Role of the Si excess on the excitation of Er doped SiO_x

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The authors have investigated the role of the Si excess on the photoluminescence properties of Er doped substoichiometric SiO_x layers. They demonstrate that the Si excess has two competing roles: when agglomerated to form Si nanoclusters (Si-nc's) it enhances the Er excitation efficiency but it also introduces new nonradiative decay channels. When Er is excited through an energy transfer from Si-nc's, the beneficial effect on the enhanced excitation efficiency prevails and the Er emission increases with increasing Si content. However, when pumped resonantly, the Er luminescence intensity always decreases with increasing Si content. These data are presented and their implications are discussed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734505]

Erbium doped Si nanoclusters (Si-nc's) immersed in a SiO_2 matrix have recently attracted the interest of the scientific community as a promising light source at 1.54 μm.[1–4] In fact, *e-h* pairs photoexcited in Si-nc's can decay nonradiatively by preferentially transferring their energy to a nearby Er ion which, in turn, decays by emitting a 1.54 μm photon. Luminescence intensities that are two orders of magnitude higher than in Er doped SiO_2 have been measured at room temperature[2] as a result of an increased Er excitation cross section with respect to direct photon absorption.[5] Moreover, it has been demonstrated[6] that Er is more efficiently excited if the Si excess is agglomerated to form a network of amorphous and interconnected Si-nc's instead of well separated ones, probably because the Er–Si-nc's distance is strongly reduced. In spite of the observed strong enhancement, several different reports[7–10] claim that the maximum fraction of excited Er ions in SiO_x layers is below 10%. Several different motivations have been given to explain the data. Pellegrino *et al.*,[8] for example, attribute the reduced fraction of excited Er to the small number of Er ions falling within the interaction volume around Si-nc's, while Oton *et al.*[9] consider the excited state absorption as the main likely cause.

In this letter we provide an additional point of view. In fact, by studying the luminescence properties of Er doped SiO_x layers having different Si contents, we are able to demonstrate that the Si excess has a double role. In fact it enhances the Er excitation efficiency due to the sensitization role of the Si-nc's, but, on the other side, introduces nonradiative decay channels that compete with the Er radiative relaxation. Therefore the maximum Er fraction that can be excited is a compromise between the beneficial role of energy transfer from Si-nc's (that is stronger with increasing the Si excess) and the detrimental role of defects (that reduces the Er luminescence lifetime with increasing Si content). These data are presented and discussed.

Substoichiometric SiO_x layers (with total Si concentration in the range of 35–44 at. %), 200 nm thick, were deposited by plasma enhanced chemical vapor deposition on top of a Si substrate. The details of the experimental procedure can be found elsewhere.[11] After deposition the samples were implanted with 300 keV Er ions to a dose of $5\times10^{14}/cm^2$ and finally a thermal treatment at 900 °C for 1 h under N_2 atmosphere was performed to eliminate the residual defects leftover by the implantation process and to activate Er. We[6] have demonstrated that under these experimental conditions, the Si excess is agglomerated as a network of very small and interconnected amorphous Si-nc's and that the energy transfer from Si-nc's to Er is optimized.

Photoluminescence (PL) measurements were carried out by pumping with the 476.5 nm line of an Ar^+ laser or the 980 nm line of a Ti:sapphire laser. The laser beam was chopped at a frequency of 11 Hz through an acousto-optic modulator or a mechanical chopper. The luminescence signal was focalized on the aperture of a single grating monochromator and detected by a liquid nitrogen cooled Ge detector or a Hamamatsu infrared-extended photomultiplier tube. Finally the signal coming from the detector was measured by a lock-in amplifier using the chopper frequency as a reference in order to improve the signal to noise ratio. Luminescence lifetime measurements were performed by monitoring the decay of the PL signal at 1.54 μm after pumping to steady state and switching off the laser beam. The overall time resolution of our system is of 30 ns. Photoluminescence excitation (PLE) spectroscopy measurements were performed by exciting the samples with a Xe lamp coupled to a single grating monochromator (in the wavelength region of 420–600 nm) or a Ti:sapphire laser pumped through a laser diode at 532 nm (in the wavelength region of 700–1020 nm).

In order to understand how the Si excess concentration can affect the process of energy transfer to Er, we have studied the PLE spectra of samples having the same Er content but different Si concentrations. In Fig. 1 the PL intensity at 1535 nm is reported as a function of the excitation wavelength for all the samples. It is interesting to note that, with the only exception of the sample with the lowest Si content (35 at. %) for which Er direct excitation is the dominant process (and indeed a clear peak at around 520 nm due to the

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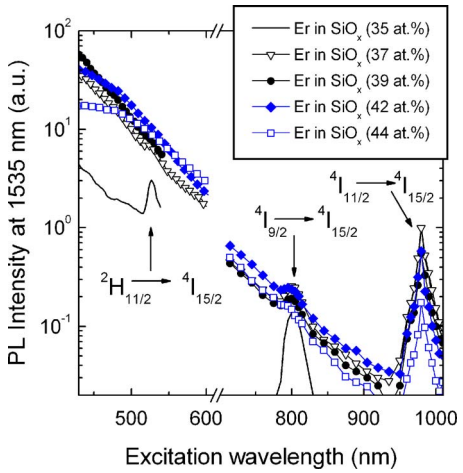

FIG. 1. (Color online) Photoluminescence intensity at 1535 nm vs excitation wavelength for SiO_x samples having the same Er content and different Si excesses. The observed Er direct transitions are indicated.

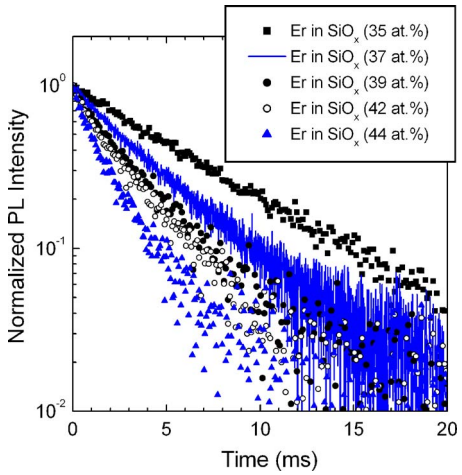

FIG. 2. (Color online) Measurements of the time decay of the PL signal at 1535 nm for SiO_x samples having the same Er content and different Si excesses. The excitation wavelength and power were 476.5 nm and 10 mW, respectively.

$^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition is superimposed to the background), in all of the other samples the PL signal monotonically decreases with increasing the excitation wavelength resembling the absorption from Si-nc's. This demonstrates that in these samples Er is excited through a carrier-mediated process. Only at wavelengths higher than 770 nm, when the absorption from Si-nc's starts to be negligible, a contribution of direct photon absorption is visible at 800 nm (corresponding to the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition) and at 980 nm (corresponding to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition). Moreover, while pumping at 980 nm (where Er is excited only through direct photon absorption) the 1535 nm PL intensity is stronger for the samples with the lower Si contents (35 and 37 at. %), in the wavelength range where carrier-mediated pumping is operative, the PL intensity is generally maximum for the samples with higher Si concentrations and an optimum Si content exists at each excitation wavelength. These results are observed, in spite of the fact that the Er content is the same for all the samples and, as we will demonstrate, can be attributed to a balance between Si-nc's sensitization and nonradiative decay processes. These data show that the Si excess has a very important role in determining the Er emission, both under direct and carrier-mediated excitations with an opposite behavior in the two cases. In order to understand what is going on, we have measured the time-decay curves of the PL signal at 1535 nm after switching off the laser beam and the results are reported in Fig. 2. The excitation wavelength was 476.5 nm (therefore out of resonance with the Er energy levels) and the pump power was 10 mW. In spite of the fact that the Er amount is the same in all of the samples, the time-decay curves are very different from one sample to another and in particular we have found that the Er PL decay time strongly decreases with increasing Si content. For the sample with the lowest Si content (35 at. %) the decay time curve can be fitted by a single exponential and a lifetime of about 6 ms. The time-decay curves for all of the other samples are characterized by a stretched exponential shape.[12] By fitting the data we have found that both the decay lifetime τ and the dispersion factor β strongly decrease with increasing the Si concentration. For example, in the sample with 44 at. % the fitting procedure gives τ=1.44 ms and β=0.73. Values of β smaller than 1 indicate that a spread of Er decay lifetime due to different Er sites is present in these samples. It should be noted that we have observed this strong decrease of the Er PL lifetime with increasing the Si concentration also in samples in which a thermal treatment at 1250 °C for 1 h was performed prior to Er implantation. In these samples the Si-nc's are larger and well separated. Indeed in these two sets of samples at a fixed Si content the Er lifetime is the same independently of the annealing process. Therefore it seems that it is not important how the Si excess is agglomerated, the only crucial parameter being its concentration.

In Fig. 3(a) the PL intensity at 1535 nm measured either by pumping with the 476.5 nm (carrier mediated) or with the 980 nm (resonant) laser line is reported as a function of the total Si concentration. While under carrier-mediated pumping the PL signal increases with increasing Si content and eventually slightly decreases only for the highest Si concentration, under resonant pumping the PL intensity at 1535 nm monotonically decreases with increasing Si. In the same figure (right hand scale) the 1535 nm Er PL decay lifetime values (as obtained by fitting the curves reported in Fig. 2) are reported. These data are compared with the lifetime of the Si-nc's luminescence measured at 700 nm in similar samples not implanted with Er (multiplied by a factor of 200 to allow the comparison). Note that, since we are measuring the decay time at a fixed wavelength (700 nm), we are observing the behavior of Si-nc's having the same size in samples with different Si excesses. The trend of the Si-nc's and Er lifetimes as a function of the Si content is identical demonstrating once again that the Si amount is the key parameter in determining the PL properties of the material (both Er doped and undoped). It is clearly interesting to note that the trend of the lifetime values versus Si content resembles that of the resonantly pumped Er PL intensity.

In order to better understand the role of the Si-nc's on the Er luminescence we have reported in Fig. 3(b) the ratio between the PL intensity at 1535 nm and the decay lifetime under both carrier mediated (476.5 nm) and resonant pumping (980 nm) as a function of the Si concentration. In the linear excitation regime we have

$$I_{\mathrm{PL}} \propto \frac{\sigma N_{\mathrm{Er}} \tau}{\tau_{\mathrm{rad}}},$$

σ being the effective excitation cross section, N_{Er} the optically active Er content, τ the lifetime, and τ_{rad} the radiative

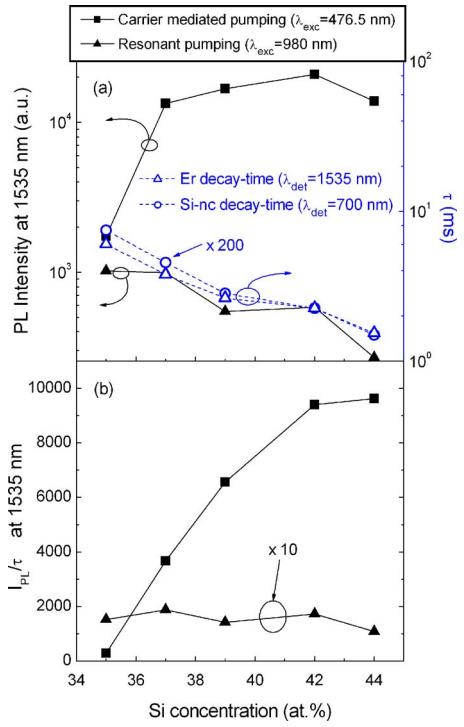

FIG. 3. (Color online) (a) (Left hand scale) Photoluminescence intensity at 1535 nm for SiO_x samples having the same Er content as a function of the Si concentration in the matrix. Data were taken under both carrier mediated (solid squares) and resonant (solid triangles) pumping. (Right hand scale) Decay lifetime of the PL signal at 1535 nm for Er doped SiO_x films (open triangles) and of the PL signal at 700 nm for undoped SiO_x layers (multiplied by a factor of 200 to allow the comparison) as a function of the Si concentration. (b) Ratio between the PL intensity and the decay lifetime at 1535 nm for SiO_x samples having the same Er content and different Si excesses as a function of the Si content. Data were taken under both carrier mediated (solid squares) and resonant (solid triangles) pumping. Data for resonant excitation are multiplied by a factor of 10 to allow the comparison.

lifetime. The ratio I_{PL}/τ gives therefore information on the product between σ and N_{Er}. While under 980 nm pumping (when Si-nc's have no role on the Er excitation) the I_{PL}/τ ratio is almost flat indicating that the observed decrease in the PL intensity can be fully ascribed to a reduced decay lifetime with no effect on σ and N_{Er}, under carrier-mediated pumping I_{PL}/τ (and therefore σN_{Er}) monotonically increases with increasing the Si concentration and eventually saturates. For the highest Si content, I_{PL}/τ (and hence σN_{Er}) increases by a factor of 100 in the case of carrier-mediated pumping with respect to resonant pumping. Since the excitation cross section σ for Er carrier-mediated pumping is three orders of magnitude higher than for resonant excitation,[5] these data indicate that, even if the Er ions are all optically active, the fraction sensitized by Si-nc's is only of the order of a few percent.

All of these data demonstrate that the presence of Si in the SiO_2 matrix has two competitive roles on the Er optical properties: it introduces nonradiative decay channels that produce a decrease of the Er decay lifetime (for all Er ions), and at the same time it increases the excitation cross section of a fraction (of the order of the percent) of the rare earth ions. These two effects act in opposite directions as the Si content increases. Therefore under resonant pumping Si-nc's are always detrimental. Under carrier-mediated pumping, the major limitation is that, though all Er ions are optically active, the fraction of Er ions that can be successfully excited through Si-nc's is rather small. Increasing this fraction is imperative to take full advantage of the sensitizing action of Si-nc's and make use of this system for the fabrication of optical amplifiers.

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