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Energy transfer between amorphous Si nanoclusters and Er^{3+} ions in a SiO_2 matrix

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We report on the energy-transfer mechanism between amorphous Si nanoclusters and erbium ions in a SiO_2 matrix. We have studied a set of optimized samples which show maximum Er^{3+} to Si-nc coupling ratio. We demonstrate that the transfer mainly occurs to the $^4I_{11/2}$ level in less than 100 ns and that higher Er^{3+} energetic levels are not involved. Furthermore, we show that there are no traces of Auger back-transfer, excited state absorption, or pair-induced quenching mechanisms in our samples, leading us to propose a model in which the short interaction distance between Si-nc and Er^{3+} ions is the limiting factor for the noncomplete excitation of the whole Er^{3+} active population.

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Erbium (Er^{3+}) -doped SiO_2 sensitized by Si nanoclusters (Si-nc) material has great potential as an active medium to fabricate cheap complementary metal-oxide-semiconductor (CMOS) compatible waveguide amplifiers and lasers operating at the telecommunication wavelength, i.e., 1.55 μm.[1] As a result of an energy-transfer mechanism between Si-nc and Er^{3+},[2] the effective excitation cross section (σ_{exc}) of Er^{3+} enhances and broadens significantly when it is placed in the close vicinity of a Si-nc, passing from values of $10^{-20}-10^{-21}$ cm^2 at the Er absorption resonances to $10^{-16}-10^{-17}$ cm^2 over a wide spectral range.[3] The presence of Si-nc within the matrix thus offers the possibility of achieving total Er^{3+} population inversion by using low-power broadband light pumping sources or even by electrical pumping. In order to optimize this material, the concentration of optically active Er^{3+} susceptible to be excited indirectly and the energy-transfer probability have become fundamental parameters, being very much dependent on the fabrication conditions. Great efforts have been made in order to understand and optimize those key issues given that encouraging results of internal optical gain have already been reported some years ago.[4]

However, in the last years the expectations generated on this material have decreased after the publication of several reports revealing what seemed to be an intrinsic limit of the material itself. Previous studies suggested that only few percents (i.e., from 0.5 to 3%) of the optically active Er population are susceptible to be excited through energy transfer from the excitons generated within the Si-nc.[5–7] Indeed, a widely spread believe is that the limitations of the indirectly excitable Er content are imposed by processes like fast Auger back-transfer from excited Er ions to excitons in Si-nc,[8,9] excited-state absorption (ESA),[10] or Er pairs induced quenching.[6] Although the latter process can be eliminated by reducing the ion concentration, the two former mechanisms would be intrinsic properties of the material that could be controlled and, thus, reduced only by carefully engineering the Si-nc band structure.

When the annealing treatment after the deposition of the active material is performed at temperatures not greater than 900 °C, the situation becomes even more complex because only amorphous Si-nc are formed. Under these annealing conditions the indirect Er^{3+} excitation is improved.[11,12] In this case the nature of the sensitizers is still under debate. Indeed, it has been recently postulated an alternative explanation to the fast amorphous Si-nc mediated excitation of Er^{3+} one, in which the presence of excess-silicon-related luminescence centers could be the source of the transfer mechanism.[13]

In this Brief Report, we address the indirect excitation mechanism in a material that has one-two orders of magnitude higher (23%) optically active Er population efficiently coupled to Si-nc than it was previously reported. This value was determined by means of quantitative measurements of the excited-state population in the steady state.[14,15] We claim, based on several experimental evidences, that the limited interaction distance between Si-nc and Er^{3+} (Ref. 7) is nowadays the main constraining factor to achieve the complete excitation of the Er^{3+} population by indirect energy transfer.

The investigated layers have been fabricated by using an approach of rf reactive magnetron sputtering under argon-hydrogen mixture of 2 inches confocal pure SiO_2 and Er_2O_3 targets.[16] Here we will report about two samples: sample A (Si excess of 5%, Er^{3+} content of 3.4×10^{20} cm^{-3}, and thickness 1.2 μm) and sample B (same deposition conditions but without Er^{3+}).[17] Both layers were annealed at 910 °C during 60 min in pure nitrogen flow. A soda-lime 1.3-mm-thick sample supplied by Corning, doped with Er to a density of 0.5×10^{20} at/cm^3, was used as a reference (sample C).

CW-photoluminescence (PL) experiments were performed at room temperature by pumping with the 476 nm line of an Ar ion laser at a photon flux density (Φ) of 10^{18} ph/cm^2 s. The infrared time-resolved (TR) PL measurements have been done by pumping with the $\lambda_{pump}=355$ nm (3.49 eV) line of a Nd:YAG laser (pulse duration=6 ns) with $\Phi=10^{25}$ ph/cm^2 s during the pulse. The PL spectra were resolved with a monochromator and detected with an InGaAs photomultiplier tube (10 ns temporal resolution). The visible TR-PL measurements were detected by a charge-coupled device (CCD) streak camera with picosecond resolution interfaced with a spectrometer.

Figure 1 shows the cw spectra of samples A (black) and B (gray), which are modulated by an interference pattern originated by the light reflected back by the Si substrate. The

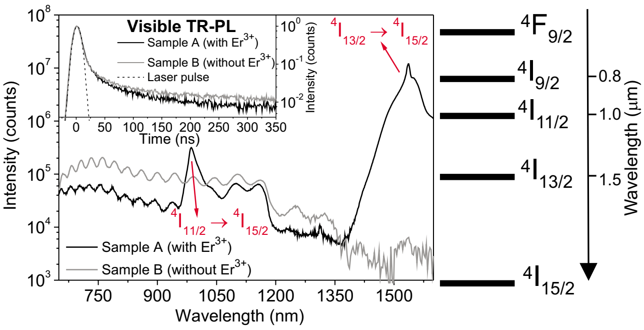

FIG. 1. (Color online) PL emission from sample A (black) and B (gray). The left inset shows the PL decay of the visible signal (0.65 to 0.95 μm) originated from the Si-nc in the first 350 ns. On the right, the Er^{3+} energy-level structure.

indirect energy transfer among Si-nc and Er^{3+} is demonstrated by two main facts: (1) the infrared transitions from $^4I_{11/2}$ to $^4I_{15/2}$ (0.98 μm) and from $^4I_{13/2}$ to $^4I_{15/2}$ (1.55 μm) are visible in sample A under nonresonant excitation; (2) the PL emission from about 0.7 μm to 0.95 μm associated to the excitonic radiative recombination in Si-nc is attenuated as a whole by about a factor 3 when Er^{3+} is included (sample A). In addition we note some contribution coming from the Si substrate at around 1.1 μm. Another interesting feature is about a faint emission observed for wavelengths longer than the Si band edge which is present in both samples, though weaker in sample A. The decrease in the emission due to Si-nc in sample A is also related with the appearance of a fast component in the exciton recombination dynamics. This is deduced by the visible TR-PL decays for samples A (black) and B (gray) shown in the inset of Fig. 1. Actually, the decay of sample B can be divided in two parts: (i) a slow process with a stretched exponential line shape (tens to hundreds of μs) that is typical of the spontaneous emission process in Si-nc;[18] and (ii) a fast decay (tens of ns) that is associated to Auger recombination mechanisms within the Si-nc since the CW-PL intensity depends sublinearly with pump power with an exponent of about 2/3.[19] The spectral dependence of the fast decay is very similar to that of the slow process. It is worth to note that the decay line shapes are almost independent on the observation wavelength. As it will be addressed afterwards the energy transfer from Si-nc to Er ions competes with the intraband relaxation mechanism within the Si-nc, and not with the exciton recombination. The PL decay speeds up in sample A during the first tens of ns as a consequence of the transfer process.

A further indication of the excitonic origin of the fast visible PL contributions is that the intensity of both fast and slow processes decrease when Er^{3+} is incorporated (sample A). As it will be demonstrated, Er^{3+} ions indirect excitation is very fast (tens of ns) and no slow transfer (μs) mechanism is observed. This is at odds with what claimed in Ref. 13: if the transfer mechanism does not involve Si-nc as reported in Ref. 13 then the reduction in the slow PL signal cannot be explained.

Infrared TR-PL measurements are summarized in Fig. 2. Slow (μs) contributions appear at 0.98 μm and 1.55 μm associated to indirectly excited Er^{3+} transitions,[20] while the silicon substrate contribution is present at about 1.1 μm. However, the most striking feature is the appearance of a very fast (tens of ns) signal that covers the whole analyzed spectral range. We have compared these two clearly different contributions by integrating the first 200 ns of the PL signal (curve with circles of the lower panel) and from 200 ns to 2 μs (curve with squares of the lower panel): the slow part follows the expected Er^{3+} emission spectrum, while the main part of the fast signal does not come from Er^{3+} since its spectral dependence is completely different. The right panel of Fig. 2 shows the PL decay line shape at 1.535 μm (gray), which is the maximum of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. Its line shape presents a fast decaying part followed by a slow rising one. In the same panel we show also the decay line shape at 1.3 μm (black), which does not correspond to any Er^{3+} transitions: it presents only a fast component. A similar observation has been reported recently,[9] however the suggested explanations did not fit our experimental observations.[21]

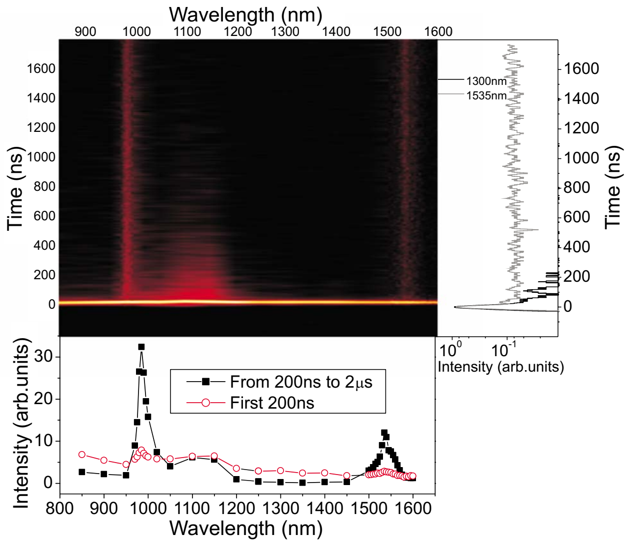

FIG. 2. (Color online) Spectral dependence of the TR-PL signal decay for sample A. The right panel shows the PL decays at 1300 nm (black) and at 1535 nm (gray). The bottom panel shows the spectral dependence of the integrated signal from 200 ns to 2 μs (black squares) and from 0 to 200 ns (red circles).

In Fig. 3 we show the temporal dependence of the spectrally resolved PL emission of sample B. In the right panel, it can be observed the usual μs decay of the $\lambda < 0.95$ μm signal and only a fast (tens of ns) component in the IR region. The spectral analysis of the first 200 ns after the pump pulse (lower panel) shows that the fast components of both sample A and B have very similar spectral dependences, just being that of sample B about three times more intense. This further demonstrates that the IR fast component is not related to the Er^{3+} presence in sample A. At this stage we can only speculate on its origin: recombination of defect centers either in the silica matrix or at the interface with the Si-nc or maybe to intraband recombination mechanisms that can lead to some light emission. It is also worth noting that the presence of Er^{3+} clearly quenches this emission so the transfer process appears to be a competitive process with that which gives origin to the fast IR component.

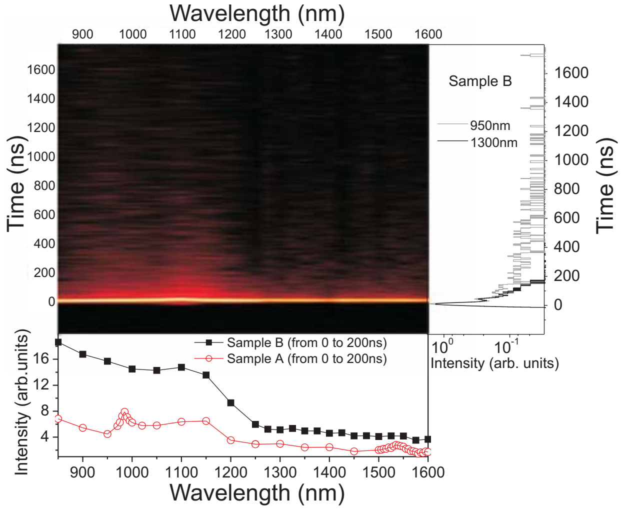

FIG. 3. (Color online) Spectral dependence of the TR-PL signal decay for sample B. The right panel the PL decay at 950 nm (gray) and at 1300 nm (black). The bottom panel shows the spectral dependence of the integrated signal from 0 to 200 ns for sample B (black squares) and from 0 to 200 ns for sample A(red circles).

Annealing the sample at high T (1100 °C for 1 h), i.e., promoting crystallization of the Si-nc, does not change the overall picture described by Fig. 2 and 3. A fast component is observed in the luminescence decay of the Er co-doped sample which has a spectral shape not related to the Er emission. This result suggests that the fast component is not related to the amorphous phase of the Si-nc. The temporal dependence of the 0.98 μm and 1.535 μm signals [Fig. 4(a)] allows getting some insights on the Er^{3+} levels involved in the resonant energy-transfer process. Neglecting the non-Er related fast contribution, the 0.98 μm signal is a single decaying exponential with 4.6 ± 0.2 μs lifetime. The maximum of the $^4I_{11/2}$ level population is achieved in less than 100 ns since the detected 0.98 μm signal is always decreasing after the first tens of ns as it is clearly shown in Fig. 4(b). This result is in agreement with the shortening of the decay in the Si-nc exciton dynamics (inset of Fig. 1). We thus conclude that the indirect excitation transfer time to this level is lower than 100 ns. We exclude both the presence of a slower (μs) transfer process and a repopulation due to relaxations from higher energetic levels since if it was the case a deviation from the single exponential behavior should be observed (the $^4I_{9/2}$ level lifetime, for example, is few μs). On the other hand, the 1.535 μm signal increases with a rise time of few μs and then decays with a ms long lifetime.

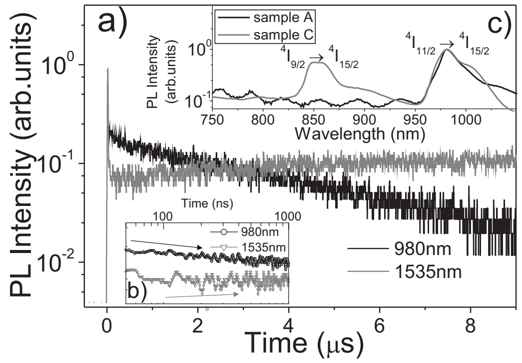

FIG. 4. Panel a) Integrated TR-PL decays at 0.98 μm (black) and 1.535 μm (gray) of sample B. Panel (b) Zoomed part of the 980 nm (black with circles) and 1535 nm (gray with inverted triangles) decays in the first μs. Panel (c) CW-PL signal from sample A (black) and sample C (gray) for the same Φ.

In order to better analyze these results, let us define N_3 and N_2 the populations of the $^4I_{11/2}$ and $^4I_{13/2}$ levels, respectively, being $N_3(t=0)$ the population just after the pump pulse. If we assume that N_2 is only due to the relaxation of N_3, after some simplifications the temporal dependence of N_2 reduces to

$$N_2(t) \approx N_3(t=0)(e^{-t/\tau_{21}} - e^{-t/\tau_{32}}), \tag{1}$$

where τ_{21} and τ_{32} are the lifetimes of the corresponding transitions, the former one being 5.5 ms independently of the Φ, as reported in Ref. 14 (pair induced quenching effects are thus very weak if present). From Eq. (1), N_2 cannot be higher than $N_3(t=0)$. We cannot strictly compare the two curves since the PL signals ($I_{PL,i\to1}$, i denoting the initial level) are inversely proportional to the radiative recombination probability ($I_{PL,i\to1}\alpha N_i/\tau_{rad,i\to1}$). However, it is clear that the 1.535 μm signal ($I_{PL,2\to1}$) is never higher than the initial 0.98 μm one ($I_{PL,3\to1}$) and that the extracted τ_{32} (2–5 μs) is comparable to the 0.98 μm signal lifetime extracted before. This result means that the $^4I_{13/2}$ level is populated mainly by the de-excitation of the $^4I_{11/2}$. Although we cannot exclude, in addition to the previous process, the presence of a slightly faster transfer process (no faster than 1 μs) that populates directly the $^4I_{13/2}$ level, its impact would be at most of the same order of importance than the transfer to the $^4I_{11/2}$ level. On the basis of all the results showed up to now we do not have any evidence that the energy could be transfer back to the Si-nc; hence, no signs of Auger back-transfer mechanisms are detected, in contradiction to what claimed in Refs. 8 and 9.

Figure 4(c) reports the comparison between the CW-PL measurements of sample A and sample C under the same pumping conditions, being the signals normalized to the 0.98 μm emission. It is evident the absence of emitted light at about 0.82 μm due to the $^4I_{9/2}\to{}^4I_{15/2}$ transition in sample A. This is a further support to our previous conclusion that the transfer is not occurring to levels higher than the $^4I_{11/2}$. Moreover, since the signal coming from higher levels is totally absent, ESA mechanisms are not relevant, contrary to what proposed in Ref. 10.

Having excluded Auger back-transfer, ESA and induced pair quenching as the main limiting issues to achieve population inversion, we propose a model in which the short-range energy-transfer interaction distance (~0.5 nm) between Si-nc and Er^{3+} (Ref. 7) restricts the Er^{3+} content indirectly excitable via the Si-nc to 23%.

Even though we have demonstrated that the transfer occurs mainly to the $^4I_{11/2}$ level, it has been measured that the PL signal coming from Si-nc attenuates with no spectral dependence. We believe that this is a consequence of the carrier intraband recombination nature of the transfer, which competes with the thermal intraband relaxation process. As predicted by Allan *et al.*[22] the energy gap in amorphous Si clusters can be even below that of crystalline silicon, allowing high energetic intraband transitions that could fit with the required excitation energy. The nature of the transfer mechanism would be much faster than the predicted by a Förster type one (dipole-dipole interaction).[9] In addition, the presence of Auger processes within the Si-nc re-excite carriers to levels from which they could transfer again, effectively decreasing the population of the Si-nc emitting levels and speeding up the visible PL. Thus, Auger mechanisms could be considered more as a feedback than a detrimental process. They are effective until the carrier population in the emitting level decreases to a point in which Auger is no more a probable process, so relaxation occurs through other intrinsic interband recombination paths.

In conclusion, we have performed a thorough experimental study of the transfer mechanism in Er-doped SiO$_2$ sensitized by amorphous Si-nc, determining that only fast transfer mechanisms are present with transfer times lower than 100 ns and that the transfer mainly occurs to the $^4I_{11/2}$ level. From these results, we also conclude that there is no appreciable sign of fast Auger back-transfer, ESA, or pair-induced quenching mechanisms in our samples and, hence, these processes are not immediate issues to be addressed. These findings are related to the high optically active Er^{3+} content indirectly excitable (23%) we have reported recently,[14] which could be improved by placing the Er^{3+} ions close to the Si-nc surface according to a model in which the limited interaction distance between Si-nc and Er^{3+} is the limiting factor.

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[21] Weak peaks at 0.98 μm and 1.55 μm appear in the first 200 ns associated to the recombination of indirectly excited Er^{3+} ions.

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