidis, T. Gregorkiewicz, C.A.J. Ammerlaan, M. Godlewski, F. Scholz, and B. Lambert, J. Appl. Phys. **77**, 1523 (1995); I. Tsimperidis, T. Gregorkiewicz, and C.A.J. Ammerlaan, to be published.
9. W. M. Chen, I.A. Buyanova, A. Henry, W.-X. Ni, G.V. Hansson, and B. Monemar, Mat. Sci. Forum **196-201**, 473 (1995).
10. T. Gregorkiewicz, B.J. Heijmink Liesert, I. Tsimperidis, I. de Maat–Gersdorf, C.A.J. Ammerlaan, M. Godlewski, and F. Scholz in Rare Earth Doped Semiconductors, edited by G.S. Pomrenke, P.B. Klein, and D.W. Langer (Mater. Res. Soc. Proc. 301, Pittsburgh, PA 1993), pp. 239-250.
11. I. Tsimperidis, T. Gregorkiewicz, and C.A.J. Ammerlaan, Mat. Sci. Forum **196-201**, 591 (1995).
12. M.S. Bresler, O.B. Gusev, I.N. Yassievich, and B.P. Zakharchenya, to be appear in Solid State (Fizika Tverdogo Tela 38, 5 (1996).
13. D.T. Xuan Thao, T. Gregorkiewicz, and C.A.J. Ammerlaan, to be published.
14. E. Efeoglu, J.H. Evans, T,E. Jackman, B. Hamilton, D.C. Houghton, J.M. Langer, A.R. Peaker, D. Perovic, J. Poole, N. Ravel, P. Hemment, and C.W. Chan, Semicond. Sci. Technol. **8**, 236 (1993).
15. J. Michel, J. Palm, F. Gan, F.Y.G. Ren, B. Zheng, S.T. Dunham, and L.C. Kimerling, Mat. Sci. Forum **196-201**, 585 (1995).
16. M.S. Bresler, O.B. Gusev, M.I. Macoviichuk, P.E. Pak, E.O. Parshin, E.I. Shek, N.A. Sobolev, I.N. Yassievich, and B.P. Zakharchenya in Tenth Feofilov Symposium on Spectroscopy of Crystals Activated by Rare-Earth and Transitional-Metals Ions, edited by A. Ryskin and V.F. Masterov, Proc. SPIE 2706, pp. 31-37 (1996).
17. J. Palm, F. Gan, and L.C. Kimerling in - see Ref.[16].
18. Jung H. Shin, G.N. van den Hoven, and A. Polman, Appl. Phys. Lett. **67**, 377 (1995).
19. S. Coffa, G. Franzò, F. Priolo, A. Polman, and R. Serna, Phys. Rev. B **49**, 16313 (1994).
20. N.A. Sobolev, O.V. Alexandrov, M.S. Bresler, O.B. Gusev, E.I. Shek, M.I. Makoviichuk, and E.O. Parshin, Mat. Sci. Forum **196-201**, 597 (1995).
21. N.A. Drozdov, A.A. Patrin, V.D. Tkachev, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 651 (1976); Sov. Phys. JETP Lett. **23**, 597 (1976).
22. R.H. Vebbing, P. Wagner, H. Baumgart, and H.J. Queisser, Appl. Phys. Lett. **37**, 1078 (1980).
23. R. Sauer, J. Weber, J. Stolz, E.R. Weber, K.-H. Küsters, and H. Alexander, Appl. Phys. A**36**, 1 (1985).