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Direct and indirect excitation of Nd^{3+} ions sensitized by Si nanocrystals embedded in a SiO_2 thin film

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The luminescence properties of Nd-doped SiO_x layers containing silicon nanocrystals (Si-ncs) were investigated by steady state, time-dependent and power-dependent photoluminescence spectrometry and photoluminescence excitation experiments. Both direct and indirect excitation processes of Nd^{3+} ions have been evidenced. The energy transfer mechanism between Si-ncs and Nd^{3+} ions is favored by the overlap between the emission spectrum of confined excitons in Si-ncs and the Nd^{3+} absorption from the ground state to $^4F_{5/2}$ electronic level. The more intense Nd-related emission was obtained in samples containing 0.5 at. % of Nd and characterized by an indirect excitation cross section equal to 8×10^{-15} cm^2. © *2011 American Institute of Physics*. [doi:10.1063/1.3667286]

I. INTRODUCTION

To circumvent the inability of bulk silicon (Si) to emit light, great efforts have been devoted to the study of light emitting Si nanostructures.[1] Doping with optically active ions is an alternative approach to obtain optical emission from Si-based materials.[2] In particular, because of their potential use for telecom applications, Si-based materials doped with Er^{3+} ions have been strongly investigated. In the presence of silicon nanocrystals (Si-ncs), the Er-related PL at room temperature is strongly improved, which is attributed to a strong coupling between Er^{3+} ions and Si-ncs.[3,4] The Er^{3+} ions can then be indirectly excited by Si-ncs that have an absorption cross section several orders of magnitude higher than that of direct Er excitation. Few models describing an energy transfer from the exciton in Si-ncs to the Er^{3+} ions were proposed.[5–7] In these models, photogenerated excitons in Si-ncs can either transfer their energy to Er^{3+} ions or give rise to a luminescence in the visible range. Similarly to the case of erbium, Nd^{3+} ions present several technologically important luminescent bands including the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ 4*f*-shell transitions which are, respectively, the basis of 1.06 μm Nd lasers, a second lasing transition at 900 nm, and a 1.3–1.4 μm band in the second optical fiber transparency window. The transitions at 900 nm and 1 μm also render Nd^{3+} ions suitable for photovoltaic applications. Indeed Nd^{3+} doped Si-based materials could be used as down-converter layers, allowing the photonic conversion of ultraviolet photons to near infrared ones. Similarly to Er, Nd is a good candidate to benefit from the indirect excitation by Si-ncs because the energy of the intra 4*f* electronic transition from the ground state to the $^4F_{5/2}$ states, equal to around 1.55 eV in different glasses,[8,9] is very close to that of the exciton in Si-ncs. Few studies report on the PL properties of Nd^{3+} ions in layers containing Si-ncs. An Nd-related luminescence has been observed in silica gel films,[10] silicon oxide alloys prepared by plasma-enhanced chemical vapor deposition,[11] sputtering[12,13] or evaporation.[14] The Si excess and the structure of the Si nanoparticles in the silica matrix are of prime importance in the efficiency of the energy transfer process. Former results, reporting on samples annealed at temperature lower than that needed to form Si-ncs, suggest that amorphous Si particles could be efficient sensitizers for Nd^{3+} ions.[11,14]

In this study, the attention is focused on Nd-doped SiO_x samples containing Si nanocrystals. Samples were investigated by steady state PL, PL excitation (PLE) spectrometry, time-dependent and power-dependent PL experiments.

II. EXPERIMENTAL DETAILS

The films were prepared by co-evaporation of SiO powder from a thermal cell and of SiO_2 powder from an electron beam gun in a high-vacuum chamber. The thickness of the films was equal to 200 nm. The Nd evaporation was performed from an effusion cell, heated around 1200 °C. The prepared samples have the composition $SiO_{1.5}$ and the Nd concentration was varied from 0.1 to 4 at. %. The Si clusters are generated by annealing post-treatments, which involves in the demixtion of the SiO_x film following the reaction $SiO_x \rightarrow Si + SiO_2$. Further information on the SiO_x demixtion and the formation of Si-ncs can be found in our previous publications.[15] For this study, the samples were annealed at 1100 °C under a N_2 atmosphere. For the PL experiments, the samples were excited by the 325 nm line of a He-Cd laser, by the 355 nm line of a frequency-tripled YAG:Nd laser or by an optical parametric oscillator (OPO) laser. The laser pulse frequency and the duration were typically equal to 10 Hz and 5 ns, respectively. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by an InP/InGaAs photomultiplier tube cooled at 190 K. For experiments using the OPO laser, the PL emission from the samples was obtained by integrating the time-dependent luminescence. The response of the detection systems was precisely calibrated with a tungsten wire calibration source.

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III. RESULTS AND DISCUSSION

Figure 1(a) shows the room temperature PL spectra for $SiO_{1.5}$ samples annealed at 1100 °C and doped with different Nd concentrations. The Nd-doped SiO_2 sample is also represented, as a reference sample which does not show any Nd-related PL, nor Si-ncs-related peak. The undoped $SiO_{1.5}$ sample shows the characteristic wide PL band of Si-ncs around 800 nm. This energy is correlated to Si-ncs having a mean size around 3 nm.[16] It has been previously verified that the PL wavelength is an increasing function of Si excess in the SiO_x alloys, in agreement with the quantum confinement effect. The $SiO_{1.5}$ composition was chosen for this study because it avoids a too large overlapping with the Nd-related PL band at around 920 nm. For the doped samples, the characteristic PL emissions of Nd are obtained. Emissions at 920, 1100 and 1300 nm are due to transitions from the $^4F_{3/2}$ excited state to the $^4I_{n/2}$ levels with n equal to 9, 11 and 13, respectively. The results show that the Si-ncs PL intensity is a decreasing function of the Nd concentration. As reported in Fig. 1(b), the Nd-related PL intensity is an increasing function of the Nd concentration up to 0.5 at. % and then it decreases for higher concentration. This behavior can be interpreted in terms of energy transfer processes from Si-ncs to Nd^{3+} ions. Indeed, two competitive mechanisms are likely to occur. The radiative relaxation of excitons leads to the emission at 800 nm. On the other side, if Si-ncs and Nd^{3+} ions are coupled, the energy transfer process from Si-ncs to Nd^{3+} ions is a non-radiative de-excitation of excitons involving in excitation of Nd^{3+} ions. For a Nd concentration up to 0.5 at. %, the increase of Nd^{3+} ions number leads to an increase of the Nd-related PL. For higher Nd content, the decrease of the Nd PL emission is due to the concentration quenching effect which is caused by non-radiative energy transfer processes between Nd^{3+} ions. The quenching could be explained by cross relaxation processes between close neighbors Nd^{3+} ions, as demonstrated in Nd doped silica glasses,[17] or by the formation of Nd aggregates, as proposed by Debieu et al.[18] Moreover, it is also observed that the Si-ncs PL band blueshifts as the Nd concentration increases. This behavior cannot be explained by the confinement effect because the host matrices contain the same Si excess and then Si-ncs with the same size. This could be due to the overlap between the Si-ncs PL band and the energy of the Nd^{3+} transition from the ground state to the $^4F_{5/2}$ and $^2H_{9/2}$ states. The results suggest that Si-ncs emitting at 800 nm preferentially couple with Nd^{3+} ions. The remaining Si-ncs PL could then be due to uncoupled Si-ncs which emit light at higher energy.

In a donor-acceptor mechanism, the decay time of the donor generally decreases with doping. As the PL emission at around 800 nm is due to quantum confinement in Si-ncs, we might expect that not only the Si-ncs PL intensity decreases, but also its decay time, because the energy transfer process to the rare earth ions is a non-radiative channel. Time-dependent PL intensities are represented in Fig. 2 for undoped and Nd-doped samples containing Si-ncs, for different emission wavelengths. In the wavelength range corresponding to the emission band of Si-ncs, the decay time is an increasing function of the wavelength, as a consequence of the quantum confinement model which induces in a stronger relaxation of the selection rules on the wave vector for smaller Si-ncs, and then for lower wavelength. As shown in the inset of Fig. 2, it is also observed that the decay time corresponding to the Si-ncs emission does not decrease with doping. Such an evolution has been related in Er-doped SiO_x

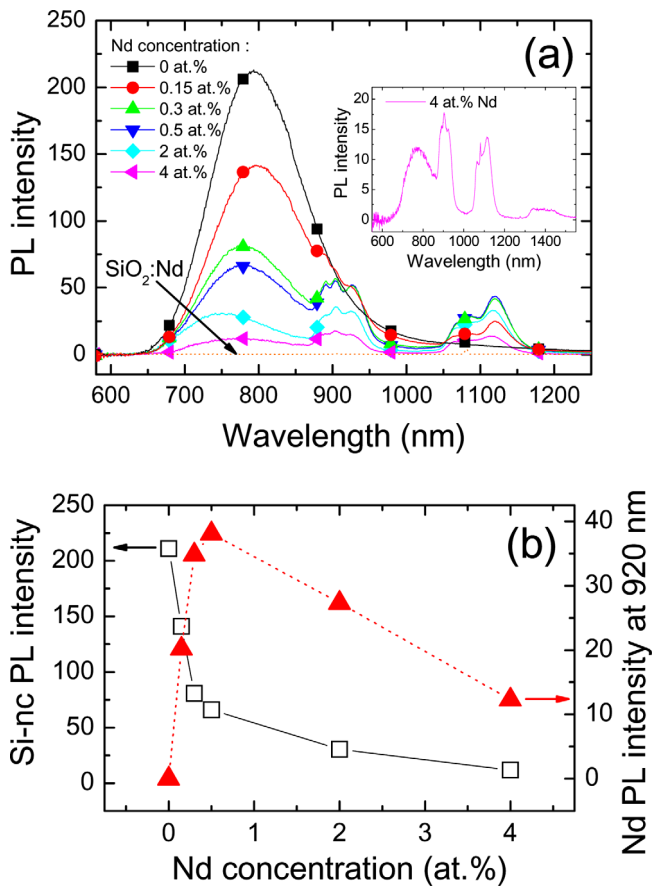


FIG. 1. (Color online) (a) Influence of the doping concentration on the photoluminescence spectra of Nd-doped layers. The inset shows the sample with a Nd content equal to 4 at. %. (b) Dependence of the PL intensity at 750 and 920 nm vs the Nd concentration.

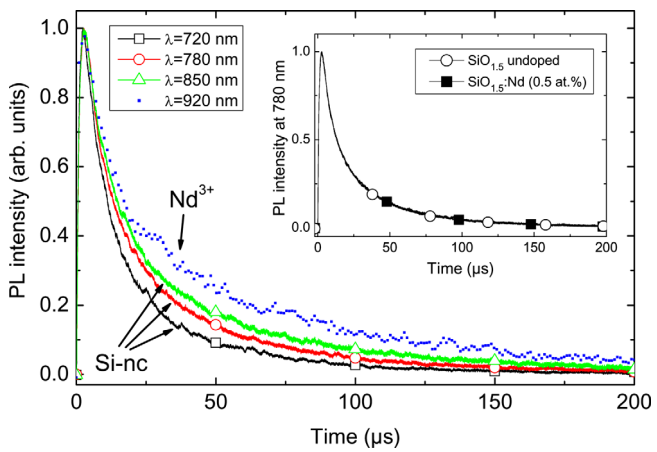


FIG. 2. (Color online) Time-dependent PL intensity measured at different wavelengths for the $SiO_{1.5}$:Nd sample doped with 0.5 at. %. The PL emission at 920 nm is due to Nd^{3+} ions. The PL emissions at lower wavelengths are due to Si-ncs. The inset presents the time dependent PL at 780 nm for $SiO_{1.5}$ and $SiO_{1.5}$:Nd samples.

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layers containing Si-ncs and was interpreted by the occurrence of an energy transfer from intrinsic luminescent centers rather than from Si-ncs.[5] In that model, the decay time of the donor center is independent on the Nd concentration. However, this interpretation can probably not be applied to our samples because the dependence of the decay time with the wavelength is in full agreement with a quantum confinement effect suggesting that the PL at 800 nm is most probably due to Si-ncs and not to luminescent centers. In our samples, we propose a different interpretation based on the existence of coupled Si-ncs and uncoupled Si-ncs. In this case, the uncoupled Si-ncs do not feel any change with the presence of rare earth and the decay time remains unchanged. For the Si-ncs, which act as sensitizers, the energy transfer process is a non-radiative channel and the decay rate should be changed. However, if we assume that this transfer process is very efficient it can be expected that the radiative efficiency of the donor tends to zero. In this extreme case, no PL from the Si-ncs can be measured or in a time scale which is very short. Consequently coupled Si-ncs do not emit measurable light. This is also in agreement with the blueshift of the Si-ncs PL band observed as the Nd concentration increases, which could be induced by the more efficient energy transfer between Si-ncs emitting at an energy close to the transition from the ground state to the $^4F_{5/2}$ excited state of Nd^{3+} ions. Considering such an assumption, for the Nd concentration equal to 0.5 at. %, almost 30% of the Si-ncs remain uncoupled. The time dependent PL measured at 920 nm is characteristic of the Nd^{3+} emission. Approximating the decay curve by a single exponential curve, the characteristic decay time is equal to 80 μs, two times higher to that reported in other works.[14]

To confirm the role of Si-ncs on the excitation of rare earth ions, PLE experiments were performed. Figure 3 shows the PLE at 920 nm for Nd-doped SiO_2 and Nd-doped $SiO_{1.5}$ layers with a Nd content equal to 4 at. %. The mean laser power was equal to 50 mW. For the SiO_2 sample, which does not contain any Si-ncs, the spectrum evidences the direct excitation of Nd^{3+} ions from the ground state to the $^2G_{9/2}$, $^4G_{7/2}$ and $^4G_{5/2}$, $^2G_{7/2}$ excited states. In presence of Si-ncs in the host matrix, the resonant excitation of ions is still visible; however, another wide contribution demonstrates an indirect excitation of Nd^{3+} ions. For this sample, the PLE spectrum at 750 nm, corresponding to Si-ncs emission, is also reported on Fig. 3. This result shows that the PLE spectrum of Si-ncs follows a very similar trend as the one of Nd^{3+} ions for the indirect contribution, suggesting that Si-ncs are the sensitizers for Nd^{3+} ions. It can be also noticed that the Nd emission intensity after a resonant excitation at 585 nm or after an indirect excitation at 420 nm is almost the same, similarly to what has been reported in Nd-doped triethoxysilane films.[10] This result must be carefully analyzed in relation with the laser excitation power because of the possible saturation of the Si-ncs which act as donors, as shown in a previous study.[19] The power dependence of the Nd-related PL emission at 920 nm with a resonant excitation at 585 nm and a non-resonant excitation at 430 nm is represented in Fig. 4(a). For the resonant excitation, the emission intensity of Nd^{3+} ions leads to a linear dependence with the excitation power in the whole studied range. However, for the indirect excitation via Si-ncs, the Nd^{3+} emission shows a linear dependence only for power values less than 15 mW and the indirect excitation is about three times more efficient than the resonant one to promote Nd^{3+} ions in excited states. For higher power values, the Nd^{3+} emission shows a pronounced saturation. To understand these results, we assume that the excited states dynamics of Si-ncs and Nd^{3+} ions can be described by the following rate equation:

$$\frac{dN_2}{dt} = \sigma\Phi N_1 - \frac{N_2}{\tau}.$$

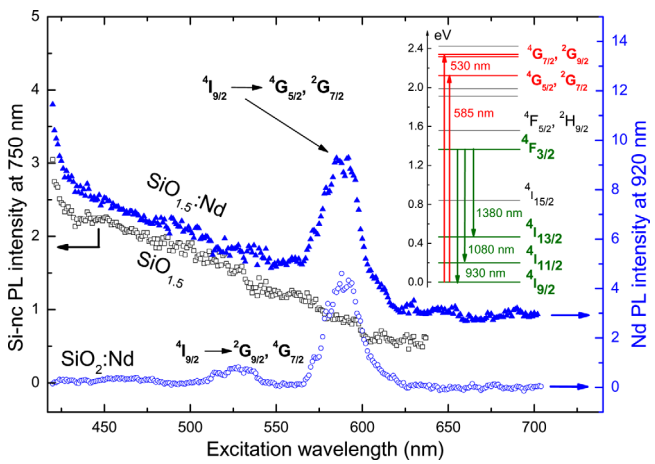


FIG. 3. (Color online) PLE spectra at 920 nm for a SiO_2: Nd sample and at 750 and 920 nm for a $SiO_{1.5}$: Nd sample, both annealed at 1100 °C. The inset shows the energy levels of Nd^{3+} ions.

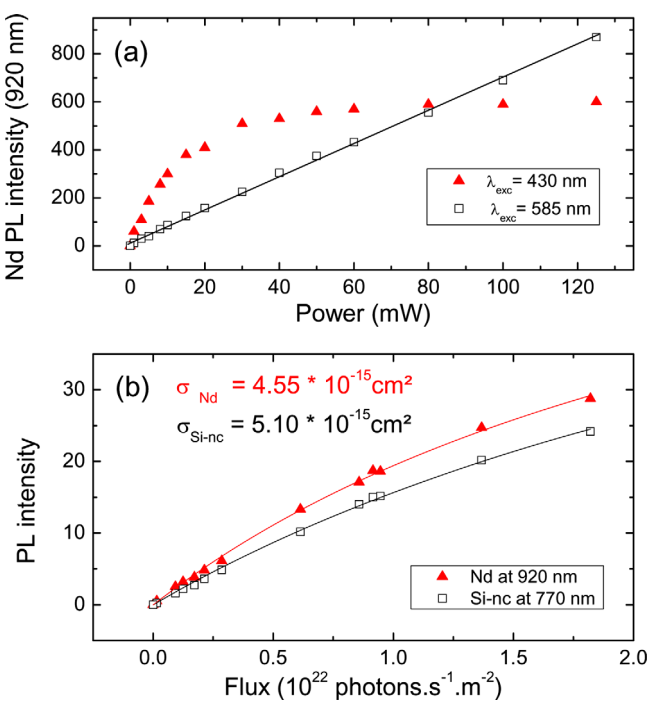


FIG. 4. (Color online) Power-dependent PL of a $SiO_{1.5}$: Nd sample, (a) measured at 920 nm with an OPO laser excitation at 430 and 585 nm, (b) measured at 920 and 770 nm with a CW excitation at 325 nm. Continuous line is obtained from a fit according to the formula in Eq. (1).

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N_1 is the population in the ground state and N_2 is the population in the excited state that gives rise to the luminescence by relaxation to the ground state. σ, τ and Φ are the absorption cross section, the lifetime of the excited state, and the excitation photon flux, respectively. For Si-ncs, the excitation in the UV range gives rise to a high energy electron-hole pair which relaxes and gives rise to a confined exciton characterized by an energy equal to around 1.6 eV. Concerning the Nd^{3+} ions, they can be directly excited at 585 nm promoting them to the $^4G_{5/2}$, $^2G_{7/2}$ excited states. The ions immediately relaxed to the $^4F_{3/2}$ states, which is the excited state described in the rate equation. As the PL intensity is proportional to N_2, the power dependence of the luminescence intensity of Si-ncs at 770 nm with an excitation at 325 nm or of Nd^{3+} ions at 920 nm with a resonant excitation at 585 nm is then given by the relation:

$$I_{PL} \cong \frac{\sigma\Phi\tau}{1+\sigma\Phi\tau}N, \quad (1)$$

where N is equal to the sum of N_1 and N_2. With the photons flux range used for our experiments and due to the weak absorption cross section of rare earth ions, the power dependence of the Nd^{3+} PL intensity with a direct excitation at 585 nm follows a linear trend:

$$I_{PL} \cong \sigma\Phi\tau N,$$

which is in good agreement with the data reported in Fig. 4(a). As shown in this figure, a different behavior is obtained for a non-resonant excitation at 430 nm. To understand this behavior, we can assume that the energy transfer process in SiO_x:Nd is very similar to that occurring in SiO_x:Er samples. Indeed the host matrix and the Si-ncs sensitizers are identical. Moreover, Er^{3+} ions and Nd^{3+} ions present an energy level which is resonant with the excitonic energy of Si-ncs. Hence we assume that the power dependence of the Nd-related PL can be described by the relation proposed for SiO_x:Er layers[5]:

$$I_{PL} \cong \frac{\sigma_{eff}\Phi\tau}{1+\sigma_{eff}\Phi\tau}N, \quad (2)$$

where σ_{eff} is, in this case, an effective absorption cross section, taking into account of the excitation of the Si-ncs and of the energy transfer process. In the framework of this phenomenological model, we consider that σ_{eff} does not depend on the photon flux. Due to the high value of the Si-ncs absorption and to the efficient energy transfer process, σ_{eff} is several orders of magnitude higher than σ characterizing the direct excitation. The formula in Eq. (2) cannot be approximated by a linear trend. Figure 4(b) shows the PL intensity of Si-ncs at 770 nm and of indirectly excited Nd^{3+} ions at 920 nm as a function of the excitation photon flux at 325 nm. As shown by the fit of the data, the power-dependent PL is well described by the formulas presented in Eq. (1) and Eq. (2), respectively.

To estimate the absorption cross section of Si-ncs following Eq. (1), the characteristic decay time was extracted by using a stretched-exponential law ($I_{PL}=I_0\exp(-t/\tau)^{\beta}$). Such a law is generally used to describe the time dependence of the Si-ncs PL.[20,21] The β and τ values, obtained at 770 nm, are equal to 0.8 and 25 μs, respectively. With this measured decay time of Si-ncs, fitting the power dependent data leads to an absorption cross section of Si-ncs equal to 8×10^{-15} cm^2, which is in good agreement with other published values.[22] With a decay time of Nd^{3+} emission equal to 80 μs, the effective absorption cross section of Nd^{3+} ions at 325 nm is equal to 5×10^{-15} cm^2 which is several orders of magnitude higher than that of direct absorption. This value of the indirect excitation via Si-ncs is very close to that obtain for Nd in presence of amorphous Si nanoparticles.[14]

IV. CONCLUSION

In conclusion, it has been shown that Nd-relaled PL could be obtained in SiO_x samples obtained by co-evaporation of SiO and SiO_2. The Nd concentration leading to the highest luminescence is equal to 0.5 at. %. Both direct and indirect excitation processes of rare earth ions have been evidenced. The indirect excitation process occurred via Si-ncs and it is characterized by a cross section equal to 8×10^{-15} cm^2, as high as in the case of Er^{3+} ions. As such, these layers are potentially interesting for optoelectronic applications or for down-conversion layers.

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