

Direct Observation of the Two-Stage Excitation Mechanism of Er in Si

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In Er-doped silicon we have found direct evidence for the formation of the Er-related intermediate state that is a precursor of the final $4f$ -electron excited state responsible for the 0.8 eV luminescence. Time-resolved photoluminescence following band-gap illumination shows disruption of this center by a THz pulse from a free-electron laser. The decay of the intermediate state could be directly monitored in this double-beam experiment and a lifetime of approximately $100 \mu\text{s}$ has been found. In this way the most characteristic step in the excitation mechanism of the Er ion in silicon has been revealed experimentally. [S0031-9007(98)07761-8]

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With little doubt erbium doping, either by implantation or by other nonequilibrium techniques, constitutes thus far the most successful realization of silicon photonic devices. The particular attraction of the Er-in-Si system stems from the fact that its sharp atomiclike photoluminescence (PL) spectrum, which is due to internal transitions within the corelike $4f$ -electron shell, coincides with one of the absorption minima of silica fibers at $1.6 \mu\text{m}$. However, while devices based on Si:Er, such as light emitting diodes and optical amplifiers, are already being developed, many of the more fundamental aspects of the Er-in-Si system still lack sufficient understanding. These include, among others, the microscopic structure of the optically active erbium center [1,2] and also the appropriate description of the physical mechanisms responsible for the energy transfer within the system. In particular, it appears that the excitation mechanism responsible for the transitions between the spin-orbit interaction split ground and excited states of the $4f$ -electron shell has not been conclusively established. Only the thorough understanding of this mechanism might pave the way to its optimization, which is necessary for the successful event of efficient Si:Er-based optoelectronics.

Luminescence of Er in Si can be excited both optically (photoluminescence) and by carrier injection (electroluminescence) [3]. In the currently accepted models of optical excitation two important ingredients seem to be rather firmly established: the prominent role of free excitons and the formation of an Er-related donor center. The Er core excitation is then assumed to be accomplished in an Auger process comprising a nonradiative recombination of an electron-hole pair at the donor state with energy transfer to the $4f$ -electron shell [4]. This mechanism is schematically illustrated in Fig. 1 where also alternative relaxation paths competing with the Er excitation are indicated. The

free exciton participation has been postulated from an experiment where the back side of the sample has been excited [5], and the formation of an Er-related donor center has been considered by theory [6] and was also reported by deep-level transient spectroscopy measurements [7,8]. In contrast to that, the formation of the intermediate state, sometimes postulated to be an Er-related bound exciton, has been suggested based on theoretical arguments [9] and until now supported indirectly by the time delay which is observed between the termination of the excitation pulse and the decay of Er PL [10]. The properties of the intermediate state are crucial for the understanding of the physical mechanisms taking place within the Si:Er system. However, until the present, this state was not accessible experimentally.

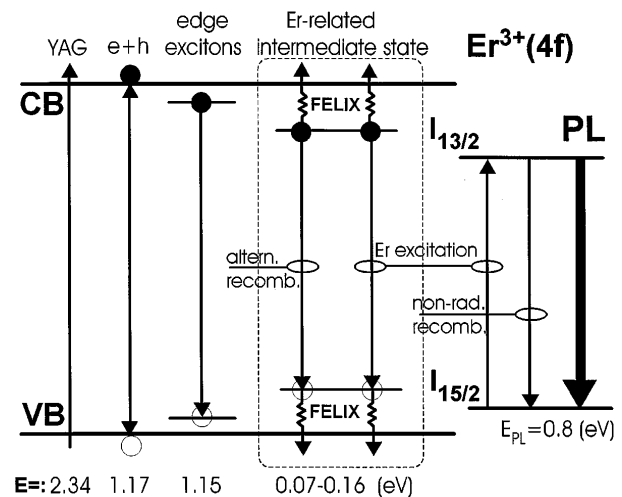


FIG. 1. Excitation scheme of Er ion in silicon.

A vast body of the currently available information on the properties of the Si:Er system has been obtained from the studies of the temperature dependence of the PL intensity and decay time. From the fitting of temperature dependencies activation energies of the individual mechanisms involved at different stages of the energy transfer process might be obtained [3]. Such results suffer, however, from considerable inaccuracy. This follows from the fact that different physical processes are active simultaneously and their individual contributions are difficult to separate. Moreover, contributions of processes with large activation energies become significant only at higher temperatures and, consequently, can be studied for a considerably reduced PL intensity.

The above problems can be avoided in a double-beam experiment, as used in the current study. In this case the individual mechanisms operational in the energy transfer process are activated by an intense infrared pulse (IR) operating additionally to the visible-light excitation; by a proper tuning of the IR beam different mechanisms were influenced independently from each other. Moreover, these can be activated regardless of temperature and therefore investigated at $T = 4.2$ K, i.e., for a large PL intensity. By using a double-beam experimental configuration we hoped to gain information pertinent to the so-far experimentally inaccessible intermediate state and reveal some of its characteristic features.

In the experiment, which is schematically illustrated in Fig. 2(a), two excitation sources have been used. The PL spectrum of an Er-doped Si sample placed at liquid-helium temperature was generated by a pulsed Nd:YAG laser operating with a repetition rate of 5 Hz at $\lambda = 532$ nm, with a pulse duration of approximately 7 ns. In order to avoid possible heating effects the averaged excitation power level was kept below ≈ 20 μ W. In addition to this above-band-gap excitation the infrared beam has been applied. This was provided by the free-electron laser for infrared experiments (FELIX) at Rijnhuizen [11]. The FELIX delivers so-called "macropulses" with a length of 5–10 μ s at a repetition rate of 5 Hz. Each macropulse consists of a train of "micropulses" with a spacing that can be set either to 1 or to 40 ns. In the study a 40 ns micropulse spacing was used with the macropulse length of approximately 7 μ s and a micropulse width of 1.7 ps. It is estimated that the energy in each micropulse was 1.7 μ J. The experimental configuration permitted the adjustments of the wavelength of the IR pulse within 7.5–17 μ m range. Also its timing with respect to the excitation laser pulse could be altered, and so different stages of the excitation/deexcitation process of Er ions could be influenced. In order to avoid a possible penetration of shorter wavelengths present in the FELIX beam due to the generation of higher harmonics a cutoff 7.2 μ m filter has been placed before the sample. The emerging PL was collected from the laser-irradiated surface and passed through a bandpass filter centered at $\lambda = 1548.8$ nm and

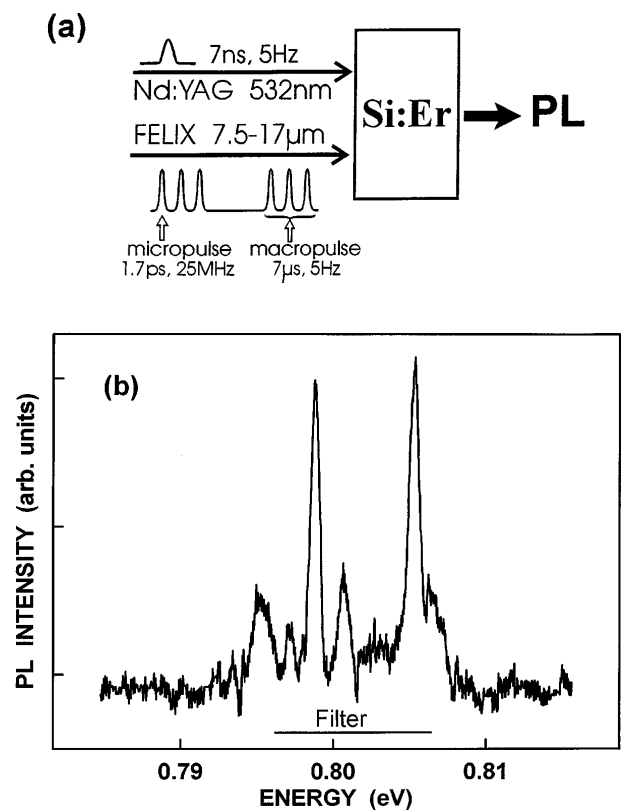


FIG. 2. (a) Schematic illustration of the experiment. (b) PL spectrum of the sample used in the experiment, $T = 4.2$ K. The bandpass filter range is indicated.

with a bandwidth of 20 nm. The filter has been chosen to select the most intense component of the Er-related PL spectrum emitted by the sample. The PL has been detected by a germanium detector whose response has been experimentally established as 5 μ s on the rising slope and 75 μ s for the decay time. The signal from the detector was amplified and accumulated by a digital oscilloscope. By using the bandpass filter rather than a monochromator a better signal-to-noise ratio could be achieved. In this case the experimentally measured signal corresponds to the total emission of all the spectral components appearing in the filtered range.

The sample used in the experiment was prepared from $\langle 100 \rangle$ -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 Ω cm. It has been implanted at 500 $^{\circ}\text{C}$ with Er^{2+} ions of 1100 keV energy to a dose of 10^{13} cm^{-2} ; no further heat treatment has been given. The PL spectrum of this material is shown in Fig. 2(b) where also the filter range is indicated.

Upon application of the excitation pulse characteristic Er-related PL appears. The time development of the PL response of the sample is shown in Fig. 3(a). As can be seen, the PL intensity first increases steeply,

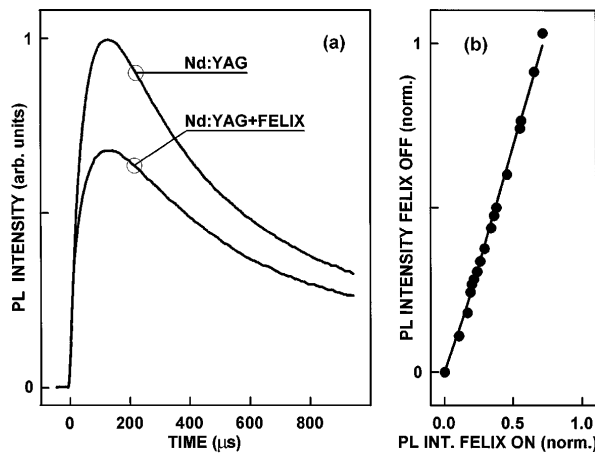


FIG. 3. Comparison of the PL signals observed following the YAG-laser excitation pulse with and without simultaneous application of the FELIX quenching pulse: (a) Time development; (b) mutual correlation. $\lambda_{\text{FELIX}} = 9.5 \mu\text{m}$, $T = 4.2 \text{ K}$.

attains a maximum after approximately $100 \mu\text{s}$, and then diminishes exponentially. The second curve in Fig. 3(a) depicts the time dependence of the PL signal when a short infrared pulse (in this case of the wavelength $\lambda = 9.5 \mu\text{m}$) has been applied simultaneously with the excitation. As can be seen, the FELIX pulse leads to a considerable quenching of the intensity of the PL signal. In order to conclude on the nature of the effect that the FELIX pulse exerts on Er PL we now plot the mutual relation between the two signals, i.e., PL intensity as measured with and without the quenching beam for the same time delay with respect to the excitation pulse—see Fig. 3(b). By inspecting the figure we note that the experimental points clearly fall on a straight line cutting through the origin. This implies that the total number of Er ions attaining the excited state following the Nd:YAG laser pulse is reduced as a result of the IR pulse.

In order to now understand the actual role played by the IR pulse, we should establish which stage of the excitation process is affected. Following the theoretically considered energy transfer models, one could imagine that the populations of free carriers, of free excitons, or of the intermediate state centers could be lowered by the FELIX pulse. Yet another possibility to account for the diminished PL intensity would be a direct interaction of the IR beam with the $4f$ -electron core effectively lowering the number of excited Er ions. Since all of the aforementioned states are characterized by different lifetimes, a further insight into the actual role of the quenching IR pulse is gained by monitoring its effect on the Er PL signal as a function of the delay with respect to the excitation pulse. In Fig. 4(a) the result of such an experiment is shown: the time dependence of the Er PL is depicted with the FELIX being fired 10, 50, 100, and $200 \mu\text{s}$ after the YAG laser. As can be concluded, the quenching effect diminishes gradually with the increasing

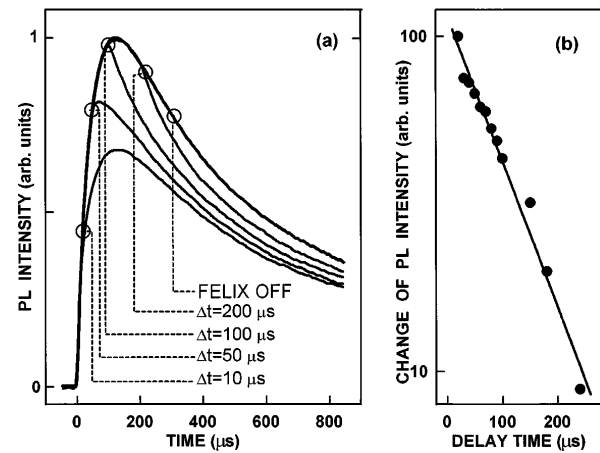


FIG. 4. Quenching effect of the FELIX pulse, $\lambda_{\text{FELIX}} = 9.5 \mu\text{m}$, $T = 4.2 \text{ K}$: (a) Illustration of the effect with the pulse applied 10, 50, 100, and $200 \mu\text{s}$ after the YAG-laser excitation; (b) intermediate state lifetime determination: the solid line corresponds to a single-exponential decay with a time constant $\tau \approx 100 \mu\text{s}$.

time separation between the two pulses. For delay times longer than approximately $250 \mu\text{s}$ practically no decrease of PL could be detected. We conclude that the IR pulse does not influence the population of the excited Er ions; at $t = 250 \mu\text{s}$ these are still present in a significant concentration, as evidenced by the PL intensity. On the other hand, the fact that the quenching effect is observed for delay times of tens of microseconds clearly argues against a mechanism in which the IR beam would interact with free carriers or free excitons, whose lifetimes are much shorter. In view of the above we conclude that the quenching effect must happen at an intermediate stage of the excitation path and that the FELIX pulse affects the postulated Er-related intermediate state responsible for the energy transfer to the Er core. Therefore we can use the magnitude of the quenching, defined as the integrated difference of the PL signal as induced by the application of the IR pulse, to monitor the decay kinetics of that intermediate state center. Figure 4(b) shows the dependence of the quenching effect as a function of the delay time between the excitation and the quenching pulses. No change of PL is seen if the FELIX is fired before the YAG laser. Since thermal effects have relaxation times of an order of milliseconds, this serves as an independent indication that lattice heating by the IR pulse does not take place. The quenching effect sets in as the two pulses overlap and gradually diminishes with increasing delay time. Based on the presented reasoning we attribute the observed time decay of the quenching to the decay of the Er-related intermediate state, which is thus directly monitored in the experiment. In this way the result presented in Fig. 4 serves as an immediate experimental evidence for the existence of the intermediate state giving its lifetime and thus supporting

theoretical models of the Er excitation mechanism based on that assumption. When the data of Fig. 4(b) is fitted by an exponential function, as commonly assumed in the rate equations describing the Er excitation process [3,4], a decay time constant $\tau = 100 \pm 10 \mu\text{s}$ is obtained, which in our model corresponds to the characteristic time τ_{TR} of the energy transfer between the monitored intermediate center and the Er $4f$ shell. This is considerably longer than assumed in current descriptions of the Er excitation mechanism. We note further that the identification of this time constant as the energy transfer time τ_{TR} relies on the assumption that Er excitation is the main decay mechanism of that center. In principle the experimentally measured value corresponds to the effective lifetime of the intermediate state; this should be strongly influenced by relaxation paths alternative to Er excitation—see Fig. 1. Moreover, it is commonly accepted that different Er-related complexes might be characterized by different lifetimes; one should also expect that excitation time will depend on local properties of the given center. In this case the decay curve of the intermediate state will contain contributions from different types of centers, with slower and faster components, very similar to the situation usually faced in the lifetime measurements of the excited Er state [3,8], and the measured value of τ_{TR} corresponds to the slowest excitation process significantly contributing to PL intensity. Finally, we point out that the lifetime value determined in this study for the Er-related intermediate state is similar to those found for excitons bound to isoelectronic centers in silicon [12]. Therefore, the presented results support identification of the intermediate state as an Er-related bound exciton.

In an attempt to establish the dissociation energy of the intermediate state we have checked whether the observed quenching effect was dependent on a particular wavelength of the IR beam. We have found that the dissociation of the intermediate state was taking place within the whole experimentally available wavelength range, i.e., between 7.5 and 17 μm . This sets the upper limit on the dissociation energy of the intermediate state at approximately 70 meV. The physical properties of the quenching process and the wavelength dependence of its efficiency are currently being investigated.

In summary, we have directly confirmed the two-stage excitation mechanism of Er in Si by photo dissociation

of the intermediate state for which the decay time of approximately 100 μs and dissociation energy not exceeding 70 meV have been established. Both parameters are similar to those found for bound exciton states.

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