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PHOTOLUMINESCENCE STUDY OF ERBIUM IN SILICON WITH A FREE-ELECTRON LASER

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Abstract The influence of intense infrared (IR) radiation in the range 7–17 μm on the photoluminescence (PL) of erbium in silicon has been investigated. To excite the PL a pulsed Nd:YAG laser operating in the visible with a wavelength of 532 nm has been used. The infrared beam was generated by a free-electron laser. In the experiment the intensity and decay kinetics of the low-temperature PL of Er-doped silicon were monitored as a function of the wavelength of the quenching beam and its delay with respect to the excitation pulse of the visible-light laser. The experiments show quenching of the PL by the IR pulse only at delays shorter than approximately 250 μs. The result is interpreted as dissociation of the Er-related bound-exciton (BE) state whose effective lifetime is then estimated as approximately 100 μs. A special quenching feature for $\lambda \approx 12.5$ μm is detected indicating a possible "back-transfer" mechanism involving the excited Er state. For still longer delay times a small transient increase of Er PL is observed.

Introduction

The presence of an incompletely filled 4f shell distinguishes rare earth (RE) atoms from other elements. The spin-orbit interaction within this shell gives rise to a very characteristic splitting of the energy levels which can be experimentally observed in photoluminescence due to transitions between the (lowest) excited and the ground states. When placed within a solid the emissions can further be influenced by the local crystal field; this effect is, however, usually small due to screening of the 4f electron shell. Consequently, the PL spectrum of a RE dopant is very similar to that of a free atom, with rather narrow lines and a very limited dependence on the host crystal. Further, being due to internal atomic transitions, the emissions have a temperature-stable wavelength. These characteristic features make RE's very attractive for practical applications and they stimulated intensive investigations. In case of the erbium-in-silicon system the interest is fortified by potential applications as the sharp, atomic-like emission of Er coincides with the absorption minimum of glass fibers commonly used in telecommunications. Currently Er doping of silicon is among the most promising approaches to photonics of this basic electronic material.

However, the successful development of Er-based optical silicon devices requires high-efficiency emission at room temperature. In order to achieve that, mechanisms responsible for the excitation of the intrashell and its recombinations (both radiative and non-radiative) have to be thoroughly understood [1]. Here especially the energy transfer between the silicon host and the Er core appears complex, since the Er atom, which embedded in Si assumes an Er^{3+} charge state, most probably does not introduce any energy levels in the bandgap. Based on numerous experimental and theoretical studies [2] an energy transfer mechanism has been proposed which involves creation of an intermediate state when an exciton becomes bound to an Er ion by a local potential [3]. The properties of this state, such as its lifetime and generation and recombination paths, are crucial for the Er excitation process and govern the PL intensity. Following exciton localization the core excitation is then accomplished in an Auger process involving the nonradiative recombination of the bound

exciton with a simultaneous energy transfer to an electron localized in the 4f shell and compensation of (a possible) energy mismatch. The efficiency of this indirect energy transfer is additionally hampered by an alternative quenching of the BE system. A low PL intensity follows further from the fact that the internal 4f transitions are parity-forbidden and become only partially allowed due to crystal-field-induced mixing of states. Consequently, the radiative recombination time is long. The decay time is effectively shortened by 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 been suggested. Due to the low probability of the radiative recombination the PL efficiency is additionally hampered by the so-called "back-transfer" process reversing the excitation by regeneration of the intermediate BE state.

In the current study we probe the PL mechanism of Er in Si with intense far-infrared radiation provided by a free-electron laser. In view of the complex character of the energy transfer mechanism one might expect that different stages of this process may be influenced. In particular, this novel approach could reveal information on the so-far experimentally inaccessible intermediate BE state and on the back-transfer process.

Experimental conditions

The experiments were performed at the FOM Institute for Plasma Physics "Rijnhuizen".

Two excitation sources have been used. The PL spectrum was generated by a pulsed Nd:YAG laser operating at λ=1064 nm, with a pulse duration of approximately 7 ns and a repetition rate of 5 Hz. The pulse was passed through a second-harmonic generator; consequently the sample was exposed to the green laser beam of 532 nm. In the experiment the averaged excitation power level was kept below $\approx$20 μW. In addition to this over-the-bandgap excitation the infrared probing beam has been applied. This was provided by the Free Electron Laser for Infrared Experiments (FELIX) at Rijnhuizen. The FELIX delivers so-called "macropulses" with a length of 5-10 μs at a maximum repetition rate of 10 Hz. Each macropulse consists of a train of "micropulses" with a spacing that can be either 1 or 40 ns (1 GHz or 25 MHz operation mode). In the study a 40 ns micropulse-spacing was used with the macropulse length of approximately 7 μs and a micropulse width of 1.7 ps. It is estimated that the energy in each micropulse is 1.7 μJ. The sample was mounted inside a variable temperature cryostat operated within a 4-40 K range and with a stability of $\pm$0.1 K. In the infrared beam a cut-off 7.2 μm filter has been used in order to block the shorter wavelengths present due to the generation of higher harmonics. Both laser beams were coincident on the sample. The emerging PL was collected from the laser-irradiated surface and passed through a band pass filter centered for λ=1548.8 nm and with a bandwidth of 20 nm. The PL has been detected by a germanium detector. The signals were then amplified and analyzed by a digital oscilloscope. The experimentally detected response of the system was 5μs on the rising slope and 75 μs for the decay time. We note that in a chosen experimental configuration the measured signal corresponds to the total emission integrated over the filtering range. Therefore the information contained in the form of the spectrum, e.g., individual spectral lines, is not accessible. The decision to use the band-pass filter rather than a monochromator was necessary in order to achieve a satisfactory signal-to-noise ratio.

The sample used in the experiment was prepared from <100>-oriented, n-type, phosphorus-doped float-zoned silicon, with a donor concentration of approximately 6×10^{15} cm^{-3} and a room-temperature resistivity between 0.7 and 0.9 Ωcm. It has been implanted with Er^{2+} ions to a dose of 10^{13} cm^{-2} with an energy of 1100 keV. The implantation has been performed at a temperature of approximately 500 °C; no further heat-treatment has been given.

Experimental results and discussion

A. Preliminaries

In the past the PL of the Si:Er system has been intensively investigated. In order to study the de-excitation mechanism the decay characteristics as well as the temperature quenching of the PL intensity and decay time are usually investigated [3,4]. The results reveal that the temperature dependencies are governed by a set of activation energies; their particular values appear to be different in FZ- and Cz-grown Si. These differences are especially evident for the quenching processes which become important at an elevated temperature and are characterized by activation energies in the 100–150 meV range. For the identification of the particular mechanism responsible for this process two

possibilities are currently considered: the ionization of an electron at the Er-related trap [5], and the already mentioned back-transfer process. Regardless of the actual mechanism it is evident that this activation energy value contains information on a most characteristic step in the energy transfer mechanism between the silicon crystal and the Er core. Unfortunately, in the temperature range where this quenching process is important the PL intensity is already very low and, consequently, this informative parameter is poorly determined. In the current experiment the IR pulse provides the possibility to induce the back-transfer process at low temperature, i.e., for high intensity of the PL emission.

Preliminary to the current experiments the temperature dependence of the PL intensity of the sample has been measured. It was found to be controlled by two activation energies: $E_1 \approx 15$ meV and $E_2 \approx 110$ meV [6]. Also the decay time was investigated and no significant change in the temperature range up to 70 K was found. In the present study we start by measuring the time development of an Er PL signal upon a single pulse of the Nd:YAG laser, as depicted in Fig.1. The points represent experimental data averaged over 100 excitation pulses. The solid line represents a computer fit according to the formula

$$I_{PL}(t) = A\,[exp(-t/\tau_R) - exp(-t/\tau_{TR})]\,, \qquad (1)$$

which can be derived from the set of rate equations for the excitation model where the existence of an intermediate BE state is assumed [2]. In the formula τ_R and τ_{TR} correspond to the Er radiative recombination time constant and the excitation transfer time between the intermediate BE state and the Er core, respectively. A is a proportionality constant. As can be seen, a good agreement with τ_{TR}=45 μs and τ_R=580 μs can be obtained for almost the entire time window used in the depicted measurement. The discrepancy appearing for t>600 μs is due to a slower decaying component whose existence is not incorporated in the rate equation set from Ref.[2], and which could be due to a different species of Er-related PL centers [7]. We conclude that in the investigated sample the effective lifetime of the intermediate state responsible for the excitation of the Er core has a relatively high value, similar to those found for excitons bound to isoelectronic centers.

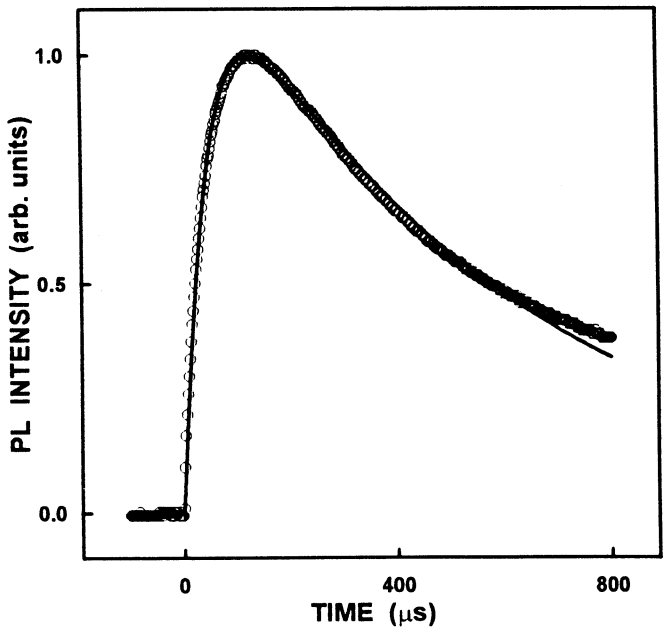

Figure 1: *The time development of the Er PL signal generated by the Nd:YAG laser pulse. The experimental points were fitted according to Eq.(1) with τ_{TR}=45 μs and τ_R=580 μs.*

B. Effect of the IR beam - quenching of Er PL

Upon application of the infrared beam the intensity of the Nd:YAG-excited PL changes. This is illustrated in Fig.2. The broken line corresponds to the original PL signal, while the solid ones,

labeled A, B, C, and D, show the effect of the free-electron laser pulse (λ=9.5 μm) which is fired 10, 50, 100, and 200 μs after the Nd:YAG pulse, respectively. As can be seen, the intensity of the signal quenches, with the effect becoming smaller as the time difference between the two pulses increases. For longer delay times, $\Delta t > 50$ μs, the form of the signal indicates that upon the IR pulse the excitation of Er is terminated immediately and only the decay takes place. For still larger delays, $\Delta t > 250$ μs, no influence of the IR beam on the PL signal can be observed.

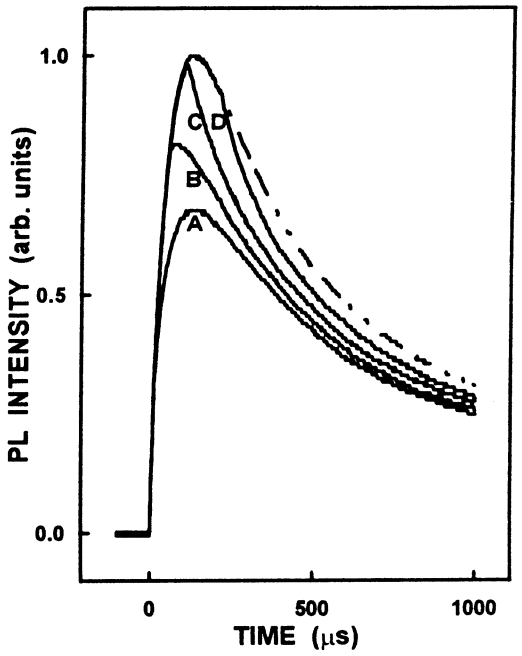

Figure 2: *Quenching of the Er PL signal (broken curve) with the λ=9.5 μm FELIX pulse. Curves A, B, C, and D correspond to delay times of 10, 50, 100, and 200 μs, respectively.*

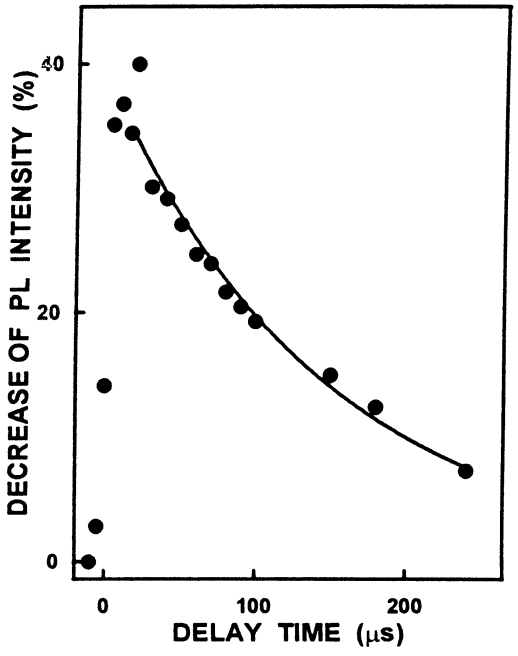

Figure 3: *Dependence of the quenching effect on the delay time for λ=9.5 μm. The solid line has been fitted as a single-exponential decay yielding a time constant $\tau_{TR} \approx 100$ μs.*

The results depicted in Fig.2 are readily understood if we assume that the infrared beam affects not the excited Er state but the transient BE state intermediating Er excitation; the effect diminishes as the concentration of these centers decreases and the excitation is transferred to Er. In such an interpretation the difference between the undisturbed signal (broken curve) and curves A through D corresponds to the number of Er atoms whose excitation is prevented by the IR pulse. If we assume that the total PL is proportional to the number of intermediate BE centers available at the beginning of the excitation, then the magnitude of the quenching effect for different delay times will monitor the actual number of these centers. In Fig.3 the magnitude of the FELIX-induced quench is plotted versus the delay time between both laser pulses. As can be seen, the quenching effect has a sharp onset and reaches its maximum for $\Delta t \approx 10$ μs, which corresponds to the situation when the Nd:YAG is fired immediately following the FELIX (macro) pulse, which has approximately 7 μs duration. In this case the IR pulse quenches the Er-related photoluminescence to approximately 60% of its total intensity. For longer delays the effect gradually ceases to exist, in agreement with Fig.2, and can no longer be detected for $\Delta t > 250$ μs. If we assume, as outlined before, that the quenching effect is proportional to the number of intermediate BE states available at the moment of the pulse, then the lifetime of these centers can be estimated from Fig.3. A satisfactory computer fit can be obtained for $\tau \approx 100$ μs. The factor 2 difference between this effective lifetime value of the intermediate BE state and that estimated from the form of the PL signal, Fig.1, is most probably indicative of the approximations used in developing the quantitative description of the energy transfer process expressed by Eq.1. In any case we note that, according to the assumed energy transfer model, the

effective lifetime of the intermediate BE state should depend on relaxation paths alternative to Er excitation (e.g. nonradiative energy transfer to the conduction band) and, as such, could be strongly time-dependent, following the development of conduction electron concentration, see, e.g., Ref.2.

C. A special quenching feature for $\lambda \approx 12.5$ μm

The quenching effect of the Er-related BE state outlined in the preceding section has been investigated as a function of the wavelength of the IR laser beam. The experiments were performed for various delay times. For a short delay of $\Delta t=5$ μs (maximum quench) no significant differences were found, except for a general lowering of the effect for $\lambda > 16$ μm, presumably due to water absorption in air. However, for $\Delta t=50$ μs an additional feature around the wavelength $\lambda \approx 12.5$ μm was detected: following the IR pulse the PL signal remained stable for approximately 30-40 μs before starting to decrease, as observed for other wavelengths. This resulted in a somewhat smaller quench monitored as total integrated PL signal. The effect is depicted in Fig.4, where the PL signal remaining after the FELIX pulse is plotted - a local maximum centered around $\lambda=12.5$ μm can be concluded. For still longer delay times the $\lambda=12.5$ μm feature gradually disappears, as does also the total quenching effect.

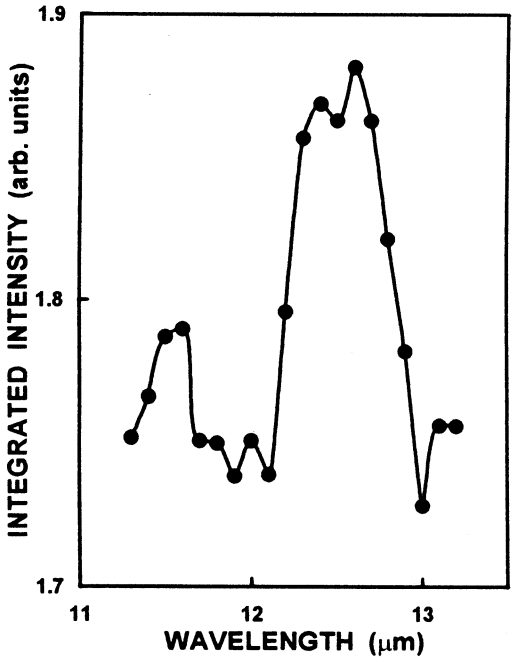

Figure 4: *Quenching effect as observed for the delay time $\Delta t=50$ μs. A reduced quenching for $\lambda \approx 12.5$ μm can be noted.*

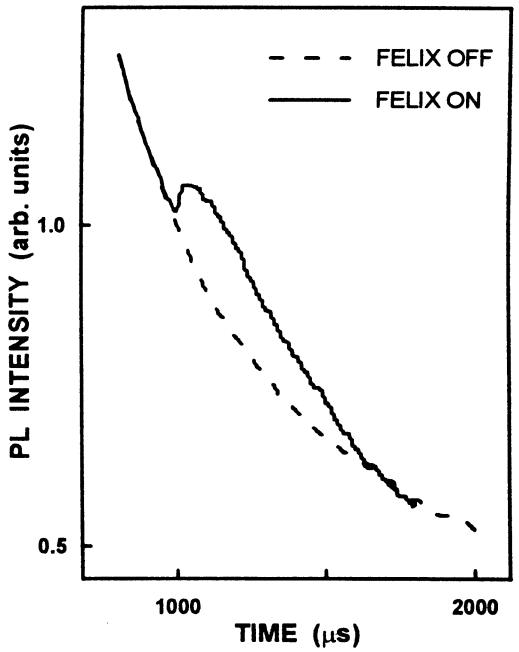

Figure 5: *An increase of the PL signal by the IR pulse observed for large delay times; $\Delta t=1$ ms, $\lambda=9.6$ μm.*

While the experimental finding reported here is a matter of current investigation and requires further confirmation, it is certainly tempting to relate it to the back-transfer process outlined in the introductory section. In case that this process would be induced, one might expect that part of the energy of the IR beam would now be absorbed by excited Er atoms converting them back into the intermediate BE state. This could lead to an additional excitation of Er after termination of the IR pulse, thus generating an effect of "delayed PL". Taking into account the available detector decay time, such a feature could result in a smaller recorded quench of the total signal. If the observed effect would indeed be related to the back-transfer mechanism then it could take place only when a considerable concentration of excited Er would become available; this could explain why it is not observed immediately following the Nd:YAG pulse ($\Delta t=5$ μs). We note further that no quenching can be observed for $\Delta t > 250$ μs. To this end we recall that recent theoretical work [4] suggests

that the back-transfer process requires participation of an electron in the conduction band; in our experiment conduction electrons are present immediately after the excitation, or, alternatively, they can be generated by the IR pulse due to the dissociation of the intermediate Er-related BE state. In the latter case the back-transfer process could not be observed after decay of the BE state, in agreement with the experiment. Finally, we point out that the photon energy for which the described special quenching feature takes place is very similar to one of the activation energies as determined from the temperature dependence of the PL intensity for the same sample [7].

D. Enhancement of PL intensity for long delay times

For long delay times between the two pulses, $\Delta t \geq 800$ μs, a different effect has been observed. This is illustrated in Fig.5. As can be seen, the IR pulse applied when the intensity of PL has already decayed to below 50% causes a transient increase of PL; following that, the signal continues to decay with, possibly, a somewhat shorter time constant. The enhancement effect, clearly observed here, needs to be further investigated in more detail. Its origin is at present unclear, as no such feature has been predicted by the existing models of Er-related energy transfer mechanisms.

As mentioned before, it has been suggested in the past that within the PL of Er in silicon two components can be separated with different decay time constants [6]. According to that interpretation, after a delay of more than 800 μs the PL would be dominated by a "slow" species giving a long-lasting, weak emission. An effect as depicted in Fig.5 could take place if the IR laser pulse would be capable of converting the slow-decaying species into the fast ones. At this moment, however, such a mechanism remains purely speculative and it is evident that more research is required.

Conclusions

In the performed study the influence of an intense IR illumination on intensity and decay characteristics of the PL signal generated by a visible laser pulse in Er-doped silicon has been investigated. The quenching of the PL signal was concluded. This effect has been related to the dissociation of the Er-related BE state rather than to the decrease of the concentration of the excited Er centers. A special quenching feature was found for λ=12.5 μm; this could be a manifestation of the back-transfer process converting excited Er centers into the BE state intermediating the energy transfer to the 4f shell. If confirmed, the observed effect would indicate that conduction electrons are required for the back-transfer process. Investigations currently on the way will further elucidate the reported issues [8].

Acknowledgements

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