

Strong exciton-erbium coupling in Si nanocrystal-doped SiO₂

P. G. Kik,^{a)} M. L. Brongersma,^{b)} and A. Polman

FOM Institute for Atomic and Molecular Physics, 1098 SJ Amsterdam, The Netherlands

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Silicon nanocrystals were formed in SiO₂ using Si ion implantation followed by thermal annealing. The nanocrystal-doped SiO₂ layer was implanted with Er to a peak concentration of 1.8 at. %. Upon 458 nm excitation the sample shows a broad nanocrystal-related luminescence spectrum centered around 750 nm and two sharp Er luminescence lines at 982 and 1536 nm. By measuring the excitation spectra of these features as well as the temperature-dependent intensities and luminescence dynamics we conclude that (a) the Er is excited by excitons recombining within Si nanocrystals through a strong coupling mechanism, (b) the Er excitation process at room temperature occurs at a submicrosecond time scale, (c) excitons excite Er with an efficiency >55%, and (d) each nanocrystal can have at most ~1 excited Er ion in its vicinity. © 2000 American Institute of Physics. [S0003-6951(00)03517-8]

Erbium-doped silica glass is used in optical telecommunication technology as an amplification medium. The Er³⁺ ions in the glass matrix exhibit a number of sharp emission lines due to electronic transitions within the 4*f* shell. The transition from the first excited state to the ground state occurs at 1.53 μm, a standard wavelength in optical telecommunication. Optical amplification at this wavelength can be achieved if sufficient Er can be brought into the first excited state. Unfortunately, the optical cross sections for the intra-4*f* transitions are rather small, typically on the order of 10⁻²¹ cm². For this reason there is considerable interest in sensitizing the Er³⁺ ions by adding a strongly absorbing species that can transfer energy efficiently to Er. Examples of such sensitizers are the rare earth ion ytterbium¹ and various organic dyes.²

Recently, Fujii *et al.* reported that the presence of Si nanocrystals in Er-doped SiO₂ considerably enhances the effective Er absorption cross section.³ Following this observation, a number of articles appeared that showed similar results for samples prepared by means of cosputtering,⁴ pyrolysis,⁵ and ion implantation.^{6,7} Although the exact structural properties of the nanocrystals depend on the fabrication method employed, all observations strongly suggest that energy is transferred from Si nanocrystals to the Er. A possible excitation model is shown in Fig. 1(a), which shows a schematic band diagram of SiO₂ containing a Si nanocrystal and Er³⁺. First a photon is absorbed by the nanocrystal, which causes generation of an exciton inside the nanocrystal. This exciton can recombine radiatively, emitting a photon with an energy that depends on the nanocrystal size. If an Er ion is present close to the nanocrystal, the exciton can recombine nonradiatively by bringing Er into one of its excited states.

Although the excitation model sketched in Fig. 1(a) is often referred to, the following issues have not been solved: (1) the *lifetime paradox*: recently Franzò *et al.*⁷ found that the nanocrystal luminescence decay time is not affected by the presence of Er. They argued that this would be inconsis-

tent with the model in Fig. 1(a), since in this model erbium adds a nonradiative decay path for exciton recombination, which should lower the nanocrystal lifetime. (2) The *temperature dependence*: the nanocrystal luminescence intensity and the Er luminescence intensity are thought to be proportional to the excited concentration of excitons. Nevertheless, in temperature dependent measurements,^{4,7} the Er luminescence intensity has repeatedly been observed to behave independently of the nanocrystal luminescence intensity. (3) The *excitation efficiency*: it is not known how efficiently the exciton energy can be transferred to Er. (4) The *excitable Er fraction*: excitation via Si nanocrystals enhances the Er luminescence intensity, but it is not known which fraction of the Er is actually excitable. This knowledge is essential for the design of optical amplifiers and lasers based on Er and nanocrystal doped SiO₂. In this letter these four points will be addressed and resolved.

Silicon ions were implanted at 35 keV to a fluence of 6 × 10¹⁶ cm⁻² into a 100 nm thick SiO₂ layer that was formed by wet thermal oxidation of a lightly *B*-doped Si(100) substrate. The material was subsequently annealed at 1100 °C for 10 min in vacuum at a base pressure below 3 × 10⁻⁷ mbar. This procedure is known to produce well passivated Si nanocrystals in the size range 2–5 nm.⁸ The corresponding nanocrystal concentration is approximately 10¹⁹ nanocrystals/cm³. The nanocrystal-doped region was

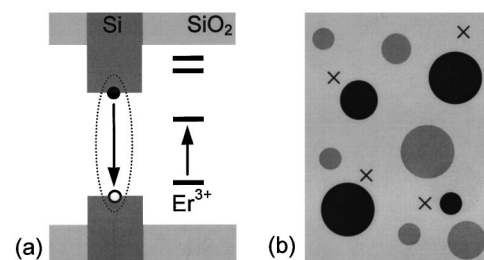


FIG. 1. (a) Schematic Er excitation model, showing the electronic band structure of Si nanocrystal-doped SiO₂ and the Er 4*f* energy levels. An optically generated exciton (dotted line) confined in the nanocrystal can recombine and excite Er³⁺. (b) Schematic representation of SiO₂ containing Er (crosses) and nanocrystals (circles). The nanocrystals that couple to Er (black circles) show no exciton luminescence.

^{a)} Author to whom correspondence should be addressed; electronic mail: Kik@amolf.nl

^{b)} Present address: California Institute of Technology, Pasadena, CA 91125.

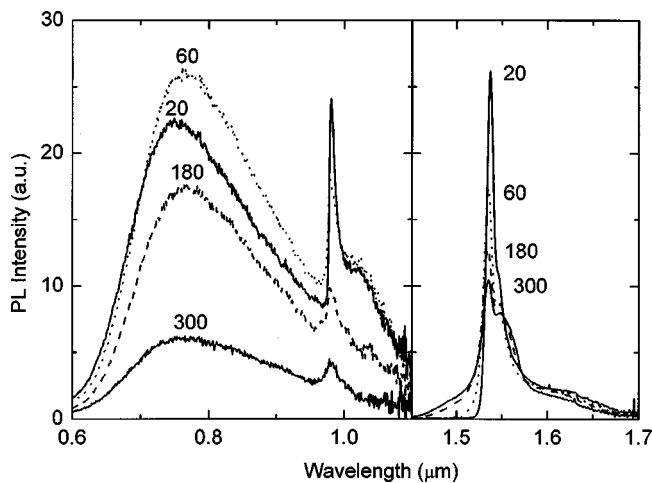


FIG. 2. Photoluminescence spectra at 20, 60, 180, and 300 K showing a broad nanocrystal spectrum in the range 0.6–1.1 μm , and two clear Er luminescence lines at 982 and 1536 nm.

then implanted with $5.1 \times 10^{15} \text{ Er/cm}^2$ at 125 keV, resulting in an Er peak concentration of 1.8 at % at a depth of 50 nm. This material was annealed at 1000 $^\circ\text{C}$ in vacuum in order to remove implantation-induced damage. To further reduce defect-related luminescence, the material was passivated by performing an anneal at 800 $^\circ\text{C}$ for 30 min in forming gas ($\text{H}_2:\text{N}_2$ at 1:9) at atmospheric pressure.

Photoluminescence (PL) spectra were measured using an Ar laser at 457.9 nm as an excitation source. The excitation power was 1–10 mW in a ~ 1 mm diam laser spot. The laser beam was modulated at 11 Hz using an acousto-optical modulator. The PL was focused onto the entrance slit of a 96 cm monochromator and detected using standard lock-in techniques. Luminescence spectra were measured in the 600–1150 nm range using a AgOCs photomultiplier tube, and in the range 1100–1700 nm using a liquid nitrogen cooled Ge detector. All spectra were corrected for the system response. PL decay traces were recorded using either a photomultiplier in combination with a photon counting system, or a Ge detector in combination with a digitizing oscilloscope. The system response time in the two cases was 150 ns and 160 μs , respectively. The sample temperature was controlled between 20 and 300 K using a closed-cycle He cryostat.

Figure 2 shows PL spectra taken at 20, 60, 180, and 300 K at a pump power of 10 mW. At all temperatures a broad luminescence band is observed extending from 0.6 to 1.1 μm , which is attributed to radiative recombination of excitons inside Si nanocrystals.⁸ The exciton luminescence appears at energies above the band gap energy of bulk Si due to quantum confinement.⁹ The large spectral width of the nanocrystal luminescence is the result of the rather broad nanocrystal size distribution (2–5 nm diameter).

Superimposed on the nanocrystal luminescence spectrum a relatively sharp peak is observed at 982 nm, corresponding to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} . Another clear emission line is observed at a wavelength of 1536 nm, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} . Photoluminescence excitation spectra (not shown) indicate that the Er is not excited directly by absorption of pump photons, but indirectly via an energy transfer process from Si nanocrystals, as was shown before.^{3,4,7} At a fixed pump power, the

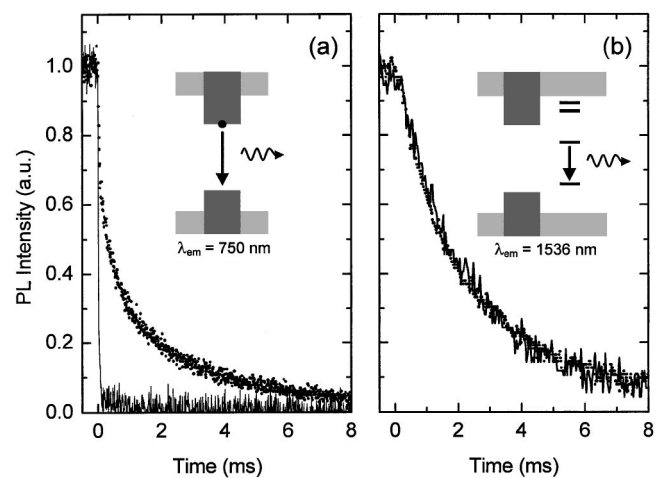


FIG. 3. Luminescence decay measurements taken at 15 K (dots) and at 300 K (drawn lines) of: (a) nanocrystal luminescence at 750 nm and (b) Er^{3+} luminescence at 1536 nm.

nanocrystal luminescence intensity and the Er luminescence intensity increase by a factor of 2 when the excitation wavelength is decreased from 514 to 459 nm. We attribute this to the increasing nanocrystal optical absorption cross section for increasing photon energy, leading to a higher exciton generation rate. It is tempting to conclude that the luminescent nanocrystals are the nanocrystals that are responsible for the Er excitation. This turns out not to be true, as will be shown below.

In Fig. 2 it can be seen that increasing the temperature from 20 to 300 K first causes the nanocrystal luminescence to increase by 16% and then to decrease by 75% upon going from 60 to 300 K. This kind of temperature dependence is commonly observed for Si nanocrystals, and can be fully described¹⁰ by a model that takes into account the temperature dependent population of the exciton singlet and triplet states (with low and high radiative decay rate, respectively) in competition with nonradiative processes. The Er luminescence peak at 1.536 μm exhibits an entirely different temperature dependence. The temperature increase only induces spectral broadening due to the thermal redistribution over the Stark levels, while the integrated intensity remains constant within 10%. These observations contradict any model that directly links the observed nanocrystal and Er luminescence intensities.

Figure 3 shows luminescence decay curves of the nanocrystal luminescence at 750 nm and the Er luminescence at 1536 nm, measured at 15 and 300 K at a pump power of 1 mW. It is found that the nanocrystal decay rate [Fig. 3(a)] increases from 1.5×10^3 to $4.8 \times 10^4 \text{ s}^{-1}$ upon going from 15 to 300 K, which is consistent with the exciton singlet-triplet decay model.⁸ The Er decay time at 1.536 μm [Fig. 3(b)] is found to be 2.1 ms at all temperatures between 20 and 300 K, which implies that the Er luminescence efficiency is temperature independent.

A consistent description of the observed temperature dependencies can be obtained if we assume *strong coupling* between a Si nanocrystal and Er. If the energy transfer from a nanocrystal to Er is fast, we expect to see no luminescence from a nanocrystal that is coupled to Er, since any generated exciton will immediately recombine nonradiatively by excit-

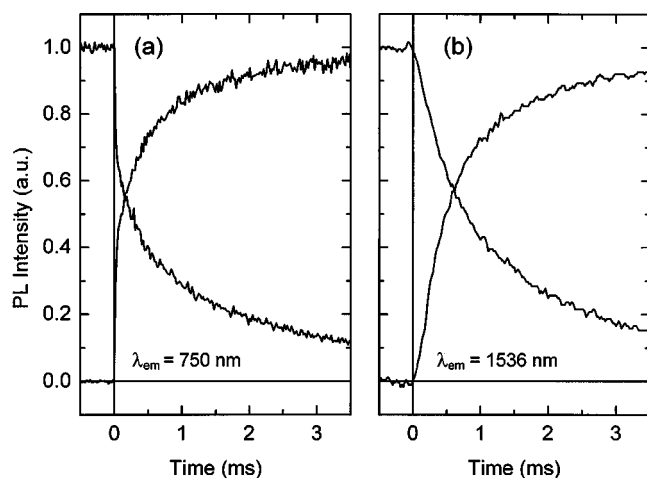


FIG. 4. Luminescence rise time and decay measurements at 5 mW pump power at 15 K for: (a) nanocrystal luminescence at 750 nm and (b) Er luminescence at 1536 nm.

ing Er. Such fast transfer might occur because at the high nanocrystal density ($\sim 10^{19}/\text{cm}^3$) the maximum distance between an Er ion and the nearest nanocrystal is ~ 1 nm. The Er luminescence intensity will then be determined by the product of the nanocrystal absorption cross section, which is approximately temperature independent and the Er luminescence efficiency, which is also temperature independent [Fig. 3(b)].

The fact that the Er luminescence is constant up to room temperature implies that the energy transfer to Er must occur well within the nanocrystal decay time at 300 K, which is 21 μs . Consequently the transfer rate constant must be larger than $\sim 10^6 \text{ s}^{-1}$ at room temperature. This fast transfer explains the paradox encountered by Franzò *et al.*, who found that while the incorporation of Er does reduce the nanocrystal luminescence, it does not affect the nanocrystal decay time. This behavior is now expected, since in the strong-coupling case all observed nanocrystal luminescence originates from nanocrystals that do not couple to Er, while nanocrystals that do couple to Er show no luminescence. This model is shown schematically in Fig. 1(b).

In order to determine the Er excitation efficiency, we measured both the nanocrystal and the Er luminescence $1/e$ rise time τ_r and decay time τ at 5 mW pump power [see time dependent data in Fig. 4(a)]. From these two time constants we can deduce the excitation rate $R = (1/\tau_r - 1/\tau)$, assuming that the Er and the nanocrystals effectively behave as two level systems. At a pump intensity of 5 mW/mm² we find for the nanocrystal excitation rate $R_{\text{nc}} = 940 \text{ s}^{-1}$ and for the Er excitation rate $R_{\text{Er}} = 570 \text{ s}^{-1}$. Note that this Er excitation rate may contain a contribution of excitation into the higher lying Er energy levels, followed by nonradiative relaxation to the first excited state. Comparing the nanocrystal and Er excitation rates, we conclude that at least 55% of the generated excitons recombine by transferring energy to Er.¹¹ This high conversion efficiency is in agreement with the strong coupling picture.

The high excitation efficiency also raises a new question. At the peak concentration of 1.8 at.% Er, the Er-to-nanocrystal ratio is approximately 100:1, which implies that in principle many Er ions compete for the same exciton.

Nevertheless the observed Er excitation rate is close to that of a single nanocrystal. This leads to the conclusion that a single nanocrystal can effectively excite only ~ 1 Er ion. This behavior can be explained in the following way: if an exciton is formed inside a nanocrystal which has just excited one of the surrounding Er ions, the Er ion may decay nonradiatively through an Auger process¹² in which the exciton is excited to higher energy. After thermal relaxation, the exciton can recombine by exciting an Er ion. If the Auger process is sufficiently fast, it will limit the amount of excitable Er per nanocrystal to one.

The findings in this letter have important implications for the design of nanocrystal-sensitized Er-doped lasers or optical amplifiers operating at 1.54 μm . In these devices the Er could be pumped efficiently using a broad range of pump wavelengths. It may also be possible to pump such a device by electrically supplying electrons and holes. At a nanocrystal density of 10^{19} cm^{-3} and 1 Er ion per nanocrystal, the maximum gain of such a device will be 0.1 dB/cm, assuming a typical Er emission cross section of $3 \times 10^{-21} \text{ cm}^2$. Note that the highest maximum gain can be obtained when the sample preparation method is optimized to yield a high density of small nanocrystals. We have recently fabricated Er and Si nanocrystal doped waveguides in SiO₂, in which the index contrast is provided by the Si nanocrystals. The first measurements on these devices show excellent mode confinement and low optical losses. Optical gain measurements on these samples are underway.

In conclusion, we have shown evidence for strong coupling between excitons and Er in Si nanocrystal-doped SiO₂. The energy transfer takes place at a submicrosecond time scale. The exciton-to-Er energy transfer efficiency is larger than 55%, and the maximum number of excitable Er ions around a single nanocrystal is near unity.

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¹M. P. Hehlen, N. J. Cockroft, T. R. Gosnell, and A. J. Bruce, *Phys. Rev. B* **56**, 9302 (1997).

²S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. Van Veggel, D. N. Reinhoudt, L. H. Slooff, A. Polman, and J. W. Hofstra, *J. Appl. Phys.* **86**, 1181 (1999).

³M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, *Appl. Phys. Lett.* **71**, 1198 (1997).

⁴M. Fujii, M. Yoshida, S. Hayashi, and K. Yamamoto, *J. Appl. Phys.* **84**, 4525 (1998).

⁵J. St. John, J. L. Coffey, Y. Chen, and R. F. Pinizzotto, *J. Am. Chem. Soc.* **121**, 1888 (1998).

⁶C. E. Chrystou, A. J. Kenyon, T. S. Iwayama, C. W. Pitt, and D. E. Hole, *Appl. Phys. Lett.* **75**, 2011 (1999).

⁷G. Franzò, V. Vinciguerra, and F. Priolo, *Appl. Phys. A: Mater. Sci. Process.* **69**, 3 (1999).

⁸M. L. Brongersma, A. Polman, K. S. Min, E. Boer, T. Tambo, and H. A. Atwater, *Appl. Phys. Lett.* **72**, 2577 (1998).

⁹C. Delerue, G. Allan, and M. Lannoo, *Phys. Rev. B* **48**, 11024 (1993).

¹⁰M. L. Brongersma, P. G. Kik, and A. Polman, *Appl. Phys. Lett.* **76**, 351 (2000).

¹¹We assume that the nanocrystal absorption cross section and spontaneous lifetime are not affected by the presence of Er.

¹²F. Priolo, G. Franzò, S. Coffa, and A. Carnera, *Phys. Rev. B* **57**, 4443 (1998).