Multilevel sensitization of Er$^{3+}$ in low-temperature-annealed silicon-rich SiO$_2$

Oleksandr Savchyn,$^{1,4}$ Ravi M. Todi,$^2$ Kevin R. Coffey,$^{2,4}$ and Pieter G. Kik$^{1,4}$

$^1$CREOL, The College of Optics and Photonics, University of Central Florida, 4000 Central Florida Blvd., Orlando, Florida 32816, USA
$^2$Advanced Materials Processing and Analysis Center (AMPAC), University of Central Florida, 4000 Central Florida Blvd., Orlando, Florida 32816, USA

(Received 31 October 2008; accepted 18 November 2008; published online 12 December 2008)

The dynamics of Er$^{3+}$ excitation in low-temperature-annealed Si-rich SiO$_2$ are studied. It is demonstrated that Si-excess-related indirect excitation is fast (transfer time $\tau_f < 27$ ns) and occurs into higher lying Er$^{3+}$ levels as well as directly into the first excited state ($^4I_{13/2}$). By monitoring the time-dependent Er$^{3+}$ emission at 1535 nm, the multilevel nature of the Er$^{3+}$ sensitization is shown to result in two types of excitation of the $^4I_{13/2}$ state: a fast excitation process ($\tau_f < 27$ ns) directly into the $^4I_{13/2}$ level and a slow excitation process due to fast excitation into Er$^{3+}$ levels above the $^4I_{13/2}$ level, followed by internal Er$^{3+}$ relaxation with a time constant $\tau_{rel}$ > 2.3 $\mu$s. The fast and slow excitations of the $^4I_{13/2}$ level account for an approximately equal fraction of the excitation events: 45%–50% and 50%–55%, respectively. © 2008 American Institute of Physics.

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The continued technological implementation of Si photonics requires the development of a cost effective Si-compatible light source.\textsuperscript{1–4} The use of Si nanocrystals (NCs) as sensitizers of Er$^{3+}$\textsuperscript{5} and the subsequent demonstration of Si-sensitized gain at 1.54$\mu$m (Ref. 6) have drawn significant attention since this approach could potentially enable the realization of an on-chip laser under excitation with a low-cost broadband light source. Despite significant promise of this approach, the presence of Si NCs was found to result in low concentration of optically active erbium ions\textsuperscript{7,8} and to introduce significant confined carrier absorption\textsuperscript{9–11} as well as scattering.\textsuperscript{12} Recently it has been shown that broadband sensitization of Er$^{3+}$ can also occur in Si-doped SiO$_2$ annealed at temperatures well below those required for NC formation.\textsuperscript{7,8,13} This phenomenon has been attributed to Er$^{3+}$ excitation by Si-excess-related luminescence centers (LCs) in the SiO$_2$ matrix.\textsuperscript{7,8} Such low-temperature-annealed samples were found to contain a higher density of optically active Er$^{3+}$ ions compared to Si-NC-doped samples with similar total Si and Er concentrations.\textsuperscript{7,8} In addition, the absence of Si NCs in low-temperature annealed samples could minimize scattering as well as confined carrier absorption typically induced by Si NCs during optical pumping.\textsuperscript{9,10} These factors make low-temperature-annealed Er-doped Si-rich SiO$_2$ an interesting candidate for the realization of amplification at 1.54$\mu$m under broadband excitation. The evaluation of this material as a gain medium requires a detailed understanding of the observed Er$^{3+}$ excitation process. The present study discusses the dynamics of the LC-mediated Er$^{3+}$ excitation mechanism in low-temperature-annealed Er-doped Si-rich SiO$_2$.

An Er-doped Si-rich SiO$_2$ film (thickness 110 nm) containing 12 at. % of excess Si and 0.63 at. % of Er was deposited by magnetron cosputtering onto a Si wafer. The sample was annealed for 30 min in N$_2$ at 600 °C and subse-

\textsuperscript{4}Electronic mail: osavchyn@mail.ucf.edu.
\textsuperscript{5}Also at the Physics Department, University of Central Florida.

0003-6951/2008/93(23)/233120/3/$23.00
93, 233120-1 © 2008 American Institute of Physics

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substrate. At this pump power, no Er-related PL signal could be detected during either continuous wave (cw) excitation or pulsed excitation from a reference sample containing a similar concentration of Er (0.49 at. %) but no excess Si. This demonstrates that the observed Er3+ emission is predominantly excited indirectly via a Si-excess-related mechanism. Power-dependent cw and pulsed PL measurements (not shown) indicated that second order processes such as cooperative upconversion and excited state absorption do not significantly contribute to the observed 981 nm emission in these experiments.

Figure 2 shows the PL decay trace detected at 981 nm under pulsed excitation. The signal shows a sharp initial peak followed by a slow multiexponential decay. The decay after the initial peak was fitted with a stretched exponential function of the form \( I(t) = I_0 \exp\left(-t / \tau_3\right)^\beta_3 \), with a decay time \( \tau_3 = 2.38 \pm 0.07 \) μs and dispersion factor \( \beta_3 \).

FIG. 1. (Color online) PL spectrum of low-temperature-annealed Er-doped Si-rich SiO2 measured at 15 K. Emission from LC and Er3+ ions is indicated schematically on energy diagrams.

FIG. 2. (Color online) Time-dependent PL intensity at 981 nm under pulsed excitation (\( I_{pl} \), solid line) with the corresponding fit (\( N^{fit} \), dashed line), including the individual time-dependent contributions due to excitation by the fast (\( N_{fast}^{fit} \)) and slow (\( N_{slow}^{fit} \)) mechanisms. The Er3+ level diagram indicates possible excitation pathways. The inset shows the same data in the range of 0–27 μs.

FIG. 3. (Color online) Time-dependent PL intensity at 1535 nm under pulsed excitation (\( I_{pl} \), solid line) with the corresponding fit (\( N^{fit} \), dashed line), including the individual time-dependent contributions due to excitation by the fast (\( N_{fast}^{fit} \)) and slow (\( N_{slow}^{fit} \)) mechanisms. The Er3+ level diagram indicates possible excitation pathways. The inset shows the same data in the range of 0–27 μs.
that all emission at 1535 nm observed after the initial peak is due to Er$^{3+}$ emission from the first excited state. The similarity between the decay time of the second excited state (≈2.38 μs) and the duration of the slow excitation of the first excited state (≈2–3 μs) suggests that the slow excitation results from internal relaxation of the Er$^{3+}$ ion from the $^4I_{11/2}$ to the $^4I_{13/2}$ level.

Based on the experimental observations, it appears that the time-dependent emission from the first excited state [and thus its total population $N_2^{\text{tot}}(t)$] contains the two following contributions: emission from Er$^{3+}$ ions excited into the first excited state via a fast excitation mechanism ($N_2^{\text{fast}}$) and emission from Er$^{3+}$ ions excited via a slow excitation mechanism ($N_2^{\text{slow}}$) due to the relaxation of Er$^{3+}$ ions from the second excited state (characterized by the population $N_3$) to the first excited state. The time-dependent populations are described by the following rate equations:

$$\frac{dN_3(t)}{dt} = -\frac{N_3(t)}{\tau_3},$$

$$\frac{dN_2^{\text{flow}}(t)}{dt} = \frac{N_3(t) - N_2^{\text{flow}}(t)}{\tau_2},$$

$$\frac{dN_2^{\text{fast}}(t)}{dt} = -\frac{N_2^{\text{fast}}(t)}{\tau_2},$$

(1)

where $\tau_3$ is the decay time of the first excited state and $\tau_2$ is the relaxation time from the second to the first excited state. These equations lead to the following time-dependent total intensity $I_2^{\text{tot}}$ of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition:

$$I_2^{\text{tot}} \approx N_2^{\text{fast}}(0)e^{-(\beta_2)\tau_2} + \frac{N_3(0)}{\tau_2} \left[ e^{-(\beta_2)(\tau_3 - \tau_2)} - e^{-(\beta_2)\tau_3} \right],$$

(2)

where the dispersion factors $\beta_2$ and $\beta_3$ have been added to account for the multiexponentiality of the decay. Setting both dispersion factors to 1 reduces Eq. (2) to the analytical solution of Eq. (1). Fitting the trace measured at 1535 nm with Eq. (2) yields the following parameter values: $\tau_3 = 20.7 \pm 1.9$ μs, $N_3(0)/[\tau_2N_2^{\text{flow}}(0)] = (4.93 \pm 0.52) \times 10^5$ s$^{-1}$, $\tau_3 = 2.33 \pm 0.05$ μs, $\beta_2 = 0.49 \pm 0.01$, and $\beta_3 = 0.63 \pm 0.02$. The corresponding fit to the experimental trace and the respective time-dependent contributions to the population of the first excited state $N_2^{\text{fast}}$ and $N_2^{\text{slow}}$ are included in Fig. 3. The decay time $\tau_3 = 2.33$ μs found from this fit and the value $\tau_3 = 2.38$ μs found independently in Fig. 2 are equal within the experimental error. This observation provides strong support for the attribution of the slow excitation process to internal $^4I_{11/2} \rightarrow ^4I_{13/2}$ relaxation and not to a slow LC-mediated excitation process. Taking into account that $\tau_1^{-1} = \tau_3^{-1} + \tau_{12}^{-1}$, with $\tau_{12}^{-1}$ the relaxation rate from level $^4I_{11/2}$ to the ground state, we find that the relaxation time $\tau_{12}$ is longer than 2.3 μs. Time integration of the functions $N_2^{\text{fast}}$ and $N_2^{\text{slow}}$ yields a quantity proportional to the number of Er$^{3+}$ ions excited into the first excited state via the two excitation mechanisms. Performing this integration shows that ~45%–50% of the optically active sensitized Er$^{3+}$ ions are excited directly into the $^4I_{13/2}$ level by LCs, while ~50%–55% are excited into the $^4I_{13/2}$ after LC-mediated excitation of the $^4I_{11/2}$ level followed by internal relaxation of the Er$^{3+}$ ions. The presence of a large contribution of excitation via the $^4I_{11/2}$ level implies that the interval relaxation rate $\tau_{12}^{-1}$ will have a significant effect on the maximum net LC-mediated excitation rate of the $^4I_{13/2}$ level.

In summary, the mechanism of Er$^{3+}$ excitation in low-temperature-annealed Er-doped Si-rich SiO$_2$ was studied. Er$^{3+}$ excitation by LC was shown to occur directly into the $^4I_{13/2}$ level, as well as into higher lying levels, with a typical time constant of <27 ns. The presence of such a multilevel sensitization results in two types of excitation of the $^4I_{13/2}$ level of Er$^{3+}$: fast direct excitation ($\tau_1 < 27$ ns) by the LCs and slow excitation due to the fast excitation of Er$^{3+}$ ions into the higher energy levels with subsequent relaxation to the first excited state with a time constant $\tau_{12} > 2.3$ μs. It is shown that an approximately equal percentage of Er$^{3+}$ ions are excited into the $^4I_{13/2}$ level by the fast (45%–50%) and slow (50%–55%) processes.

This work was supported by the National Science Foundation Career No. ECCS-0644228. We are grateful to Dr. R. E. Peale for providing us with access to the Nd:YAG laser used in these studies.