

# Excitation and deexcitation of Er<sup>3+</sup> in crystalline silicon

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Temperature dependent measurements of the 1.54  $\mu\text{m}$  photoluminescence of Er implanted N codoped crystalline Si are made. Upon increasing the temperature from 12 to 150 K, the intensity quenches by more than a factor thousand, while the lifetime quenches from 420 to 3  $\mu\text{s}$ . The quenching processes are described by an impurity Auger energy transfer model that includes bound exciton dissociation and a nonradiative energy backtransfer process. Electron and hole trap levels are determined. Direct evidence for a backtransfer process follows from spectral response measurements on an Er-implanted Si solar cell. © 1997 American Institute of Physics. [S0003-6951(97)00313-6]

With the increasing importance of combining optical and electronic technology, the need for an effective light source in silicon grows. One way of realizing such a light source is by optical doping, in which optically active elements are incorporated in the silicon matrix. Erbium is an interesting optical dopant, as its intra- $4f$  transition from the first excited state ( $^4I_{13/2}$ ) to the ground state ( $^4I_{15/2}$ ) causes luminescence at 1.54  $\mu\text{m}$ , a standard wavelength in telecommunication.

Erbium luminescence in crystalline silicon has been extensively studied in the past five years.<sup>1-5</sup> In most cases, the erbium is excited by photogenerated carriers, using above-band-gap laser illumination. The luminescence intensity is found to decrease rapidly upon going to higher temperatures. This luminescence quenching can be described using the model<sup>3</sup> depicted in Fig. 1. In this model, electrons are trapped at a deep level in the silicon band gap, where they form ( $F$ ) bound excitons. The deep level can, for example, be an impurity induced level<sup>3</sup> or a level corresponding to a hybridization between the Er<sup>3+</sup>  $5d$  state and silicon conduction band states.<sup>6</sup> Recombination of a bound exciton can excite ( $E$ ) the Er<sup>3+</sup>  $4f$ -shell in an Auger process. The erbium ion can then decay radiatively, resulting in 1.54  $\mu\text{m}$  luminescence. Due to the donor character of erbium, the hole capture process is usually the rate limiting step in the exciton formation.

The observed luminescence intensity and lifetime quenching are thought to be caused by the reverse of processes  $F$  and  $E$ . The dissociation of bound excitons ( $D$ ) reduces the *excitation* efficiency. The energy backtransfer from an excited erbium ion to a trapped carrier state ( $B$ ) decreases the excited state lifetime, and with it the *luminescence* efficiency. To account for the energy differences involved in the quenching mechanisms  $B$  and  $D$ , both steps have to be phonon assisted. This is the origin of the temperature dependence of the luminescence quenching. Quenching can also occur by Auger energy transfer to free carriers,<sup>7</sup> if these are present in sufficiently high concentrations.

Although the model outlines above has been used to describe the luminescence quenching of erbium in crystalline silicon, no direct proof of the dissociation and backtransfer processes has been supplied. Furthermore, few reports have

been made of the position of the relevant deep levels in the bandgap. In this letter, we provide direct experimental evidence for the backtransfer process in crystalline silicon, obtained from room temperature (RT) spectral response measurements on an erbium implanted silicon solar cell. From measurements of the temperature dependence of the erbium photoluminescence intensity and lifetime in nitrogen codoped crystalline silicon, we acquire information on the position of the energy levels involved in excitation and deexcitation of the erbium. The obtained values for the level positions show that independent optimization of excitation and deexcitation efficiencies might be possible.

A single crystal Czochralski-grown silicon wafer ( $p$ -type, B-doped, [100], 1–10  $\Omega$  cm) was implanted with Si, N, and Er at room temperature, at a pressure below  $10^{-6}$  mbar. Silicon was implanted at 450 keV to a fluence of  $3.5 \times 10^{15}$ . Nitrogen was coimplanted at 225 keV to a fluence of  $1 \times 10^{15}$   $\text{cm}^{-2}$ , followed by an erbium implant at 1.46 MeV to a fluence of  $1.6 \times 10^{14}$   $\text{cm}^{-2}$ . The sample was annealed in vacuum for 2 h at 490 °C and for 1 h at 600 °C, to recrystallize the implanted layer. Rutherford backscattering spectrometry showed that the Er has a Gaussian depth distribution at a depth of 490 nm, with a full width at half-maximum (FWHM) of 310 nm and a peak concentration of  $5 \times 10^{18}$   $\text{cm}^{-3}$ .<sup>8</sup> The nitrogen concentration profile as determined from secondary ion mass spectrometry peaks at a depth of 580 nm and show a FWHM of 200 nm and a peak concentration of  $6 \times 10^{19}$   $\text{cm}^{-3}$ .

Photoluminescence (PL) measurements were done using the 515 nm line of an Ar ion laser as a pump beam. The pump beam was modulated by an acousto-optic modulator. The sample was mounted in a closed cycle helium cryostat, using silver paint to ensure good thermal contact. The PL signal was focused into a 48 cm monochromator, and collected by a liquid nitrogen cooled Ge detector. The signal was determined using standard lock-in techniques. Luminescence decay traces were obtained by averaging the detector signal on a digital oscilloscope. The system response time was 0.5  $\mu\text{s}$ . Measurements were taken at temperatures ranging from 12 to 170 K.

The erbium doped silicon wafer shows a PL spectrum typical for erbium in silicon,<sup>8</sup> peaking at 1.535  $\mu\text{m}$ . Figure 2 shows an Arrhenius plot of the integrated PL intensity (open

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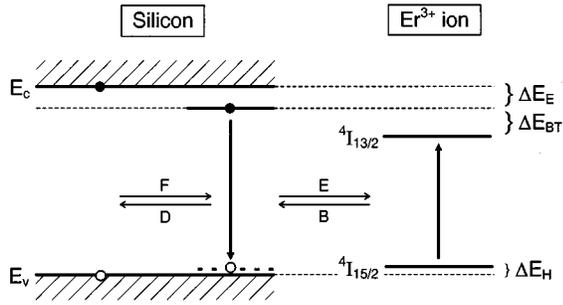


FIG. 1. Model of excitation and deexcitation of  $\text{Er}^{3+}$  in Si, including bound exciton formation ( $F$ ) and dissociation ( $D$ ),  $\text{Er}^{3+}$  excitation ( $E$ ), and energy backtransfer ( $B$ ).

circles). To achieve optimum signal to noise ratio, the data in Fig. 2 were taken at different pump powers in the range of 1–100 mW, and then normalized to pump power. All data were taken in the regime where PL intensity depends linearly on pump power, precluding effects of beam heating, erbium excited state saturation, and free carrier Auger quenching of the  $\text{Er}^{3+}$  excited state. A slight intensity quenching is observed up to a temperature of 85 K, above which a much stronger quenching sets in.

Luminescence decay measurements were performed at  $1.535 \mu\text{m}$ , at temperatures ranging from 12 to 170 K. At low temperatures, a nearly single exponential decay is observed. For higher temperatures the decay becomes strongly nonexponential. The  $1/e$  times  $\tau_{\text{Er}}$  are included in Fig. 2 (crosses). A strong decrease in lifetime is observed above 85 K, indicating that a decrease in *luminescence* efficiency is an important factor in the measured intensity quenching. The slight intensity decrease observed in going from 12 to 85 K is not accompanied by a decrease in lifetime, indicating that this intensity quenching is caused by a change in *excitation* efficiency, and not by a change in luminescence efficiency. This might be due to the detrapping of holes weakly bound to a filled trap.

The observed temperature dependence of the lifetime can be described using the model in Fig. 1. Once excited, an Er ion can decay through two pathways: either by emitting a  $1.54 \mu\text{m}$  photon, or by energy backtransfer into a deep level in the gap. The total decay rate  $W$ , equal to  $1/\tau_{\text{Er}}$ , is then given by

$$W = W_0 + W_{\text{BT}} e^{-\Delta E_{\text{BT}}/kT}, \quad (1)$$

in which  $W_0$  represents the measured erbium decay rate at low temperatures, where phonon assisted deexcitation does not occur. The exponential term accounts for the phonon assisted backtransfer process, where  $W_{\text{BT}}$  is a prefactor and  $\Delta E_{\text{BT}}$  the energy difference involved in the backtransfer process (see Fig. 1). From the high-temperature slope of the lifetime curve, we find  $\Delta E_{\text{BT}} = 135 \pm 5 \text{ meV}$ . Furthermore, fitting Eq. (1) to the lifetime data we find  $W_{\text{BT}} = 10^8 - 10^{10} \text{ s}^{-1}$ .

It should be noted that the trap level mentioned in the discussion of the model is not the only carrier recombination center present in the silicon. In reality, dislocations and point defects introduced during the implantation process are likely

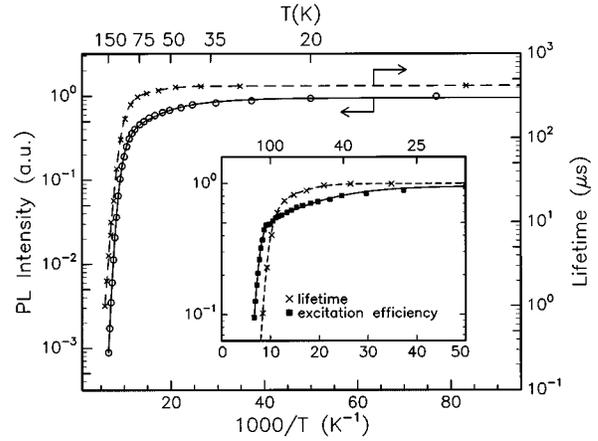


FIG. 2. Temperature dependence of the  $1.54 \mu\text{m}$  PL intensity (circles, left axis) and the  $1/e$  luminescence lifetime (crosses, right axis) of Er implanted crystalline Si.

to dominate the minority carrier lifetime  $\tau_p$ . Inserting this in the model, we find the following low pump power behavior for the PL intensity:

$$I_{\text{PL}} \propto \frac{1}{W} \frac{G \tau_p}{1 + C e^{-\Delta E_H/kT} + D e^{-(\Delta E_H + \Delta E_E)/kT}}, \quad (2)$$

where  $\Delta E_H$  is the hole binding energy at a filled trap,  $\Delta E_E$  the depth of the electron trap,  $G$  the carrier generation rate, and  $\tau_p$  the minority carrier lifetime. The prefactors  $C$  and  $D$  are given by  $C = W_H/R_T$  and  $E = W_E/R_T$  with  $W_H$  the hole capture rate constant,  $W_E$  the electron trapping rate constant, and  $R_T$  the rate constant for exciton recombination at the trap. In general,  $C$  and  $D$  depend on temperature, as both  $W_H$  and  $W_E$  contain the carrier velocity and their respective carrier capture cross sections. Depending on the type of trap, it follows that  $W_{H,E} \propto T^\alpha$  with  $-1.5 < \alpha < 0.5$ .

Equation (2) shows that in the low pump limit, the luminescence efficiency and the excitation efficiency are decoupled. To obtain the Er excitation efficiency, given by the second term in Eq. (2), the intensities were divided by the measured luminescence lifetimes. This was done using a spline fit through the lifetime data (dashed lines, Fig. 2). The resulting excitation efficiency is shown in the inset in Fig. 2 (squares). The efficiency data were then fitted using the second term in Eq. (2), by varying  $\Delta E_H$ ,  $\Delta E_E$ , and the prefactors  $C$  and  $D$ , as well as the absolute scaling. Assuming a temperature independent  $\tau_p$ , and taking into account the allowed range for  $\alpha$  in the prefactors  $C$  and  $D$ , we find  $\Delta E_E = 125 \pm 3 \text{ meV}$  and  $\Delta E_H = 12 \pm 6 \text{ meV}$ . The fitting result for  $\alpha = -1/2$  is shown in the inset in Fig. 2 (solid line). It is clear that the proposed model describes the excitation process quite well.

The mismatch between the  $\text{Er}^{3+}$  excited state ( ${}^4I_{13/2}$ ) energy and the silicon band gap amounts to  $\sim 300 \text{ meV}$ . The fitted activation energies together bridge only  $272 \pm 10 \text{ meV}$ . This suggests that in N codoped Si, erbium excitation occurs through a level different from that involved in the deexcitation process. An explanation might lie in the nature of the different energy levels. Impurity related levels such as those introduced by nitrogen, are spatially rather extended, and couple strongly to conduction band states. Such levels are

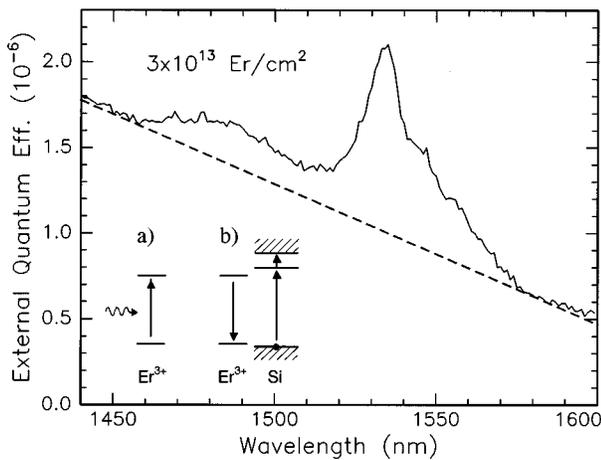


FIG. 3. Spectral response of an erbium implanted PERL solar cell, derived from data in Ref. 10. The dashed line is a linear interpolation of the background signal. Schematically indicated are the processes of Er excitation (a) and energy backtransfer followed by exciton dissociation (b).

effective electron-hole recombination centers, which makes them probable *excitation* channels for the erbium (see Fig. 1). The predicted Er related  $5d$ -like level<sup>6</sup> however, is localized near the erbium, resulting in a weak coupling to conduction band states, and a relatively strong coupling to the first excited state of the erbium. Carrier recombination at the latter erbium related energy level could therefore be the main *deexcitation* channel. This implies that the erbium PL emission may be optimized by increasing the excitation rate using different impurities and reducing the deexcitation rate by changing the local structure around the erbium.

In order to further investigate the backtransfer process, spectral response measurements on a passivated emitter, rear locally diffused (PERL) Si solar cell<sup>9</sup> were analyzed. The cell was implanted with 3.5 MeV Er ions to a fluence of  $3 \times 10^{13} \text{ cm}^{-2}$ . After implantation, the cell was annealed at 1060 °C for 1 h and at 1000 °C for 75 min. The solar cell was made at the University of New South Wales, and its detailed electrical characteristics are reported in Ref. 10.

The RT solar cell spectral response was converted to the absolute external quantum efficiency, defined as the number of collected electron-hole pairs per incoming photon. The result, derived from data in Ref. 10, is shown in Fig. 3. Superimposed on a decreasing background signal, which is attributed to absorption by implantation induced defects, a pronounced RT erbium absorption spectrum is observed, peaking at a wavelength of  $1.535 \mu\text{m}$ . These data are direct experimental evidence for a backtransfer process leading to the generation of free carriers from an excited state in  $\text{Er}^{3+}$ .

The spectral response measurement in Fig. 3 can be used to estimate the erbium deexcitation efficiency. Assuming a linearly decreasing background (dashed line), we find a

maximum external quantum efficiency  $\eta_{\text{ext}}$  of  $\sim 10^{-6}$ . This  $\eta_{\text{ext}}$  is given by  $\eta_{\text{ext}} = N_{\text{Er}} \cdot \sigma_{\text{abs}} \cdot \eta_{\text{BT}} \cdot \eta_{\text{D}}$ , with  $N_{\text{Er}}$  the optically active Er fluence,  $\sigma_{\text{abs}}$  the  $\text{Er}^{3+}$  intra- $4f$  absorption cross section at  $1.535 \mu\text{m}$ , and  $\eta_{\text{BT}}$  and  $\eta_{\text{D}}$  the quantum efficiencies for backtransfer and dissociation. Assuming all implanted Er is optically active and taking as an estimate<sup>11</sup>  $\sigma_{\text{abs}} = 6 \times 10^{-20} \text{ cm}^2$ , we find  $\eta_{\text{BT}} \cdot \eta_{\text{D}} \approx 50\%$ , showing that the backtransfer process can be quite efficient. The obtained estimate yields an upper limit for  $\eta_{\text{BT}} \cdot \eta_{\text{D}}$ , as internal reflections in the solar cell were neglected in this analysis. It should be noted that the backtransfer efficiency might depend on the specific anneal treatment.

In conclusion, the  $1.54 \mu\text{m}$   $\text{Er}^{3+}$  luminescence intensity in crystalline Si, codoped with  $6 \times 10^{19} \text{ N cm}^{-3}$ , quenches by three orders of magnitude as the temperature is increased from 12 to 150 K, while the luminescence lifetime decreases from 420 to 3  $\mu\text{s}$ . Using an impurity Auger model to describe the data, electron detrapping with an activation energy of  $125 \pm 3 \text{ meV}$  and hole detrapping with an activation energy of  $12 \pm 6 \text{ meV}$  are found to reduce the Er excitation rate at high temperatures. In addition, a nonradiative erbium deexcitation process, with an activation energy of  $135 \pm 5 \text{ meV}$  reduces the erbium luminescence efficiency at high temperatures. From these activation energies it is concluded that the level causing erbium excitation is different from the level causing erbium deexcitation. Direct experimental evidence is found for a nonradiative  $\text{Er}^{3+}$  deexcitation process, resulting in the generation of free carriers.

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