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The Nd-nanocluster coupling strength and its effect in excitation/de-excitation of Nd 3+ luminescence in Nd-doped silicon-rich silicon oxide
Evidence of two sensitization processes of Nd$^{3+}$ ions in Nd-doped SiO$_x$ films

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This paper aims to study the excitation mechanism of Nd$^{3+}$ ions in Nd-SiO$_x$ (x < 2) films. The films were deposited by magnetron co-sputtering followed by a rapid thermal annealing at temperature $T_A$ ranging from 600 to 1200 °C. Two different photoluminescence (PL) behaviors have been evidenced in SiO$_x$ layers depending on the annealing temperature. For low $T_A$ ($T_A < 1000$ °C), the recorded visible PL originates from defects energy levels while for high $T_A$ ($T_A > 1000$ °C), the visible emission emanates from recombination of excitons in Si nanoclusters. When doped with Nd$^{3+}$ ions, the visible PL behaviors of Nd-SiO$_x$ films follow the same trends. Nd$^{3+}$ PL was investigated and its decay rate was analyzed in detail. Depending on the annealing conditions, two types of sensitizers have been evidenced. Finally, maximum Nd$^{3+}$ PL emission has been achieved at around 750 °C when the number of Nd$^{3+}$ ions excited by the two types of sensitizers reaches a maximum.

I. INTRODUCTION

As a leading semiconductor material in the microelectronic industry, silicon has received significant attention on its optical functionality in these last years aiming at integrating photonics with semiconductor microelectronics. 1,2 However, suffering from the indirect nature of its band gap, bulk Si shows poor emission efficiency. Fortunately, two important results have been achieved by decreasing the Si grain size to the nanoscale range. On one hand, the nature of Si band gap changes from indirect to quasi-direct with the decrease in grain size. 3 This quasi-direct band gap allows room temperature photoluminescence (PL) of Si nanoclusters (Si-ncs) without any phonon assistance. This emission is ranging in the visible spectra from 700 to 900 nm depending on the Si-ncs size. 3–6 On the other hand, Si-ncs can play the role of sensitizer towards rare earth (RE) ions such as Er$^{3+}$ ion 7–12 or Nd$^{3+}$ ion. 13 Hence, the effective excitation cross section of RE ions is enhanced by several orders of magnitude and broadened spectrally in the visible range. 14,15 This result provides the possibility to manufacture less-cost and miniaturized Si-based optoelectronic devices.

To better understand the limiting factors for achievement of such optoelectronic devices, huge effort has been focused on the mechanism of energy transfer from Si-ncs towards Er$^{3+}$ ions. It appears that the Si-ncs:Er$^{3+}$ interaction distance should be less than 2 nm 16 for an effective coupling whose efficiency decreases exponentially with the increasing of distance. 10 Fujii et al. 17 observe the coexistence of two processes for Si-ncs:Er$^{3+}$ energy transfer depending on the sizes of the sensitizers. A fast process is attributed due to the large Si-ncs sensitizer, while a slow one is found to depend on the recombination rate of excitons in small Si-ncs. In contrast, Savchyn et al. 12 demonstrate the existence of two excitation processes for Er$^{3+}$ $4_{13/2}$ level involving multi-levels sensitization: fast direct excitation by Si-excess-related luminescence centers and slow excitation related to the fast excitation of Er$^{3+}$ ions up to the higher energy levels such as $4_{F_{0/2}}$ and $4_{I_{0/2}}$ with subsequent slow relaxation to the $4_{13/2}$ level. These works agree the origin of Er$^{3+}$ excitation from recombination of generated excitons within Si-ncs and subsequent energy transfer to the nearby Er$^{3+}$ ions. Even though a great number of papers have been published on the Si-based matrices co-doped with Er$^{3+}$ and Si-ncs, evidence of the achievement of net gain from such a system has been presented in only one report. 18 This is due to the nature of the three-level electronic 4f structure for the Er$^{3+}$ ions leading to a threshold power necessary to get population inversion and to the possibility of reabsorption of photon emitted by the neighboring Er$^{3+}$ ions. In contrast, the Nd$^{3+}$ ions emitting in four-level configuration (1.06 µm) do not have a threshold pump power for inversing population and there is no reabsorption of the emitted light at 1.06 µm. Moreover, the up-conversion is negligible with Nd$^{3+}$ ions emitting at 1.06 µm compared to Er$^{3+}$ ions emitting at 1.53 µm. Consequently, net gain should be achievable with Nd$^{3+}$ ions in easier way than with Er$^{3+}$ ions.

However, the study on excitation mechanism of Nd$^{3+}$ ions in Nd-SiO$_x$ films is still rather rare by comparison to its Er$^{3+}$ ions counterpart. After the discovery of energy transfer from Si-ncs to Nd$^{3+}$ ions, several groups 21–23,24 investigated the energy transfer with the goal of improving the Nd$^{3+}$ emission properties. Our previous work 21 evidences that high Nd$^{3+}$ content incorporated into the layers would form Nd$_2$O$_3$ clusters leading to the quenching of the Nd$^{3+}$ PL. Moreover, Watanabe et al. 25 point out that the Si-ncs size plays an important role in the Si-ncs:Nd coupling. The authors show that the Si-ncs:Nd energy transfer is more effective with smaller Si-ncs. This is explained by a good match of energy band gap in small Si-ncs with Nd$^{3+}$ excited energy levels (higher than $4_{F_{3/2}}$). Therefore, the discussion on excitation mechanism of Nd$^{3+}$ ions should include an investigation of Si-ncs PL properties. Two main models on the origin of Si-ncs emission have been proposed on the basis of both experimental and theoretical studies. The first

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model depicts the quantum confinement effect,\textsuperscript{26} which in general explains the evolution of Si-ncs PL versus its size depending on the Si excess and/or annealing treatment.\textsuperscript{27} The second model considers that the Si-ncs PL is correlated to the presence of defects at the interface between Si-ncs and SiO$_2$ matrix in SiO$_x$ layers,\textsuperscript{28,29} supporting the PL peak position size-independent.\textsuperscript{30}

In this paper, we investigate the optical properties of SiO$_x$ and Nd-SiO$_x$ films annealed using rapid thermal annealing (RTA) process. The influence of Si-ncs PL origins on the excitation mechanism of Nd$^{3+}$ ions is investigated depending on the annealing conditions.

II. EXPERIMENT

Undoped- and Nd-doped-SiO$_x$ ($x<2$) films of about 350 nm thick were deposited by magnetron co-sputtering of two (SiO$_2$) or three (Nd-SiO$_x$) confocal cathodes under a plasma of pure argon. The p-type monocrystalline Si or fused silica substrates were used and maintained at 500°C during the growth. The plasma power density for Nd$_2$O$_3$, Si, and SiO$_2$ targets were fixed at 0.30, 1.48, and 8.88 W/cm$^2$, respectively. After deposition, the films were submitted to RTA process under N$_2$ for variable durations, $t_A$, and different temperatures, $T_A$, ranging from 1 min to 1 h and 600 to 1200°C, respectively. The microstructural characteristics were obtained by RAMAN and Fourier transform infrared (FTIR) spectroscopies. The optical properties were achieved by means of PL experiments. These latter were carried out using the 488-nm-line of a CW Ar$^+$ laser (Innova 90C laser) pumped by a YAG:Nd laser) set at 488 nm with a repetition rate of 10 Hz. The focusing beam was 500 $\mu$m with an average energy of 15 mJ. The PL decay was recorded with an appropriated electronic and detector (PM R5509-73 Hamamatsu) on a digital oscilloscope (Tektronix tds 3012).

III. RESULTS AND DISCUSSION

The two kinds of films, SiO$_x$ and Nd-SiO$_x$, object of the present study, have the same value of O/Si ratio ($x=1.74$). The $x$ value was calculated as shown in our previous paper\textsuperscript{32} using the equation

\begin{equation}
x = 0.02v - 19.3, \tag{1}
\end{equation}

where $v$ is the transverse optical (TO$_3$) peak position in FTIR spectrum collected at normal incidence. As a consequence, the Si excess ($Si_{ex}$) is found to be 4.7 at. % using the following relation:

\begin{equation}
Si_{ex}(\text{at} \%) = [(2-x)/(2+2x)]100. \tag{2}
\end{equation}

This silicon excess value has been confirmed by Rutherford backscattering experiments, which have given a Nd content of about $5 \times 10^{19}$ Nd cm$^{-3}$.

FIG. 1. The PL spectra of SiO$_x$ films annealed at the indicative temperature with 1 min duration. The left (a) corresponds to $T_A$ lower than 1000°C while the right (b) to high $T_A$ higher than 1000°C. AD is the abbreviation of as-deposited.

A. Photoluminescence properties of SiO$_x$ films

The PL properties of SiO$_x$ films were investigated as a function of $T_A$. The spectra are separately shown in Figure 1(a) for low $T_A$ less than 1000°C and Figure 1(b) for high $T_A$ more than 1000°C. As noticed on these two graphs, the emission bands peak at different wavelengths depending on the $T_A$ range. Thus, the emission peaks obtained for low $T_A$ will be defined as $E_L$; while for high $T_A$, the recorded emission peaks will be called $E_H$. To easily catch the evolution trend, both integrated peak intensity and maximum peak position have been determined and are presented in Figure 2. The $E_L$ peak intensity first increases to reach a maximum for $T_A = 750°C$ before decreasing for higher annealing temperatures. This could be explained by a passivation of some non-radiative centers with increasing $T_A$ up to 750°C and for $T_A$ above 750°C by a decrease of the number of emitting centers at the origin of the $E_L$ peak emission. Its position does not change with $T_A$ peaking at around 720 nm. The exact origin of this $E_L$ peak is still unclear. Wang \textit{et al.}\textsuperscript{30} and Wora Adeola \textit{et al.}\textsuperscript{33} have separately observed the very similar $E_L$ peak in their samples. The former attribute it to surface states while the latter to band tails states. Therefore, at this level of discussion, we ascribe this $E_L$ peak to defects related radiative states which origin will be specified later in this paper. Comparatively for $T_A$ higher than 1000°C, the $E_H$ peak

FIG. 2. Peak intensity (left scale) and position (right scale) of SiO$_x$ films versus $T_A$. 

\[\text{Peak position (nm)}\]
\[\text{Peak intensity (a.u.)}\]
\[\text{Peak intensity (a.u.)}\]
intensity rises up abruptly till a maximum at $T_A = 1100^\circ C$ and thereafter drops down to a very low value for the highest annealing temperature ($T_A = 1200^\circ C$). However, the maximum $E_{HH}$ intensity is more than three times higher than the one achieved for $E_{HL}$ peak after annealing at $T_A = 750^\circ C$. The band positions red-shift from 756 to 836 nm with increasing $T_A$, allowing of attributing the $E_{HH}$ peak to the quantum-confined excitonic states in Si-ncs. This evolution of $E_{HH}$ intensity versus $T_A$ is related both to the passivation of non-radiative channels and the Si-ncs density increase up to $1100^\circ C$. If the former continues for higher annealing temperature, the latter will decrease due to a Si-ncs size growth over the quantum confinement limit. Such an oversize growth explains the quench of the PL observed for temperature as high as $1200^\circ C$. Note that both $E_{HL}$ and $E_{HH}$ peaks are related to the Si excess incorporated in the SiO$_2$ matrix as no emission was observed from pure SiO$_2$ sputtered films annealed at any $T_A$.

To further analyze the different PL behaviors between low- and high-$T_A$ layers, two typical annealing temperatures ($750$ and $1100^\circ C$) corresponding to the maximum PL intensities achieved were set to study the effect of annealing time $t_A$. The evolutions of peak intensity as a function of $t_A$ are presented in Figure 3. It can be noticed that the $E_{HL}$ peak intensity gradually decreases with time for the $750^\circ C$-annealed samples while $E_{HH}$ peak significantly increases for the $1100^\circ C$-ones, for the same range of time. This PL evolution is another evidence of different excitation-de-excitation mechanisms: radiative defects controlled at $750^\circ C$ while quantum confinement controlled at $1100^\circ C$. When the annealing duration is increased, the radiative defects are quenched at $750^\circ C$ probably due to the rearrangement of Si and/or O atoms, while the $1100^\circ C$-extended annealing could mainly passivate the non-radiative defects such as stressed bond angles, distorted bond length in host. In high temperature range, Garrido Fernandez et al. have obtained the same PL behavior versus $t_A$. They observe that during annealing process the nucleation and growth of Si-ncs are almost completed in a few minutes and the average Si-ncs diameter remains constant for longer annealing times. Thus, increasing annealing time up to 30 min favors achievement of high Si-ncs density but remains sufficiently short to avoid the growth of large Si-ncs, which are detrimental for the quantum confinement process. Moreover, such extra annealing time favors the recovering of the non-radiative channels.

B. Microstructural characterization

To understand the above PL properties, the evolution of film microstructure versus $T_A$ has been analyzed by means of RAMAN spectroscopy (Figure 4). Each curve has a broad band peaking at $\sim 480 \text{ cm}^{-1}$ attributed to amorphous Si agglomerates. Such a result is in agreement with previous work showing that the formation of amorphous Si agglomerates in similar thin films starts to occur at about $600^\circ C$. By increasing $T_A$ up to $1100^\circ C$, a sharp peak at around $521 \text{ cm}^{-1}$ assigned to crystalline Si-ncs appears while, in the same time, the $480 \text{ cm}^{-1}$-band intensity decreases. This convincingly certifies that the $T_A = 1100^\circ C$ annealing promotes the formation of Si nanocrystals. The results of RAMAN experiments on the Nd-doped SiO$_x$ thin films (not shown here) follow the same trends as results obtained on undoped films. This is supported by the fact that the low Nd content incorporated may not affect the formation of either amorphous or crystalline Si-ncs.

Figure 5 shows the evolution of FTIR spectra for SiO$_x$ films annealed at different temperatures. There are two main
bands attributed to longitudinal optical (LO3) and TO3 phonons of Si-O bonds. The relative intensity of the former peaking in the 1230–1255 cm\(^{-1}\) range increases with TA up to 1050 °C, and then slightly decreases for higher TA. According to the work of Olsen and Shimura,\(^{37}\) LO3 band intensity corresponds to the number of Si-O-Si bonds at 180° present at the Si/SiO\(_2\) interface. Consequently, this is the signature of the increasing formation of Si-ncs in our film upon annealing temperature up to 1050 °C. The continuously increase of TA will then favor the growth of Si-ncs size leading to the decrease of the Si-ncs density and thus the number of Si-O-Si bonds at the Si/SiO\(_2\) interface. As a consequence, a slight decrease of the LO3 mode intensity is noticed. Concerning the TO3 mode, it blue-shifts from 1052 to about 1081 cm\(^{-1}\) with increasing TA. This progressive shift towards the stoichiometric position of amorphous SiO\(_2\) (1081 cm\(^{-1}\)) is indicative of the phase separation between Si and SiO\(_2\) occurring in the film. This is confirmed by the decrease of the disorder in the matrix as evidenced by the evolution of the intensity of the LO4 and TO4 pair modes with TA.

C. Comparison of Nd-SiO\(_x\) PL properties with SiO\(_x\) films

To study the excitation mechanism of Nd\(^{3+}\) ions in Nd-SiO\(_x\) system, the PL experiments are performed on Nd-doped SiO\(_x\) layers annealed at 750 and 1100 °C which correspond to the two temperatures allowing achievement of the maximum intensity for E\(_L\) and E\(_H\) peaks, respectively. Figure 6(a) shows the PL spectra of Nd-SiO\(_x\) and SiO\(_x\) films annealed at 750 °C during 1 min. The significant Nd\(^{3+}\) PL peak from the de-excitation from the \(^{4}F_{3/2}\) to \(^{4}I_{9/2}\) level at around 920 nm is observed for Nd-doped layer excited with the non-resonant 488 nm-Ar laser wavelength. This implies the existence of Nd\(^{3+}\) sensitizers present in the SiO\(_x\) matrix. The occurrence of an energy transfer from sensitizers to Nd\(^{3+}\) ions is evidenced by the concomitant lowering E\(_L\) peak intensity compared to that from undoped SiO\(_x\) layer.

To confirm this behavior, investigation of the visible and Nd\(^{3+}\) PL intensities as a function of annealing duration has been carried out (Figure 7). One can noticed that the visible E\(_L\) peak intensity decreases versus TA for both SiO\(_x\) and Nd-SiO\(_x\) films. As explained above, this evolution can be ascribed to the recovering of the radiative defects. For at least TA ≤ 30 min, the E\(_L\) peak intensity from Nd-doped SiO\(_x\) layer annealed at 750 °C shows a lower value than that of undoped one. Such a behavior is an evidence of an efficient energy transfer from these radiative defects to Nd\(^{3+}\) ions states, playing the role as Nd\(^{3+}\) sensitizers as mentioned above. Concerning the Nd\(^{3+}\) emission evolution at 920 nm, it increases until 15 min of annealing and saturates afterward. Such saturation may be attributed to (i) the passivation of some non-radiative defect and/or (ii) the existence of another type of sensitizers. Moreover, we have observed in the Figure 3 a decrease of the low TA type Nd\(^{3+}\) sensitizer (E\(_L\) peak) with longer annealing, which should contribute to a decrease of the Nd\(^{3+}\) PL intensity. Consequently, these trends of visible and Nd\(^{3+}\) PL intensities are a signature of the existence of another type of sensitizers that also excite efficiently the Nd\(^{3+}\) ions (Figure 6(b)). As demonstrated in our previous work,\(^{38}\) such sensitizers present at low TA contain a few Si atoms (less than 15 atoms) and will be here named atomic scale sensitizers (ASSs). They differ from the luminescence centers proposed by Savchyn et al.\(^{39}\) Since using also a RTA of 100 s, they observed always a PL peak position shift, which is in disagreement with our results (seen Figure 1(a)).

When annealed at higher temperature (1100 °C), the intensity of E\(_H\) peak falls down by about 8 times after Nd incorporation (Figure 8). It is thus supposed that most of emitters transfer energy to their nearby Nd. One can notice that the position of E\(_H\) peak shifts from about 790 to 730 nm after Nd incorporation. This shift is probably explained by the two Nd\(^{3+}\) absorption bands peaking at about 750 and 808 nm\(^{31}\) and is a confirmation of the energy transfer process involved. Nevertheless, the Nd\(^{3+}\) PL intensity achieved at such TA appears very low. This demonstrates the E\(_L\) peak emitters formed at this high temperature act as sensitizer of Nd\(^{3+}\) ions, but unfortunately, this efficient energy transfer process suffers from Nd\(_2\)O\(_3\) clusters formation and/or a too large sensitizer-Nd\(^{3+}\) distance. This can explain that the drop of Si-ncs PL does not lead to a high PL emission of the Nd\(^{3+}\) ions.

FIG. 6. PL spectra of Nd-SiO\(_x\) and SiO\(_x\) films annealed at 750 °C during (a) 1 min and (b) 1 h.

FIG. 7. Integrated peak intensities of Nd-SiO\(_x\) and SiO\(_x\) films annealed at 750 °C versus TA.
ions. In addition, the effect of annealing duration was investigated at 1100°C. The EH peak intensity of Nd-SiOx film gradually increases with increasing tA (data not shown here), presenting thus a similar trend to that achieved for undoped layer (Figure 3).

This paragraph will address the effect of TA on Nd3+ PL properties (Figure 9). Even though the as-deposited layer clearly shows PL, the intensity increases with TA and is enhanced by a factor 2.5 upon annealing at 750°C before decreasing for higher TA. The optimized temperature at 750°C corresponding to maximum Nd3+ PL may be explained by the fact that both matrix ordered degree and coupled Nd3+ number evolve in opposite trend with annealing temperature. For the former, the FTIR spectra reported in Figure 5 have evidenced the attenuation of LO4 and TO4 pair mode with increasing TA. Such an evolution implies that the film matrix gradually becomes ordered, which would favor the Nd3+ emission by decreasing the non-radiative paths.

The concomitant increase of the LO3 intensity with TA up to 1050°C suggests an increase of Si-ncs density also favoring an enhancement of Nd3+ emission. For the latter, the visible EL peak (Figure 1(a)) is quenched with TA higher than 750°C attesting the decreasing of radiative defect. When TA ≥ 750°C, the Nd3+ ions were consumed by the formation of Nd2O3 clusters decreasing the coupled Nd3+ ions as evidenced by lifetime measurements detailed below. Therefore, a maximum Nd3+ PL is reached at the moderated temperature (TA = 750°C). Moreover, it is worth to note that the Nd3+ PL at TA = 900°C is still remarkable and only decreases by less than 1.5 times in contrast to that at TA = 750°C. However, the defects emission (EL peak) almost completely quenches at about 900°C as shown in Figure 1(a). This again evidences the existence of atomic scale sensitizers apart from the radiative defects.

D. Analysis of both visible PL and Nd3+ infrared PL decay curves

Lifetimes τ measured on EL and EH peaks do not show a single exponential trend, therefore as a first approach the integrated Eq. (3)40 was used in order to fit the decay curve

$$\tau = \int \frac{I}{I_0} dt,$$

where I is a time dependent peak intensity while I0 is the intensity at t = 0 s. For EL peak, the lifetimes of both doped and non-doped films are low and invariable at about 2 µs as shown in Figure 10. This confirms that the visible EL peak originates from the defects.41 For EH peak from non-doped SiOx film, the lifetime increases dramatically and holds a value of 29 µs for 1100°C-SiOx film. This value is indicative that EH peak originates from the exciton recombination confined by quantum effect inside Si-ncs.42 In contrast for Nd-SiOx film annealed at 1100°C, this lifetime value decreases to 3.6 µs. This decrease is due to the energy transfer to Nd3+ ions as described by the effective lifetime deduced from rate equation43 in the sensitizer:Nd system

$$\frac{1}{\tau_{Nd-SiOx}} = \frac{1}{\tau_{SiOx}} + K N_{Nd} S_{SiOx},$$

where 1/τNd-SiOx is the EL or EH peak lifetime for Nd-SiOx film while 1/τSiOx corresponds to the non-doped SiOx film lifetime; K is the coupling constant between sensitizers and...
Nd$^{3+}$ ions; and $N_{Nd}^0$ is the Nd$^{3+}$ density in the fundamental state. The term $KN_{Nd}^0 \tau_{SiOx}$ describes phenomenologically the coupling between sensitizers and Nd$^{3+}$ ions. Therefore, the decrease of $\tau_{Nd-SiOx}$ with respect to $\tau_{SiOx}$ can be ascribed to the increasing of the coupling term $KN_{Nd}^0 \tau_{SiOx}$ and thus evidence the energy transfer to Nd$^{3+}$ ions. In Nd-SiO$_x$ films annealed at $T_A < 1000^\circ$C, the lifetime $\tau_{Nd-SiOx}$ is slightly lower than $\tau_{SiOx}$, taking into account our experimental uncertainties. For layers annealed at $T_A > 1000^\circ$C, the lifetime $\tau_{Nd-SiOx}$ is 10 to 20 times lower than SiO$_x$ lifetime (Figure 10). Consequently, for low $T_A$, Nd-SiO$_x$ layers have a weaker coupling term $KN_{Nd}^0 \tau_{SiOx}$ compared to higher one. The efficiency $\eta$ of energy transfer can be estimated by the following equation:

$$\eta = 1 - \frac{\tau_{Nd-SiOx}}{\tau_{SiOx}}. \tag{5}$$

One can obtain that in Nd-SiO$_x$ films annealed at $T_A < 1000^\circ$C, the efficiency is lower than 10%, while $\eta$ reaches about 90% for 1100$^\circ$C-annealed layer. Notwithstanding, the weaker sensitizer:Nd coupling regime and lower efficiency for the low $T_A$, the highest PL intensity is achieved. Such a feature can be explained by the larger number of sensitized Nd$^{3+}$ ions due to the larger density of both radiative defects and atomic scale sensitizers (low $T_A$) than that of Si-ncs sensitizers (high $T_A$).

The decay rate of Nd$^{3+}$ infrared PL at 920 nm has a non-exponential nature as seen from the Figure 11 inset (a). For all the films, the Nd$^{3+}$ PL decay rate was fitted by a two-exponential decay model

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right). \tag{6}$$

Fast ($\tau_1$) and slow lifetimes ($\tau_2$) have been reported in Figure 11, and the corresponding component of lifetime ($\frac{A_1}{A_1+A_2}$,$\frac{A_2}{A_1+A_2}$) is described in the inset (b). On one hand, the fast lifetime is shorter than 24 $\mu$s, while the slow one is in the 50–130 $\mu$s range. It is observed that both of them gradually increase followed by a dramatic decrease. The maximum is achieved after an annealing at $T_A = 800^\circ$C. This evolution versus $T_A$ is comparable to the results reported by Li et al. explaining that the local environment of Nd$^{3+}$ ions is deteriorated because of the formation of Nd$_2$O$_3$ clusters after annealing at high temperatures. Such a rare earth clusterization has been also observed in a similar sputtered system as demonstrated in our study using atom probe tomography technique. On the other hand, the component of fast lifetime decreases from 0.68 to 0.51, in Figure 11 inset (b), while the slow case increases from 0.32 to 0.49. This indicates that (i) the fast lifetime dominates the Nd$^{3+}$ emission for all the layers, and that (ii) the contribution of slow lifetime to Nd$^{3+}$ PL gradually increases with $T_A$.

### E. Energy transfer mechanism

The energy transfer from sensitizers present in SiO$_x$ matrix to Nd$^{3+}$ ions has been demonstrated using a non-resonant excitation as described above and now our purpose is to analyze this transfer process in more details (Figure 12). The absorption spectrum (Figure 12 (ii-b)) of Nd$^{3+}$ ions in Nd-doped SiO$_2$ film presents four typical absorption bands peaking at about 880, 808, 750, and 585 nm. They correspond to the transitions from the ground level $^4I_{9/2}$ to the excited level $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, and $^2G_{7/2}$, respectively. Thus, from these quantified energy levels and the positions of $E_L$ and $E_H$ emissions, one can propose a scheme of the transfer mechanism as detailed in Figure 12.

For low $T_A$-annealed Nd-SiO$_x$ layers, ASSs and radiative defects are present in the matrix. Both efficiently sensitize the Nd$^{3+}$ ions, since the intense Nd$^{3+}$ PL has been observed in both samples annealed at 750$^\circ$C for 1 min and 1 h (Figure 6). When the radiative defects are recovered with $T_A$, the atomic scale sensitizers, whose density increases with the temperature, dominate the sensitization of the rare earth ions. As a consequence, in this intermediate

![Figure 11](image1.png)

**FIG. 11.** Evolution of Nd$^{3+}$ PL lifetime at 920 nm versus $T_A$. The inset (a) is a representative decay rate of 750$^\circ$C Nd-SiO$_x$ PL, fitted by a two-exponential decay model, while the inset (b) is the component of Nd$^{3+}$ fast or slow lifetime.

![Figure 12](image2.png)

**FIG. 12.** Schematic illustrations of the Nd$^{3+}$ ions excitation. (i) Energy diagrams of ASSs and defects within the films annealed at $T_A < 1000^\circ$C. (ii) (a) energy diagram of Nd$^{3+}$ ions and (b) absorption spectrum of Nd$^{3+}$ ions doped in SiO$_2$ film, and (iii) energy diagram of Si-ncs within the films annealed at $T_A > 1000^\circ$C. ET is the abbreviation of energy transfer.
temperature range, two paths of sensitization of Nd$^{3+}$ ions will coexist and are at the origin of the radiative recombination from the $^2F_{3/2}$ to the ground state $^4I_{9/2}$ level with an emission at about 920 nm.

In the case of high $T_A$-annealed Nd-SiO$_x$ layers, the formed Si-ncs have a smaller band gap than in the case of atomic scale sensitizers. These Si-ncs can also transfer their energy to Nd$^{3+}$ ions as demonstrated by the decreasing of Ni-nc PL intensity (Figure 8) as well as its lifetime (Figure 10). But the PL intensity of Nd$^{3+}$ ions achieved after such a treatment is low. Such a feature can be attributed to two phenomena: (i) a cross relaxation process among Nd$^{3+}$ ions occurs due to the formation of Nd$_2$O$_3$ clusters as witnessed by its lifetimes (Figure 11), (ii) the formation of Si-ncs as already observed in similar sample doped with Er ions will lead to an increase of the sensitizer:Nd distance.

For all the Nd-SiO$_x$ layers, a Nd$^{3+}$ ions PL decay with a non-exponential nature was observed and fitted using a double exponential decay model leading to the determination of a fast and a slow components. They present an opposite behavior with the annealing temperature (inset (b) in Figure 11): the former decreases while the latter increases. Horak et al. have attributed the shortening of the decay time to a modification of local density of states (LDOS) brought by the Si interface. This is consequently a signature of the distance between rare earth ions and sensitizer. Considering that the annealing temperature favors the phase separation in our layers, higher the temperature is, higher the Sensitizer-Nd$^{3+}$ distance. Thus, one can explain the two components of the PL decay to the different environment of Nd$^{3+}$ ions, which is modified by the annealing treatment. This would explain the observed increase of the ratio of slow over fast components of PL decay with temperature.

**IV. CONCLUSION**

The microstructure and PL properties were investigated as a function of annealing conditions for SiO$_x$ and Nd-SiO$_x$ layers. It has been demonstrated that for the low $T_A$ ($T_A < 1000$ °C) annealed layers, the visible $E_L$ peak origins from the defects levels, while quantum confinement effect rules the visible $E_M$ peak for the layers annealed at higher temperature. For the Nd$^{3+}$ emission in Nd-SiO$_x$ layers, the former low $T_A$-layers present high intensity while the latter high $T_A$-layers have low one. The high PL intensity achieved at 920 nm has been attributed to the high density of sensitizers present in the layers that are able to transfer efficiently their energy to the rare earth ions. For increasing annealing temperatures, this 920 nm-emission decreases. It has been ascribed to both the formation of Nd$_2$O$_3$ clusters and the increasing sensitizer:Nd$^{3+}$ distance. As studied on the mechanism of excitation towards Nd$^{3+}$ ions, two kinds of sensitizers (radiative defects and atomic scale entities) would coexist for low $T_A$-annealed Nd-SiO$_x$ films, while Si-ncs were grown acting as sensitizer for high $T_A$ films. This would allow one to obtain high content of Nd$^{3+}$ ions sensitized, which is the key parameter to achieve future photonic component.

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