On optical activity of Er³⁺ ions in Si-rich SiO₂ waveguides

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Photoluminescence spectroscopy was used to explore the optical activity of Er³⁺ ions in Si-rich SiO₂ waveguides prepared by ion implantation. Measurements were performed for a series of materials characterized by different Si excess levels, Er concentrations, and annealing temperatures. The highest fraction of optically active Er³⁺ ions which can be efficiently activated by nonresonant pumping was found to be 2.6%. This was realized in a waveguide with an Er concentration of [Er]=10¹⁸ cm⁻³ and Si excess of 20%, annealed at 900 °C. This optical activity level is insufficient to realize optical gain. It is therefore clear that further material improvement is needed before optical amplification in SiO₂:Er matrices sensitized by Si nanocrystals/nanoclusters can be achieved.
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The quest for silicon-based optoelectronics continues, fuelled by the almost unlimited prospects afforded by advanced Si microelectronics technology. As is well known, while being the dominant material in microelectronics, crystalline Si (*c*-Si) is a poor light emitter with its indirect band gap not allowing for efficient radiative electron-hole recombination. As a result, much faster nonradiative mechanisms dominate carrier relaxation.¹ A possible solution is sought by use of optical dopants whose excitation is facilitated by non-radiative electron-hole recombination and which then proceed to relax radiatively. Erbium is the optical dopant of choice due to the feasibility of telecom applications in the spectral window at 1.5 μm. Although the effective cross section of the indirect excitation of Er in *c*-Si is of an order of $\sigma_{\text{eff}} \approx 10^{-14}$ cm²,² which is lower than that typical for band-to-band absorption, it is at the same time about seven orders of magnitude larger than that of direct resonant excitation of the 4*f*-electron core of Er³⁺ ions, as typically used in waveguide amplifiers of telecommunication networks. Despite this clear advantage, *c*-Si:Er has not found widespread application due to thermally induced nonradiative quenching of Er emission at higher temperatures, which practically precludes room-temperature applications.³

Currently, the most promising way to avoid temperature quenching (and also limitations in doping concentrations) seems to be offered by a combination of SiO₂ and *c*-Si, i.e., solid dispersions of Si nanocrystals or nanoclusters (Si-nc) in an Er-doped SiO₂ matrix⁴—SiO₂:(Er+Si-nc). In this case, the mechanism of Er excitation is somehow similar to that in *c*-Si:Er, i.e., it is mediated by electron-hole generation which, in this case, takes place inside Si-nc's. Si-nc's efficiently absorb the incoming photons and generate carriers by band-to-band transitions. Subsequently, these carriers recombine nonradiatively, transferring energy to excite Er³⁺ ions. Since the ions are (mostly) incorporated within the SiO₂ (in-

cluding) matrix, their relaxation proceeds radiatively and is thermally stable. The Si-nc-mediated excitation of Er³⁺ is characterized by an effective cross section of $\sigma_{\text{eff}} \approx 10^{-17}$ cm². Therefore this excitation mode is less efficient than for Er in *c*-Si but still superior to that of direct pumping into one of the higher excited states.

An important question concerns the percentage of Er dopants that can be indirectly excited via Si-nc's. Recent reports^{5,6} suggest that this number is quite small, of the order of a few percent. Yet this parameter is essential in order to estimate if net optical gain can be achieved in structures based on SiO₂:Er sensitized with Si-nc's. Results published on this issue are controversial, with observations of optical gain at 1.54 μm (Ref. 7) being counterbalanced by reports where only net losses are observed.^{8,9} In particular, different absorption bands have been reported and related to Si-nc's and implantation damage.⁹ An equally important issue is the total level of optical activity of Er dopants, that is, the percentage of "excitable" Er³⁺ ions which can attain an excited state by direct or indirect pumping and emit photons by radiative recombination. The optical activity in moderately doped SiO₂:Er is 100% but is known to be notoriously low in *c*-Si—of the order of 1%.¹⁰ The level of Er optical activity in the SiO₂:(Er+Si-nc) medium was shown to be lower than in SiO₂,⁵ but this depends on particularities of sample preparation. In order to realize net optical gain, losses and the nonradiative recombination of Er³⁺ ions have to be minimized and optical activity maximized. Also, the efficiency of the Si-nc-to-Er energy transfer has to be optimized. The controversial issue of a possible enhancement of Er absorption at 1.5 μm, allegedly induced by the local anisotropy of Si-rich SiO₂,¹¹ seems to be currently resolved.^{12,13} In contrast, the level of optical activity of Er which can be realized in the SiO₂:(Er+Si-nc) medium is not known, and it is not clear whether 100% activity can be achieved.

In the current study, we use photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies to investigate Er optical activity in a series of differently prepared waveguides based on SiO₂:(Er+Si-nc) material, character-

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FIG. 1. Luminescence intensity at $1.54\ \mu\text{m}$ as a function of the pump power. The sample has been anneal at $1150\ ^\circ\text{C}$. The inset shows a PL spectrum at a low-power regime, as indicated with an arrow. The excitation source is fixed at $522\ \text{nm}$ wavelength, resonant with an Er^{3+} $4f$ -shell transition.

ized by various levels of Si-nc and Er doping and annealing temperature, which imply different conditions of Si-nc aggregation and therefore different sizes and structures of Si-nc's. Slab waveguides were fabricated by multiple-energy coimplantation of Si and Er into a $10\ \mu\text{m}$ thick thermal oxide layer grown on a (100) silicon substrate. Details of the implantation procedure can be found elsewhere.⁹ Sets of samples with three different silicon excess levels of 10%, 20%, and 30% and two different Er concentrations of 10^{18} and $10^{20}\ \text{cm}^{-3}$ were prepared. Subsequently, each set of samples was anneal at 600 , 900 , or $1150\ ^\circ\text{C}$ for 1 h in N_2 gas. The annealing was applied in order to form Si-nc's and to optically activate Er^{3+} dopants. From numerical calculations, we have estimated that the 10% excess Si corresponds to a Si-nc concentration similar to the lower Er concentration, approximately $4 \times 10^{18}\ \text{cm}^{-3}$, while the 30% excess Si results in Si-nc's concentration somewhat lower than the higher Er concentration, approximately $10^{19}\ \text{cm}^{-3}$. Throughout the letter, samples have been labeled as ErXSiy , where $X=1,2$ for lower and higher Er concentrations, respectively, and $Y=1,2,3$ specifies the Si excess of 10%, 20%, and 30%, respectively. For reference, SiO_2 samples implanted only with erbium, with no Si excess, were prepared under identical conditions.

PL and PLE experiments were carried out at room temperature. An optical parametric oscillator was used as a tunable excitation source. It produced pulses of 5 ns duration with a 10 Hz repetition rate. 500 and 522 nm wavelengths were selected for nonresonant and resonant Er^{3+} excitations, respectively. Light emission at $1.5\ \mu\text{m}$ was collected with two lenses and resolved with a 1 m F/8 monochromator (Jobin-Yvon THR-1000) equipped with a 900 groove/mm grating blazed at $1.5\ \mu\text{m}$. Light detection was done with a visible/infrared photomultiplier tube (R5509-72 Hamamatsu Corp.). The overall response time of the detection system was set to $30\ \mu\text{s}$.

Figure 1 shows PL results for the waveguides prepared with the lower Er implantation dose and annealed at $1150\ ^\circ\text{C}$. In the inset, low resolution PL spectra for samples with different Si excesses are compared with the reference implanted only with Er^{3+} ions. The measurement has been performed under low-power excitation set to the wavelength of $\lambda_{\text{exc}} = 522\ \text{nm}$, i.e. resonant with the $^4I_{15/2} \rightarrow ^2H_{11/2}$ internal

FIG. 2. Luminescence intensity at $1.54\ \mu\text{m}$ as a function of pump power for the material with the highest Er concentration and Si excess. Samples anneal at (a) $1150\ ^\circ\text{C}$ and (b) $600\ ^\circ\text{C}$ were used. Results for resonant (522 nm) and nonresonant (500 nm) excitations are compared with those obtained for the "reference" material ($\text{SiO}_2:\text{Er}$, no Si excess, $[\text{Er}] = 10^{18}\ \text{cm}^{-3}$, and annealed at $1150\ ^\circ\text{C}$) under resonant excitation.

transition of Er^{3+} . As can be seen, under these conditions, the PL intensity in samples sensitized with nanocrystals (Si-nc's are known to be formed at annealing temperatures above $1100\ ^\circ\text{C}$) clearly exceeds that of $\text{SiO}_2:\text{Er}$. This situation changes, however, at higher pumping fluxes. The main panel of Fig. 1 shows the PL intensity for the same four samples as a function of photon flux. (The highest pump power used in the experiment was $3\ \text{mJ/pulse}$.) As can be seen, while emission from samples containing Si-nc's tends to saturate at a level which changes with Si excess, the PL intensity from the reference $\text{SiO}_2:\text{Er}$ sample grows linearly with pumping power. A comparison of the power dependence of PL intensity obtained under resonant and nonresonant pumpings yields important information. In particular, the excitation cross section and the percentage of optically active Er^{3+} ions contributing to the PL under indirect and direct pumpings can be determined.⁵ In this way the effect of different sample preparation conditions can be assessed, and structures for the realization of optical gain can be optimized. With that in mind, the power dependence of the PL intensity was measured for all samples. In Fig. 2 we show the $1.54\ \mu\text{m}$ PL intensity for material with the highest Er concentration and 30% excess Si. Significantly different behavior is observed for samples annealed at $1150\ ^\circ\text{C}$, Fig. 2(a), having well defined nanocrystals, and a sample annealed at $600\ ^\circ\text{C}$, i.e., at a temperature well below the formation of Si-nc's, Fig. 2(b). Crystallinity of nanoclusters is known to influence the energy transfer processes. Previous works¹⁴ reported that the maximum intensity of Er photoluminescence has been obtained for an intermediate annealing temperature of $800\ ^\circ\text{C}$, at which the nanoclusters are not yet completely crystallized. The data in Fig. 2 were taken under resonant (522 nm) and

FIG. 3. Fraction of the total Er contents which can emit photons upon (a) nonresonant and (b) only resonant excitations.

nonresonant (500 nm) pumpings. Results are compared to those from the SiO₂ sample with the lower Er concentration and annealed at 1150 °C which was selected as a reference. If we assume that all Er ions are optically active in the reference sample, then using the known cross section for resonant excitation $^4I_{15/2} \rightarrow ^2H_{11/2}$ of Er³⁺ in SiO₂, we can quantify PL intensity and relate it to a particular concentration of emitting Er³⁺ ions.⁵ As can be seen, the indirectly pumped Er PL clearly saturates at high excitation powers. From this saturation level, in combination with measurements of the spontaneous Er lifetime, one can deduce the actual number of Er dopants which in that case are indirectly excited via Si-nc. At the same time, we note that under resonant pumping, the PL intensity still increases linearly above this saturation level. From this notion we conclude immediately that the number of Er³⁺ ions which can be excited by Si-nc's constitutes only a minor part of all Er dopants present in the sample. By subtraction of the PL intensities under resonant and nonresonant pumpings, also shown in Fig. 2, we obtain directly the PL contribution from those Er³⁺ ions which can only be excited by direct pumping, i.e., most probably are located not in the direct vicinity of Si-nc's. Also these data can now be calibrated against the "reference" sample, so that we can conclude whether the introduction of excess Si leads to loss of optical activity, i.e., creates Er³⁺ ions which can no longer be excited to generate photons, also under resonant pumping. As can be seen from Figs. 2(a) and 2(b), in both cases the slopes of the linear dependence obtained by subtraction of resonant and nonresonant data sets are clearly lower than that of the "reference" sample, thus indicating a considerable optical activity loss. In order to calculate the percentage of Er³⁺ ions excitable via Si-nc's and those optically active (i.e., contributing to the 1.5 μm PL) for each sample, we follow a method developed previously.⁵ A summary of these procedures is presented in Fig. 3, where we show the percentages of Er dopants which (a) can be indirectly excited via Si-nc's and (b) which can be optically excited only upon direct resonant pumping, for all the samples, as function of annealing temperature. From these data we

conclude that the concentration of Er³⁺ ions which can be efficiently excited via Si-nc's in the investigated waveguides is between 2×10^{16} and 5×10^{16} cm⁻³. Therefore a higher percentage of indirectly excitable Er is obtained for waveguides prepared with the lower Er implantation dose. In this case, the highest percentage of 2.6% and 2.3% are obtained for samples with Si excess levels of 20% and 30%, respectively, annealed at 900 °C. At the same time, however, we note that in these materials about 95% and 85%, respectively, of the total amount of Er dopants are optically inactive and do not emit photons under resonant pumping. The highest percentage of optically active Er dopants (i.e., capable of emitting photons under resonant or nonresonant pumping) of ~50% is obtained for sample Er1Si1, which is characterized by the lower Er concentration and the lowest Si excess annealed at 600 °C. From Fig. 3(a) we note that for that sample only 2% of Er can be excited indirectly.

To conclude, we have found that the percentage of Er³⁺ ions whose 1.5 μm emission can be sensitized with Si-nc's, i.e., indirectly excited with a large excitation cross section, is relatively low. In the investigated waveguide structures prepared from thermally grown SiO₂ implanted with Er and Si atoms, it does not exceed 2.6%. We also show that the sensitization by Si-nc's renders an important fraction of all Er dopants optically inactive, i.e., not capable of emitting photons under direct, resonant excitation of the 4f core. While it is possible that other combination of sample preparation parameters—Er dose, Si excess, and annealing conditions—might result in better optical properties, the present results indicate that realization of optical gain in Er-doped SiO₂ material sensitized with Si-nc's will require very careful material engineering.⁹ At the same time, it is clear that in the materials for which gain has been concluded,¹¹ the percentage of indirectly excitable and of optically active Er³⁺ ions should be cross-checked. Confirmation of the high level of optical activity would add credibility to these findings, confirming the feasibility of optical gain for the investigated waveguides.

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