Distance dependent interaction as the limiting factor for Si nanocluster to Er energy transfer in silica

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Si excess, Er content, and processing parameters have been optimized in a series of cosputtered oxide layers for maximizing Er emission and lifetime. The amount of excited Er as a function of the incident photon flux has been quantified for resonant (488 nm) and nonresonant (476 nm) excitations. Results show that a maximum of 3.5% of Er ions is excitable through the Si nanoclusters (Si-nc). This low value cannot be explained only by cooperative upconversion and/or excited state absorption. A short range (0.5 nm) distance dependent interaction model is developed that accounts for this low Er population inversion. The model points to the low density of Si-nc $[(3-5)\times 10^{17}\ \mathrm{cm}^{-3}]$ as the ultimate limiting step for indirect Er excitation in this system. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2362600]

Er-doped fiber amplifiers have set the standard for long-haul optical communications. Reducing their size and cost for an integration in local area networks presents considerable advantages which require overcoming serious difficulties. Thus, the production of Er-doped planar waveguide amplifiers (EDWAs) would allow their on-chip integration in complex photonic circuits. In 1994, it was discovered that the Er emission in silica is strongly enhanced by using Si nanocrystals (Si-nc) as sensitizers.[1] In pure silica, a tuned laser is needed for pumping the Er, and its small absorption cross section ($\sigma_{abs}\sim 10^{-21}\ \mathrm{cm}^2$) and lifetime ($\tau_{Er}$ approximately in milliseconds) stand for high fluxes of about $\phi_{1/2}=1/\sigma_{abs}\tau_{Er}=10^{23}$ photons/cm^2 s to reach optical transparency (inversion of 50% of Er ions within a quasi-two-level system). For an Er concentration $N_{Er}=1\times 10^{19}\ \mathrm{cm}^{-3}$, the maximum gain G expected in silica is thus $G=\sigma_{em}N_{Er}=0.17$ dB/cm, when we assume that the emission cross section $\sigma_{em}=\sigma_{abs}$. On the contrary, a broadband source can pump the Si-nc sensitizers; their high $\sigma_{abs}\sim 10^{-16}-10^{-17}\ \mathrm{cm}^2$ in the UV-vis range implies lower $\phi_{1/2}\sim 10^{18}$ photons/cm^2 s. In the past a debate about the value of the emission cross section of Er coupled to Si-nc raised: a first report gave $\sigma_{em}\approx 8\times 10^{-20}\ \mathrm{cm}^2$, which would allow to get up to 7 dB/cm with $N_{Er}=1\times 10^{19}\ \mathrm{cm}^{-3}$,[2] then another paper seemed to confirm these figures,[3] announcing 4 dB/cm for $N_{Er}\sim 10^{19}\ \mathrm{cm}^{-3}$ and a flux of 3.6×10^{18} photons/cm^2 s. Finally, we determined by insertion loss measurements that $\sigma_{abs}\approx 5\times 10^{-21}\ \mathrm{cm}^2$ at 1.54 μm.[4,5] These cross-section data indicate that $N_{Er}\approx 3\times 10^{20}\ \mathrm{cm}^{-3}$ is needed to reach $G=7$ dB/cm. Such high doping could be problematic, since for $N_{Er}\approx 6\times 10^{20}\ \mathrm{cm}^{-3}$ a significant part of the Er can be clustered.[6] By this discussion it emerges that $N_{Er}=(2-5)\times 10^{20}\ \mathrm{cm}^{-3}$ to avoid clustering and to have large gain. However, pump and probe measurements[4] on a Si-nc EDWA with $N_{Er}\approx 4\times 10^{20}\ \mathrm{cm}^{-3}$ showed signal enhancement of 1.06 dB/cm in strong resonant pumping conditions ($\phi\sim 6\times 10^{21}\ \mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ at 488 nm) that translated into an inversion factor of only 10% of the total Er population. This letter aims at addressing the reason for this small figure trying to answer the question of how much Er is coupled to Si-nc and, thus, whether the Si-nc are really efficient sensitizers.

A set of Er-doped Si-rich silica layers with 7% of Si excess and $N_{Er}=4\times 10^{20}\ \mathrm{cm}^{-3}$ (measured by Rutherford backscattering) was deposited by reactive magnetron sputtering on thermal oxide grown on Si substrates. A careful tuning was made of the processing conditions for maximizing Er emission intensity and lifetime by annealing at 900 °C in N_2 for times between 1 and 60 min. Increasing the annealing time results in a densification of the Si rich silica film. This leads to large refractive index because of Si clustering and to higher Er emission intensity and longer lifetime. Details of the processing and structural and waveguide characterizations are provided elsewhere.[7] Photoluminescence (PL) characterization was performed by exciting the samples with the 488 nm (resonant) and 476 nm (nonresonant) lines of an argon laser. The PL setup was calibrated using reference wafers provided by Corning with known Er concentration and the use of an integrating sphere and an optical spectrum analyzer. This allowed quantifying the absolute amount of emitting Er, i.e., N_2 that is the Er density in the metastable state.

Figure 1 reports the fraction of excited Er as a function of pumping flux (ϕ) in nonresonant excitation conditions for the various samples. We find a maximum value of $N_2/N_{Er}=3.5\%$ for the 60 min annealed sample at $\phi=5\times 10^{20}$ photons/cm^2 s. Consequently, there is a strong limiting phenomenon taking place since we expect a transparency flux as two orders of magnitude lower. It is worth to mention here that for resonant pumping we got a linear dependence of N_2 on ϕ (at high pumping fluxes), and from its

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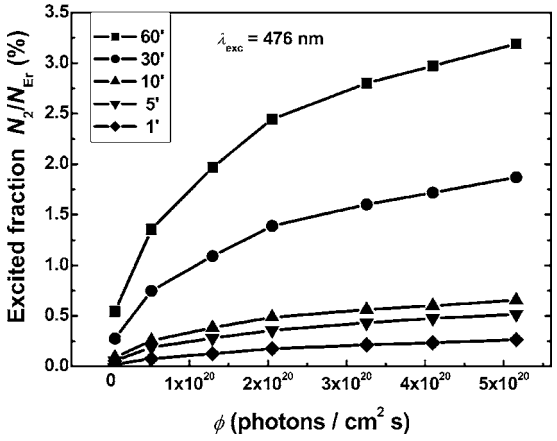

FIG. 1. Fraction of Er in the excited state as a function of incident flux at nonresonant excitation (476 nm) for the samples studied in this work.

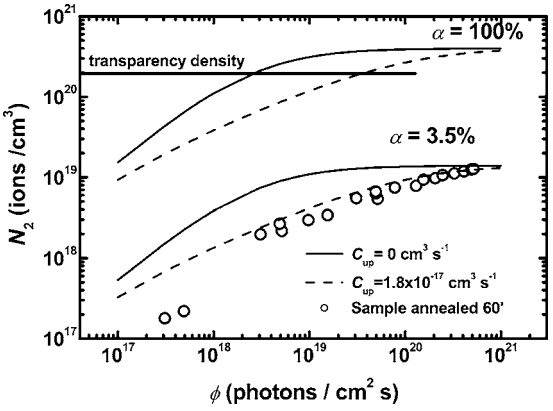

FIG. 2. Experimental data and simulation of the number of Er atoms in the excited state for sample annealed for 60 min. Solid curves account for the evolution without upconversion and a different percentage of Er coupled to the Si nanoclusters. Dashed curves included upconversion effects.

slope we deduced that all the Er introduced in the sample is optically active ($N_2 \sim N_{Er}\sigma_{abs}\tau_{Er}\phi$).

A model using rate equations and a quasi-two-level system for both Si-nc and Er provide a useful insight on the limiting phenomenon affecting the low number of excited Er. In the indirect excitation regime (low fluxes), the Si-nc pumps the Er proportionally to the number of excited Si-nc (N_{Si}^*) and to the number of Er ions in the fundamental state ($N_1=N_{Er}-N_2$). Population depletion of the first excited state, N_2, is accounted for by transition to the fundamental state (with rate τ_{Er}^{-1}) and cooperative upconversion (with rate $C_{up}N_2$), a nonradiative recombination in which the excited Er transfers the energy to another excited Er. We also include in the model the excited-state absorption (ESA), by which the Si-nc transfer the energy to Er ions already in the excited state (with a transfer coefficient K_{ESA}),

$$\frac{dN_2}{dt} = KN_{Si}^*N_1\frac{1}{1+(K_{ESA}N_2)/KN_1} - \frac{N_2}{\tau_{Er}} - C_{up}N_2^2. \qquad (1)$$

In Eq. (1), in addition to τ_{Er}, only three parameters rule the rate of excitation/deexcitation of N_2: K, the Si-nc to Er transfer rate (for which we use $K=3\times10^{-15}$ cm^3 s),[8] $K_{ESA}=1\times10^{-15}$ cm^3 s,[9] and the upconversion coefficient C_{up}. From lifetime measurements in these same samples as a function of the excited Er concentration ($1/\tau_{PL}=1/\tau_{Er}+C_{up}N_2$),[7] $C_{up}=(1-3)\times10^{-17}$ cm^3/s.[7,8]

In Fig. 2 we compare the experimental data for the 60 min annealed sample with N_2 given by Eq. (1). As N_2 is small and the term with C_{up} in Eq. (1) is squared, the contribution of upconversion is quite small. The main effect of upconversion is to increase $\phi_{1/2}$ from $\sim2\times10^{18}$ to $\sim4\times10^{19}$ photons/cm^2 s. The simulation curve does not reproduce the experimental data. Neither upconversion nor ESA helps in improving the agreement. In particular, if we consider the whole Er population coupled to the Si-nc, the relative strength of ESA with respect to indirect pumping of Er is given by the ratio $K_{ESA}N_2/KN_1$. By the literature data quoted before,[8–10] we find that ESA becomes relevant only for an Er inversion factor larger than 70%. We think that the main reason for the discrepancy between simulation and experiment is the assumption of the coupling of all the Er ions to the Si-nc. In fact, if we assume that only a fraction $\alpha=0.035$ of Er ions are effectively coupled to the Si-nc, the simulations reproduce the experimental data (see Fig. 2).

If we consider the rate equation [Eq. (1)] without making any assumption on the mechanism by which Er is pumped, we can define an effective excitation cross section σ_{eff} for Er in the following way:

$$\frac{dN_2}{dt} = \sigma_{eff}N_1\phi - \frac{N_2}{\tau_{Er}} - C_{up}N_2^2, \qquad (2)$$

hence

$$\sigma_{eff} = K\frac{N_{Si}^*}{\phi}\frac{1}{1+(K_{ESA}N_2)/KN_1}. \qquad (3)$$

σ_{eff} defined in this way includes both transfer to Er in fundamental state and ESA. It is calculated using Eq. (2) in steady state and N_2 experimental values and is found to depend strongly on ϕ. For excitation at 488 nm, σ_{eff} decreases from $\sim10^{-16}$ cm^2 at low fluxes to $\sim10^{-20}$ cm^2 at high fluxes as the number of indirectly excited Er saturates.[4,7,11,12] This is confirmed by the σ_{eff} extracted from the data of Fig. 1 and reported in Fig. 3. This result can be understood by considering that at low flux the Er are excited via the Si-nc while at high flux Er ions are not excited through the Si-nc, but are rather pumped directly. To model this and the small number of Er ions excited through the Si-nc even at low flux, we postulate that Si-nc transfers energy to Er ions with a transfer rate K which exponentially depends on the distance R between the Si-nc and the Er ion. Thus

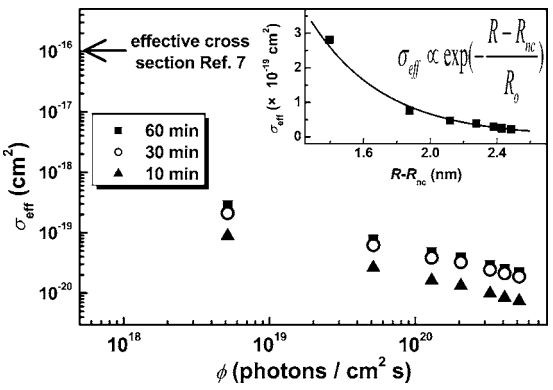

FIG. 3. Effective excitation cross section of Er as a function of the incident flux at 488 nm. The inset shows the representation of effective excitation cross section of sample annealed for 60 min as a function of the interaction radius. The characteristic distance obtained from that fitting is 0.44 nm.

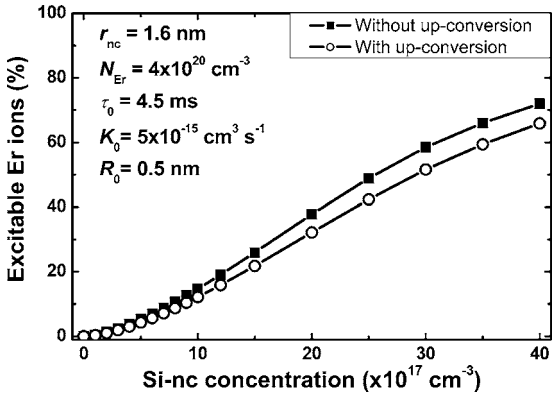

FIG. 4. Excitable Er fraction as a function of the concentration of sensitizers (Si nanoclusters) calculated from the distance dependent interaction model developed in this work.

$$K(R) = K_0 e^{-(R-R_{nc})/R_0}, \tag{4}$$

where R_{nc} is the Si-nc radius. Then if we assume that each Si-nc transfers its excitation to the closest unexcited Er ions it is possible to define an effective volume around each Si-nc which contains the excited Er ions. This volume will be defined by the interaction radius R which is

$$R = \left[\left(\frac{3}{4\pi} \frac{N_2}{N_{Si} N_{Er}} \right) + R_{nc}^3 \right]^{1/3}. \tag{5}$$

Then, by using Eq. (5) it is possible to translate $\sigma_{eff}(\phi)$ in a $\sigma_{eff}(R)$. This is shown in the inset of Fig. 3. The dependence of σ_{eff} on R can be fitted by an exponential with a parameter R_0=0.45 nm which has the meaning of a characteristic interaction length. This distance dependent interaction has been also suggested earlier in the literature with similar R_0 values.[13,14]

By using the interaction rate given by Eq. (4) and the modeling of Eqs. (1)–(3) we can evaluate the amount α (percentage of indirectly excited Er with respect to the total Er concentration) for $N_{Si}^* = N_{Si}$ and for a given distance R,

$$\alpha(R) = \frac{K(R) N_{Si}}{1/\tau_{Er} + K(R) N_{Si}}. \tag{6}$$

Then by spatial integration of Eq. (6), we get α as a function of N_{Si} (Fig. 4).

In order to compare the prediction of the model with the experimental data reported in Fig. 1, one needs to estimate the Si-nc density in our samples. By energy filtered transmission electron microscopy, we assess a Si-nc density in the range of $(3-5)\times 10^{17}$ cm^{-3}, quite close to values obtained by other authors.[15,16] For this Si-nc density we see in Fig. 4 that the model predicts a coupled Er fraction between 2.5% and 4.5%, in very good agreement with the data in Fig. 1. Optimum coupling conditions can be obtained by the extrapolation of Fig. 4 to 100% of excited Er which yields a Si-nc density of few 10^{19} cm^{-3} for the Er concentration considered here of about 4×10^{20} cm^{-3}. Then each Si-nc would excite 10–20 Er ions at most.

In summary, the distance dependent interaction model explains why only 3.5% of the total Er concentration is coupled to the Si-nc. These results have strong implications for the buildup of an optical waveguide amplifier with Si-nc and Er. A large effort is needed to engineer the material composition in order to increase the density of sensitizers (Si-nc) closely coupled to Er to accomplish the minimum 50% of their population inversion that is required for the achievement of optical gain.

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