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# Direct experimental evidence for trap-state mediated excitation of Er<sup>3+</sup> in silicon

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The time evolution of the 1.54  $\mu\text{m}$  Er<sup>3+</sup> photoluminescence intensity of Er-doped silicon following a 30  $\mu\text{s}$  excitation pulse is investigated. It is found that at 9 K, the 1.54  $\mu\text{m}$  luminescence from Er<sup>3+</sup> continues to increase up to 50  $\mu\text{s}$  after the pulse is terminated, when excess photocarriers no longer exist. This provides the first direct experimental evidence that a state in the forbidden gap of silicon acts as the gateway to the excitation of Er<sup>3+</sup>. Further analysis indicates recombination of bound excitons to be the most likely excitation mechanism. © 1995 American Institute of Physics.

Trivalent rare earth ions possess partially filled 4f shells which are shielded by outer shells. Due to this shielding, they display sharp, atomlike luminescence from intra-4f transitions when incorporated into other materials, with wavelengths that are largely independent of the host material and of the temperature. This property has attracted much research of rare earth doped materials for use in optoelectronic components.<sup>1</sup> Of the rare earth ions, Er<sup>3+</sup> is of a particular interest since one of its intra-4f transitions occurs at 1.54  $\mu\text{m}$ , which coincides with the low-loss window in silica-based optical fibers. Especially, Er-doped silicon is under intensive investigation as a possible silicon-based light source, circumventing the inefficiency of silicon in generating light due to its indirect band gap, and offering compatibility with the vast silicon-based integrated circuit technology.<sup>2</sup> Recently, room temperature electroluminescence from Er-doped silicon has been reported.<sup>3-5</sup>

Despite the amount of research, the exact excitation mechanism of Er<sup>3+</sup> in silicon is still unknown, except that it happens electrically, i.e., excitation occurs via carrier recombination and subsequent energy transfer to the Er<sup>3+</sup> ions.<sup>6-8</sup> Direct capture of an electron or a hole by the Er<sup>3+</sup> ion itself has been deemed unlikely due to the large Coulomb repulsion.<sup>9</sup> Thus, many authors have proposed that carriers are first trapped at an Er-related defect with a corresponding level in the forbidden gap of silicon, and that excitation of Er proceeds via an Auger process when the trapped carriers recombine.<sup>10,11</sup> Theoretical calculations have shown that such an excitation mechanism is possible,<sup>12</sup> and that Er<sup>3+</sup> can create a donor level 0.2 eV below the conduction band of Si.<sup>13</sup> Indeed, experiments have shown that Er acts as a donor in Si, and confirmed the presence of Er-related levels near the conduction band of Er-doped silicon.<sup>11,14</sup> Yet so far, no direct experimental evidence has shown that trapping of carriers at a state in the forbidden gap of silicon is an essential part of the excitation of Er in silicon. In this letter, we present time-resolved photoluminescence measurements which provide the first direct experimental evidence of the existence of such an intermediate step. The data also allow us to tentatively identify recombination of a bound exciton as the most likely mechanism of excitation.

Er ions were implanted at 1.5 MeV to a dose of 7

$\times 10^{14}$  cm<sup>-2</sup> into a Czochralski-grown (CZ) Si wafer ([100], doped with boron, resistivity 1–10  $\Omega$  cm). The wafer temperature during implantation was 77 K. The resulting Er-containing amorphous surface layer (820 nm thick) was recrystallized by an anneal at 600 °C for 30 min in vacuum (base pressure  $\leq 10^{-6}$  mbar). Rapid thermal annealing at 1150 °C under flowing N<sub>2</sub> atmosphere for 15 s was performed subsequently to anneal out the residual damage and activate the implanted Er atoms. This recipe was shown to create a good quality single-crystalline Er-doped Si film with optimum Er<sup>3+</sup> photoluminescence intensity, with an active (both optically and electrically) Er concentration of  $\sim 3 \times 10^{17}$  Er/cm<sup>3</sup>,<sup>7,15</sup> extending from the surface to a depth of approximately 800 nm. Photoluminescence (PL) measurements were performed using the 515 nm line of an Ar laser at a nominal pump power of 100 mW. As the 1/e penetration depth at this pump wavelength in Si is 890 nm,<sup>16</sup> we expect most of the photoluminescence signal to come from the Er-doped region. The beam was modulated with an acousto-optical modulator with a rise and fall time of 50 ns, and the luminescence signal was collected using a 48 cm monochromator, a liquid-nitrogen cooled Ge detector, and a lock-in amplifier. The time evolution of the peak PL intensity was recorded and averaged using a digitizing oscilloscope. The sample was mounted in a closed-cycle helium cryostat with silver paint to ensure good thermal contact.

Figure 1 shows the PL spectra of virgin and Er-doped Si at 9 K. The spectra are corrected for detector sensitivity. Two major features can be seen, one near 1.12  $\mu\text{m}$  and one near 1.54  $\mu\text{m}$ . The peaks near 1.54  $\mu\text{m}$  are due to intra-4f transitions from the first excited (<sup>4</sup>I<sub>13/2</sub>) to the ground state (<sup>4</sup>I<sub>15/2</sub>) of Er<sup>3+</sup> ions. The peaks near 1.12  $\mu\text{m}$  are intrinsic to Si, and are due to phonon-assisted recombination of free excitons.<sup>17</sup> Note that the exciton-related luminescence intensity of Er-doped silicon is nearly 30 times less intense than that of virgin silicon. This indicates that the carrier lifetime in Er-doped silicon is roughly 30 times shorter than that of virgin silicon, most likely due to irradiation-related defects. The attempt to measure the luminescence lifetime of the 1.12  $\mu\text{m}$  luminescence was unfruitful for both virgin and Er-doped Si, since it was shorter than the response time of the detector (30  $\mu\text{s}$ ). However, taking the response time of the detector as the

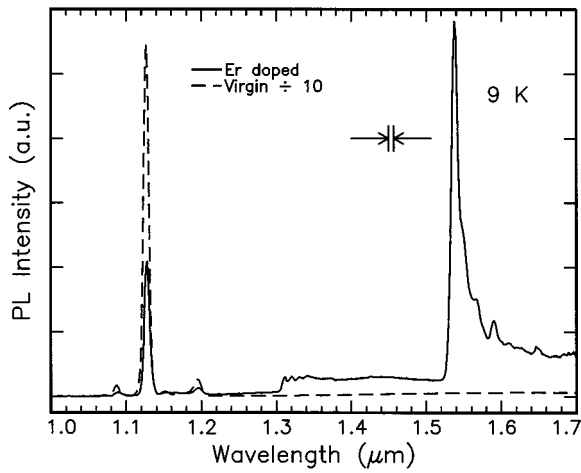


FIG. 1. Photoluminescence spectra of virgin and Er-doped silicon at 9 K. Also indicated is the resolution of the system. Notice that the spectrum of virgin silicon has been divided by 10.

upper limit, and comparing the intensities of the 1.12  $\mu\text{m}$  luminescence, we can conclude both the photocarrier lifetime and free exciton lifetime of Er-doped silicon to be  $< 1 \mu\text{s}$  even at 9 K.

Figure 2 shows the time evolution of the 1.12  $\mu\text{m}$  exciton and 1.54  $\mu\text{m}$   $\text{Er}^{3+}$  luminescence at 9 K during and after a 30  $\mu\text{s}$  excitation pulse. Also indicated is the duration of the excitation pulse. The 1.54  $\mu\text{m}$   $\text{Er}^{3+}$  luminescence *does not* decrease upon termination of the excitation pulse. Rather, it continues to increase up to  $\sim 50 \mu\text{s}$  after termination of the excitation pulse, after which it decays with a characteristic decay time of  $\sim 800 \mu\text{s}$ . This 50  $\mu\text{s}$  time lag is not related to the detector response time, as the 1.12  $\mu\text{m}$  exciton luminescence decreases as soon as the excitation pulse is turned off. The time lag thus is an indication that  $\text{Er}^{3+}$  ions are still being excited at an appreciable rate even 50  $\mu\text{s}$  after the excitation pulse is switched off. However, the above upper limit of the photocarrier lifetime of 1  $\mu\text{s}$  implies that the

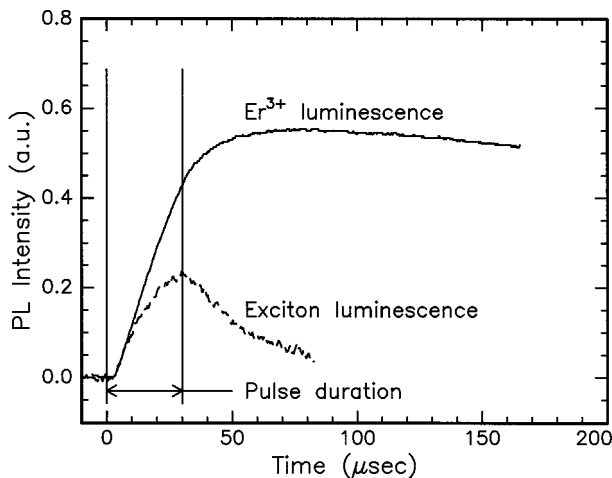


FIG. 2. Time evolution of 1.54  $\mu\text{m}$   $\text{Er}^{3+}$  luminescence and 1.12  $\mu\text{m}$  exciton luminescence intensity during and after a 30  $\mu\text{s}$  excitation pulse. Also indicated is the duration of excitation pulse.

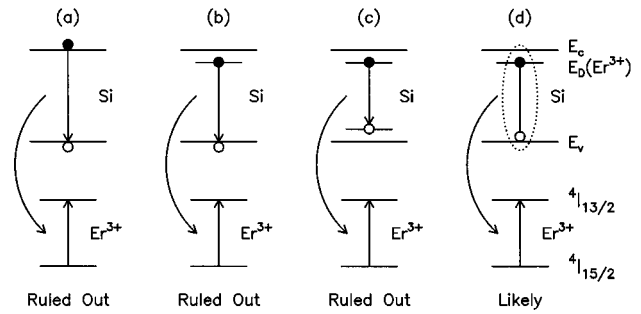


FIG. 3. Schematic representations of various possible excitation mechanism of Er in Si, and assessment of their likelihood. The excitation mechanisms shown are (a) via recombination of free carriers; (b) via recombination of an electron trapped at an Er-related level with a free hole; (c) via recombination of an electron trapped at an Er-related level with a hole trapped at an acceptor level; (d) via recombination of a bound exciton trapped at an Er-related level. The Si conduction ( $E_c$ ) and valence ( $E_v$ ) bands, and the Er-related donor level [ $E_D(\text{Er}^{3+})$ ] are indicated, as well as the  $\text{Er}^{3+}$  4f energy levels involved. The filled circles indicate electrons, and the open circles denote holes.

population of both photocarriers and free excitons in Er-doped Si is negligible 50  $\mu\text{s}$  after the excitation pulse is switched off. This rules out recombination of free carriers or free excitons as the excitation mechanism for Er. As Er in silicon is known to be excited via carrier recombination, the only remaining possibility is that  $\text{Er}^{3+}$  in silicon is excited by recombination of carriers trapped at a state in the forbidden gap of Si. Although shorter, such a time lag between the termination of the excitation pulse and the onset of the decrease of  $\text{Er}^{3+}$  luminescence intensity exists also at  $T > 100 \text{ K}$  (not shown), indicating that  $\text{Er}^{3+}$  is excited via recombination of trapped carriers also at higher temperatures.

Figures 3(a)–3(d) outline schematically the possible mechanisms of excitation of  $\text{Er}^{3+}$  in Si. Excitation of  $\text{Er}^{3+}$  via recombination of free carriers is shown Fig. 3(a). It is already ruled out as discussed in the previous paragraphs. To distinguish between other possible excitation mechanisms, we first need to consider the Fermi level of Er-doped Si. The Er-related donor concentration of  $\sim 3 \times 10^{17}/\text{cm}^3$  is more than one order of magnitude larger than the B-related acceptor concentration, which is  $< 1.5 \times 10^{16}/\text{cm}^3$ . Therefore, at 9 K, the Fermi level will be between the donor level and the conduction band, leaving both the valence band and acceptor states filled. This rules out any excitation mechanism involving isolated holes, such as excitation via recombination of a trapped electron with a free hole [Fig. 3(b)], and excitation via recombination of a trapped electron with a hole trapped at an acceptor level [Fig. 3(c)]. The conclusion does not change if the acceptor level in Fig. 3(c) is related to Er. It must be mentioned that so far, there is no experimental or theoretical evidence for such an Er-related acceptor level.

The one remaining possibility is excitation via recombination of an exciton bound to an Er-related trap site [Fig. 3(d)]. Excitons bound to impurities are well known in Si,<sup>17</sup> and such a process involving trapped excitons was calculated to be the most promising excitation mechanism of  $\text{Er}^{3+}$  in semiconductors.<sup>10</sup> We note that these bound excitons need not be free excitons trapped at the Er-related trap level. It is

also possible that these bound excitons are formed by trapping of an electron followed by Coulomb attraction of a hole.

It is interesting to note that a similar excitation mechanism has been suggested in rare earth doped III–V semiconductors such as Yb in InP,<sup>18</sup> Nd in InP,<sup>19</sup> Tm in GaAs,<sup>20</sup> and Er in InGaP,<sup>21</sup> where the rare earth ions are expected to be an isovalent trap, and also for Er-doped amorphous silicon doped with O and H.<sup>22</sup> The results presented in this letter indicate that recombination of an exciton bound to a rare earth atom related trap level in the energy gap may be an important excitation mechanism for photoluminescence of all rare earth doped semiconductors.

In conclusion, we have demonstrated experimentally that an Er-related level in the energy gap of silicon acts as the gateway for excitation of Er<sup>3+</sup> photoluminescence. The most likely excitation mechanism is recombination of excitons bound to such a level. This work is part of the research program of FOM, made possible by financial support from NWO, STW, and IOP-Electro Optics.

<sup>1</sup>See, for example, *Rare Earth Doped Semiconductors*, edited by G. S. Pomrenke, P. B. Klein, and D. W. Langer, Mater. Res. Soc. Symp. Proc. **301** (MRS, Pittsburgh, 1993).

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