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Influence of the silicon nanocrystal size on the 1.54 μm luminescence of Er-doped SiO/SiO₂ multilayers

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The influence of the silicon nanocrystal (Si-nc) size on the erbium luminescence at 1.54 μm was studied in Er-doped silicon oxide thin films containing Si-nc. Er-doped and undoped SiO/SiO₂ multilayers were prepared to control the Si-nc size. The results showed that the Er luminescence was due to an energy transfer process between Si-nc and Er ions. The proportion of Si-nc which couples with Er was dependent on the Si-nc size and the energy transfer process is maximal for a size equal to 4 nm. This preferentially coupling effect is interpreted by the existence of an optimum overlap between the Si-nc emission spectrum and the ⁴I_{9/2} multiplet of Er ions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3057386]

Er-doped silicon-based materials have attracted much attention in the scientific community because of their potential use for optoelectronics.¹ Indeed, Er³⁺ ions can emit sharp luminescence at 1.54 μm , which is the commonly used wavelength for optical communications. Er³⁺ ions can be efficiently excited through electron-hole pairs recombination or by impact of energetic carriers in crystalline silicon.^{2,3} However, such systems present a strong temperature quenching which is due to Auger dissociation of electron-hole pairs and energy backtransfer to silicon. In silica containing Si-nc, the Er-related photoluminescence (PL) is strongly improved due to a strong energy transfer from Si-nc to Er³⁺ ions.^{4–6} The Er³⁺ ions can then be indirectly excited by Si-nc that have an absorption cross section several orders of magnitude higher than that of direct Er excitation. The photogenerated excitons in Si-nc can either transfer their energy to Er³⁺ ions or give rise to a luminescence in the visible range.^{7,8} Moreover, the Er nonradiative backtransfer de-excitation process is strongly reduced in these materials. However, to obtain efficient optical amplifier, the 1.54 μm luminescence intensity has to be improved. Different quenching processes contribute to reduce the luminescence efficiency as cooperative up conversion⁹ or excited state absorption.¹⁰ Moreover it has been reported that only a small fraction of Er can be indirectly excited by Si-nc, with values around 1% or lower. This low value is attributed to the very short interaction distance between Si-nc and Er³⁺ ions needed for the energy transfer process.¹¹ This result would implicate the necessity to obtain a greater density of sensitizers, which would involve in systems preferentially containing Si-nc as small as possible. However, the influence of the Si-nc size on the coupling efficiency is not very clear. In fact, if a preferential coupling with some particular Si-nc size exists, the small fraction of Er excited through Si-nc could be due to the size distribution of Si-nc. Some authors have shown that the Er-related luminescence is a decreasing function of the Si-nc size, which is interpreted by a better energy transfer to the Er³⁺ ions for smaller Si-nc.¹² Time-resolved (TR) luminescence experi-

ments have also suggested that the energy transfer rate was greater for smaller Si-nc.¹³ However another study has shown that Si-nc with a size equal to 4 nm could be more efficient sensitizers than Si-nc of 2 nm diameter, because of a higher absorption cross section.¹⁴

In this study, the influence of the Si-nc size on the Er-related luminescence is investigated. In a previous paper,¹⁵ we have shown that a good control of the Si-nc size can be achieved by using SiO/SiO₂ multilayer structures. SiO/SiO₂ and Er-doped SiO/SiO₂ multilayers were obtained by successive evaporation of SiO powder and of fused silica glass on silicon substrates at 100 °C. The SiO active layer varies from 2 to 4 nm, whereas the SiO₂ barrier thickness is maintained equal to 5 nm. Both SiO and SiO₂ deposition rates were controlled by a quartz microbalance system and were equal to 1 Å/s. The Er doping was performed from an effusion cell during the deposition of the SiO and the SiO₂ layers. The temperature cell was calibrated by the quartz microbalance allowing us to fix the Er concentration at 0.8 at. %. For all samples, the total film thickness is equal to 200 nm. The samples were then annealed at 1050 °C in a vacuum pressure better than 10^{−6} Torr to form the Si-nc. The size of the Si-nc is well controlled by the multilayer structure and the mean size is very close to the SiO layer thickness. Moreover the size dispersion is narrow, allowing us to study the influence of the Si-nc size on the luminescence properties of Er. However, for SiO thickness greater or equal to 5 nm the size distribution becomes very broad and the Si-nc size is not controlled anymore. More details on the structural study are given in Ref. 15.

Photoluminescence experiments were performed at room temperature. For the steady state experiments in the visible range, the excitation was obtained with a 200 W mercury arc lamp source, using the ultraviolet lines at 313 and 334 nm. The PL signal was analyzed by a monochromator equipped with a 150 grooves/mm grating and by a charge-coupled device camera detector cooled at 140 K. For the experiments in the near-infrared domain, the sample was excited by a 30 mW He–Cd laser using the 325 nm line. The PL signal was analyzed by a monochromator equipped with a 600

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FIG. 1. Influence of the Si-nc size on the room-temperature PL spectra of Si-nc for the undoped samples (continuous line) and for Er-doped samples (line with symbols ■).

grooves/mm grating and by a photomultiplier tube cooled at 190 K. For the TR-PL experiments, the sample was pumped by the 355 nm line of a frequency-tripled yttrium aluminum garnet:Nd laser. The laser pulse frequency, energy, and duration were typically equal to 10 Hz, 50 μ J, and 20 ns, respectively. The detection system is the same as that used for the experiments in the near-infrared domain. The rise time of the detector is equal to around 10 ns. The response of the detection systems was precisely calibrated with a tungsten wire calibration source.

The PL in the range of 500–1000 nm is shown in Fig. 1 for the undoped and Er-doped samples, for different Si-nc sizes. The spectra show the typical broad PL band attributed to the radiative recombination of confined excitons in Si-nc. The energy of the PL is clearly a decreasing function of the size. For the undoped samples, the maximum of the PL band varies from 750 to 855 nm for Si-nc size varying from 2 to 4 nm. The Er-doped samples show a weaker PL intensity in this wavelength range. As shown in a previous study, the Er-related PL is not present in the as-deposited samples.¹⁶ This PL appears only for high annealing temperatures, corresponding to the appearance of Si-nc. For all the annealed samples, the 1.54 μ m PL band corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ intra- $4f$ transition of Er^{3+} ions is observed. As shown in Fig. 2, the Er-related PL intensity is an increasing function of the Si-nc size in the size range studied here. As the proportion of Er-doped SiO is higher for multilayers containing large Si-nc, the PL intensity values have been divided by the total SiO thickness in order to suppress the effect of the analyzed quantity of matter. PL decay time experiments were also performed at wavelengths corresponding to the maximum of the Si-nc PL band. The PL decay time curves are represented in Fig. 3 for the undoped and Er-doped samples, for Si-nc equal to 2 and 4 nm. The experimental curves show the characteristic stretched exponential decay of

FIG. 2. Room-temperature PL spectra at 1.54 μ m for the Er-doped samples with different Si-nc diameters.

Si-nc. In agreement with the quantum confinement theory, the decay time is shorter for the sample containing Si-nc with 2 nm diameter than that with Si-nc of 4 nm. It is also observed that Er doping involves in a decrease in the decay time. By fitting these decay curves with a stretched exponential function, the characteristic decay time is found around two times lower for the Er-doped samples. Such a decrease can be explained by the energy transfer toward the Er^{3+} ions, as already observed in the literature.¹² Therefore, the decrease in the Si-nc PL intensity and of the Si-nc decay time when Er is present and the existence of the Er PL only when Si-nc are present allows us to conclude that Er is indirectly excited by Si-nc.

The weak decrease in the PL decay time and the existence of remaining Si-nc related PL after doping suggest that some Si-nc are weakly coupled or non coupled to Er ions, as already suggested in previous works.^{4,13} The remaining Si-nc related PL can be used to quantify the proportion of Si-nc contributing to the energy transfer process. The experimental results shown in Fig. 1 demonstrate that, by increasing the Si-nc size, the residual PL band in presence of Er^{3+} is less important with respect to the PL of the corresponding undoped sample. As the undoped and doped samples have been prepared with the same preparation parameters, the decrease

FIG. 3. Transient of the Si-nc PL for Si-nc with diameter equal to 4 and 2 nm measured at 855 and 750 nm, respectively, for the undoped (■) and Er-doped (○) samples.

FIG. 4. Coupling efficiency parameter ζ estimated for different Si-nc sizes. The inset shows the normalized Si-nc related PL for the undoped samples and the position of the $^4I_{9/2}$ energy level of Er.

in the Si-nc PL intensity can be mostly attributed to the energy transfer process. Hence a quantitative evaluation of the coupling efficiency ζ between Er^{3+} ions and Si-nc can be expressed by the ratio between the integrated intensities of the Si-nc PL. If we assume that the total loss of the PL intensity at the Si-nc wavelength emission corresponds to an energy transfer toward Er^{3+} ions, the coupling efficiency ζ can be expressed by the following:

$$\zeta = \frac{\text{PL}_{\text{nc-Si}} - \text{PL}_{\text{nc-Si}}^{\text{Er}}}{\text{PL}_{\text{nc-Si}}} \times 100,$$

where $\text{PL}_{\text{nc-Si}}$ and $\text{PL}_{\text{nc-Si}}^{\text{Er}}$ are the integrated Si-nc related PL band for the undoped and Er-doped samples, respectively. The size dependence of ζ is shown in Fig. 4. The proportion of Si-nc that couples with Er^{3+} ions increases by increasing the Si-nc size and becomes close to 100% for the Si-nc size equal to 4 nm, while the value of the coupling efficiency is only around 15% for the sample containing Si-nc of 2 nm. According to the parameter ζ , it must be noticed that the proportion of Si-nc which present a coupling effect is ten times higher for the samples with Si-nc size equal to 4 nm compared to that with Si-nc with a size of 2 nm, whereas the Er-related PL intensity is only four times higher. The decay time at 1.54 μm has also been measured and no significant size dependence has been measured. For all the Er-doped samples, the decay time measured at 1.54 μm is around 1.7 ms and the size dependence of the 1.54 μm PL intensity cannot be explained by differences in decay times. However it was recently shown that Er^{3+} excited state absorption process could be one of the main reasons explaining the weak fraction of luminescent Er^{3+} ions.¹⁰ If a preferential energy transfer exists for the Si-nc having a diameter equal to 4 nm, the excited state absorption is likely to exist also preferentially for this diameter, leading to a weak Er luminescence even if the energy transfer is high.

The more efficient energy transfer for the sample containing large Si-nc could be explained by the shortening of the Er-Si-nc distance. However, as the silicon excess is the same for the SiO layers of all the samples, the number of Si-nc is a decreasing function of the Si-nc size. Assuming Er^{3+} ions are homogeneously distributed in the layers, the

increase in the coupling with the Si-nc size cannot be induced by the shortening of the Er-Si-nc distance. However the size-dependent energy of the confined electron-hole pair could be taken into account. Indeed, the overlap between the emission spectrum of the Si-nc and the energy levels of the $^4I_{9/2}$ multiplet is Si-nc size dependent. Assuming the transition between the ground state and the third excited state of the Er^{3+} ion give rise to an energy around 1.5 eV (830 nm), the overlap is better for Si-nc with a size in the range of 3–4 nm, as shown in the inset of Fig. 4. In this case, the weak value of ζ for the Si-nc with a diameter below 3 nm could be explained by the large energy mismatch between the Si-nc PL energy and the $^4I_{9/2}$ multiplet of Er. If the dipole-dipole interaction or the exchange interaction processes are the mechanisms of the energy transfer between Si-nc and Er, this overlap could play a major role in the transfer efficiency.

In summary, the influence of the Si-nc size on the energy transfer from Si-nc to Er^{3+} ions has been investigated. Undoped and Er-doped SiO/SiO₂ multilayers were prepared by evaporation, to control the size of Si-nc and to obtain a weak size distribution. The Er-related PL band at 1.54 μm is attributed to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ intra-4f transition of Er^{3+} ions, indirectly excited by Si-nc. The proportion of Si-nc which couples with Er^{3+} ions was quantified by analyzing the doping-induced decrease in the Si-nc related PL band. The quenching of this PL band, due to the energy transfer process to Er^{3+} ions, is Si-nc size dependent. The coupling seems to be more efficient for the Si-nc with a diameter greater or equal to 3 nm. This result is interpreted by the existence of an optimum overlap between the emission spectrum of Si-nc and the transition from the ground state to the third excited state of Er^{3+} .

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