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# Correlation between composition, microstructure, and emission properties in Nd-doped Si-rich Si oxynitride films: investigation into the nature of the sensitizer

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## Abstract

Rare earth (*RE*) ions doped in Si-based materials, compatible with Si technology, are promising compounds with regards to optical communication and energy conversion. In this article, we show the emission properties of Nd-doped Si-rich Si oxynitride (Nd-*SRSON*) films, and their dependence on the dangling bond density and the nature of the sensitizer. These films were prepared by reactive magnetron sputtering and post-annealing. The film composition, microstructure, and emission properties were investigated as a function of deposition parameters and annealing temperatures. Both Fourier transform infrared (*FTIR*) and ellipsometry spectroscopy measurements have confirmed that the sample composition (Si/N ratio) can be carefully tuned by varying the ratio of reactive nitrogen to argon in the sputtering plasma. Moreover, *FTIR* and x-ray photoelectron spectroscopy measurements demonstrate the existence of both nitrogen and oxygen dangling bonds (N<sup>·</sup> and O<sup>·</sup>) in as-deposited samples. These dangling bonds were passivated during annealing. Under non-resonant excitation at 488 nm, the films exhibit a significant photoluminescence (*PL*) signal from Nd<sup>3+</sup> ions demonstrating the occurrence of an effective sensitization of Nd<sup>3+</sup> ions in the host matrix. Both *PL* excitation and ellipsometry results (the energy band gap from new amorphous model) exclude the sensitization by an exciton with energy over the band gap, whereas the presence of Si agglomerates, at the atomic scale, have been identified as effective sensitizers towards Nd<sup>3+</sup> ions. This work not only provides knowledge to optimize Si-based materials for favorable emission properties, but also, presents a universal methodology to investigate the nature of sensitizers for *RE* emitters. This allows one to find correlations between composition, microstructure, and emission properties.

Keywords: neodymium, rare earth, Si-rich Si oxynitride, thin film, non-resonant excitation, photoluminescence

## Introduction

Silicon photonics has attracted considerable attention since it has a potential application in microelectronics and more recently in silicon-based materials for energy conversion [1–3]. For this reason, systems composed of rare earth (*RE*) ions incorporated in silicon-based host matrices have been intensively investigated [4–8]. In such systems, the presence of sensitizers such as silicon nanoparticles (Si-nps) can allow an increase of the effective excitation cross section of *RE* ions by several orders of magnitude [9, 10]. However, an effective sensitization process is governed by energy transfer (*ET*) mechanism that is strongly distance dependent. This *ET* is either a Coulombic type (Förster) or carrier exchange based (Dexter), with an interaction distance ranging from some nanometers for Förster-approach [11] to below a nanometer for Dexter-interaction [12]. A large distance between the sensitizer and the *RE* ion, as well as the clustering of *RE* ions (formation of  $RE_2O_3$  for example) in the Si-based host matrix are considered as two major factors that could limit the coupling of *RE* ions with the sensitizer. This situation requires, therefore, some nano-engineering of the material composition (i) through growing a high density of sensitizers in order to enhance the *RE*-related emission, (ii) by increasing the concentration of *RE* ions before the concentration quenching effect becomes dominant [7].

The Er-doped Si-rich Si oxide (Er-*SRSO*) system has been widely studied. Early results stated that the *ET* between Si-nps and  $Er^{3+}$  ions is optimal for crystallized Si-nps [13], but amorphous Si-nps were later shown to play an efficient sensitizing role towards the Er ions as well [14, 15], demonstrating that crystallization is not a prerequisite. From such results, it was found that crystallized Si-nps appear in general at high temperature 1100 °C, and the amorphous one at about 900 °C or below. This former would favor a coalescence of Si-nps as well as the formation of  $Er_2O_3$ , which consequently decrease the number of sensitizers, and increase the distance between them and the  $Er^{3+}$  ions. The consequence is an observed quenching of the *RE* emission [16]. At low annealing temperature (<900 °C), our previous work has evidenced the presence of Si-based sensitizers issue from the agglomeration of less than 15 Si atoms [16]. This allows to obtain a high density of sensitizers uniformly distributed leading thus to a high fraction (22%) of optically active  $Er^{3+}$  ions effectively coupled to sensitizers [17]. Up to now, the achievement of net gain from such an Er-*SRSO* system is, however, rather rare or even shown as impossible [18, 19].

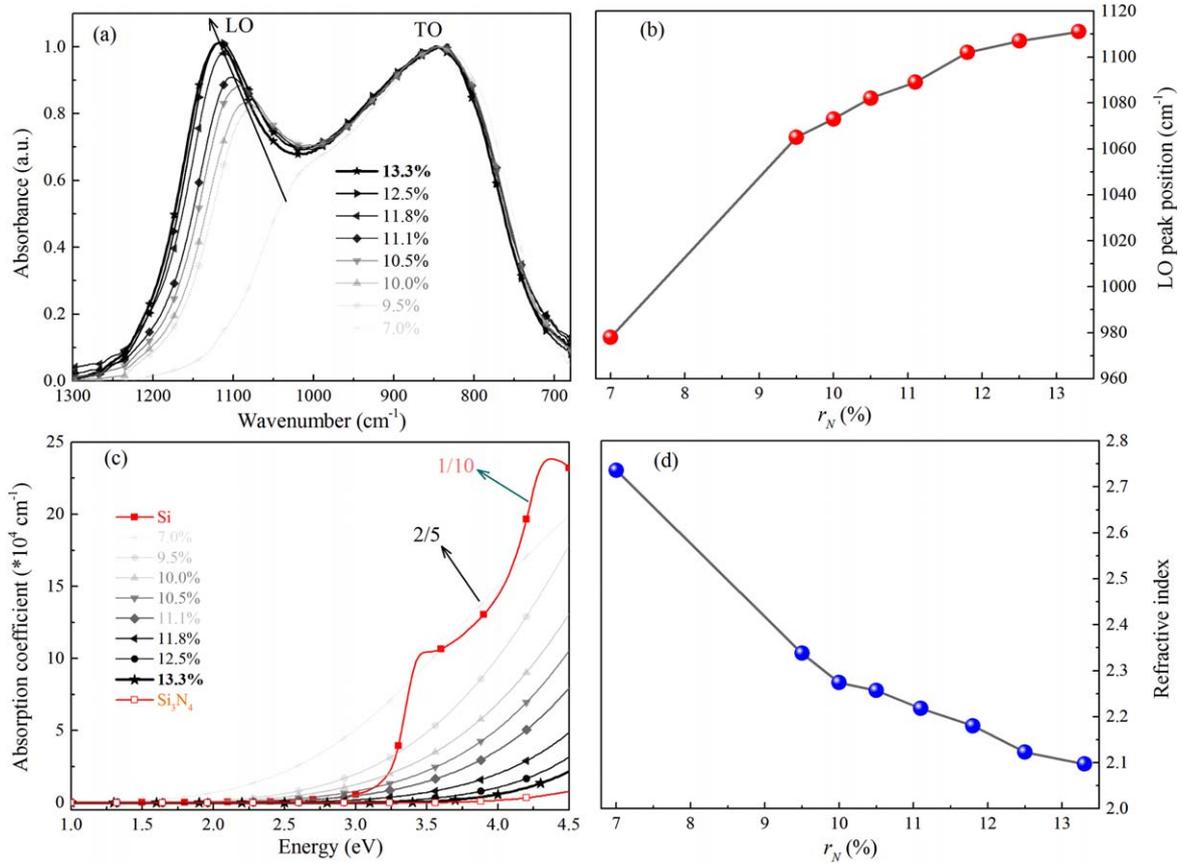
An alternative system, Nd-doped Si-rich Si nitride (Nd-*SRSN*), attracts strong interest in recent years. In contrast to the three-level electronic 4f structure for the  $Er^{3+}$  ion, in the case of the  $Nd^{3+}$  ion it is easier to achieve net gain due to its four-level configuration considering the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition leading to a 1.06  $\mu m$  emission. Our simulation work has demonstrated that a significant positive net gain up to 30 dB  $cm^{-1}$  can be achieved with the Nd-doped *SRSO* waveguide [19]. For the host matrix, the *SRSN* matrix has a much higher threshold for *RE* ions agglomeration than the oxide case. This may be due to low diffusion coefficients for

*RE* ions in a nitride matrix [20, 21]. This means that more optically active *RE* ions may potentially be present in *SRSN* than in *SRSO* matrices. Moreover, Li *et al* have observed a maximum  $Nd^{3+}$  photoluminescence (*PL*) intensity corresponding to a Si concentration of 45% [22]. These authors proposed that localized states present in high density in the band-tails act as effective sensitizers to  $Nd^{3+}$  ions for such oxygen-free Nd-*SRSN* sample. Marcus *et al* have observed that *RE* ions tend to be surrounded by oxygen atoms, an arrangement considered as crucial for the optical activation of *RE* ions in glasses, and particularly for efficient emission [23, 24]. This statement implies the importance to carefully incorporate a small amount of oxygen in the host matrix. However, the work on Nd-doped Si-rich Si oxynitride (Nd-*SRSN*) system is quite scarce. The sensitizer nature requires a deeper analysis to see whether there is a difference comparing to other Si-based systems.

In our previous work on Tb-doped N-rich Si oxynitride (Tb-*NRSON*), we have confirmed that both band-tails and  $N_4^+$  defect states can play the role of sensitizers towards  $Tb^{3+}$  ions [3]. Herein, we propose to study a different system, Nd-*SRSN* sample. It consists of an Nd-doped oxynitride Si-based matrix in which we have incorporated a Si excess. This study aims at (i) optimizing the  $Nd^{3+}$  emission through variation of deposition parameters for tuning the sample composition and annealing conditions for controlling the sample microstructure, and (ii) elucidating the  $Nd^{3+}$  ions excitation mechanisms correlated with composition and microstructure. This work has not only to do with waveguide applications in the case of  $Nd^{3+}$  ions, but also with the *RE*-doped Si-based systems as frequency conversion layers, see for example [21, 25, 26].

## Experiment

The films of about 400 nm thick were deposited by radio frequency magnetron co-sputtering of two confocal cathodes (Si and  $Nd_2O_3$ ) driven by plasma constituting of a mixture of nitrogen and argon. The p-type mono-crystalline Si or fused silica substrates were used and maintained at 200 °C during the growth. Films deposited on fused silica as substrate were developed only for Raman measurements, other experiments were carried out on films grown on Si substrate. The plasma power densities for Si and  $Nd_2O_3$  targets were fixed at 4.44 and 0.44 W  $cm^{-2}$ , respectively. The ratio of  $N_2$  to Ar gas flux ( $r_N$ ) was varied from 7.0% to 13.3%, while the gas pressure of the plasma was kept constant at 2 mTorr. Such deposition parameters allow one to incorporate a Si excess in the films. Thus, these later are named as Nd-*SRSON*, which will be confirmed below by the characterizations of their composition. After deposition, the films were submitted to a thermal annealing treatment under  $N_2$  ambient for 1 min durations, and different temperatures ranging from 600 °C to 1100 °C. The chemical composition, microstructure, and optical properties of as-deposited and annealed films were studied by x-ray photoelectron spectroscopy (XPS), Fourier transform infrared (*FTIR*), Raman, ellipsometry, transmission electron



**Figure 1.** (a) *FTIR* spectra recorded with an incidence angle of  $65^\circ$  for different  $r_N$  values, (b) the position of *LO* peak obtained by fitting the *FTIR* spectra as a function of  $r_N$ , (c) absorption coefficient versus energy, and (d) refractive index given at 1.95 eV versus  $r_N$  for as-deposited layers. In (c) absorption coefficients of pure amorphous  $\text{Si}_3\text{N}_4$  and Si are added for comparison purpose. The absorption coefficients for pure Si and  $r_N = 7.0\%$  are multiplied by  $1/10$  and  $2/5$ , respectively.

microscopy (*TEM*), *PL* and photoluminescence in excitation (*PLE*) spectroscopies.

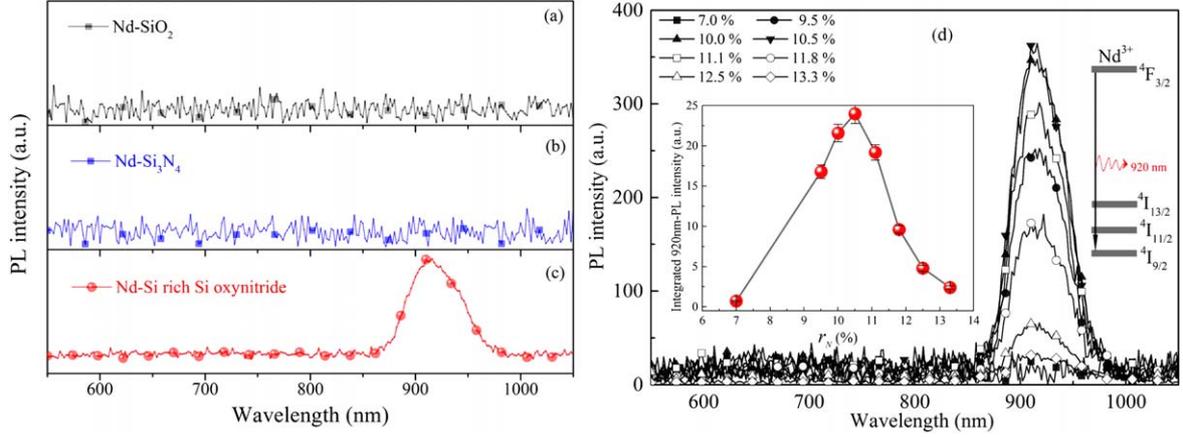
The *XPS* measurements were performed in an ultra-high vacuum *PHI-5000 VPII* system with a base pressure lower than  $5 \times 10^{-8}$  Pa using a mono-chromatic Mg  $k\alpha$  radiation at 1253.6 eV. The layer surface was cleaned (sputtered) by 2 keV  $\text{Ar}^+$  bombardment for 2 min before the measurements. The binding energy was calibrated by using the value of contaminant carbon  $\text{C}1s = 284.8$  eV as reference. For *FTIR* measurements, the spectra were recorded at  $65^\circ$  incidence angle in the  $500\text{--}4000$   $\text{cm}^{-1}$  range using a Nicolet Nexus 470 spectrometer. In case of Raman characterization, the incident laser wavelength was 532 nm. The ellipsometry experiments were carried out by means of an *UVISSEL* Jobin–Yvon ellipsometer with an incident angle of  $66.2^\circ$ . The experimental spectra were recorded on a  $1.5\text{--}5$  eV range with 0.01 eV resolution. The absorption coefficient, refractive index, and thickness were deduced from the experimental data by fitting with the new amorphous dispersion formula which is derived from the Forouhi–Bloomer model for amorphous semiconductors using the *DeltaPsi2* software [27]. The model takes into account the use of crystalline Si substrate, an amorphous Si oxynitride, a rough surface layer composed of a mixture of void space and Si oxynitride. The *TEM* measurements were performed in bright and dark field

modes on a cross-sectional sample using a JEOL 2010F (200 kV) microscope. The *PL* experiments were carried out using the 488 nm-line of a *CW* Argon laser (*Innova 90 C Coherent*), which is a non-resonant wavelength for  $\text{Nd}^{3+}$  ions [28]. Finally, the *PLE* spectra were collected by means of Jobin–Yvon Fluorolog spectrophotometer using a Xe lamp as excitation source. The *PLE* spectra shown below have been calibrated to the spectrum of the Xe lamp used.

## Results and discussion

### Effect of composition

As nondestructive techniques, both *FTIR* spectroscopy and spectroscopic ellipsometry were adopted to study the microstructural and optical properties of dielectric films. Figure 1(a) shows the evolution of the *FTIR* spectra recorded for as-deposited films prepared with the indicative  $r_N$ . Two main vibrations bands are clearly visible, peaking at about  $830$   $\text{cm}^{-1}$  and between  $970$  and  $1150$   $\text{cm}^{-1}$ . They correspond to the transverse and longitudinal optical (*TO* and *LO*) vibrations bands from Si–N bond, respectively. All spectra are normalized to the intensity of  $\text{TO}_{\text{Si-N}}$  band position. The  $\text{TO}_{\text{Si-N}}$  band position slightly changes with  $r_N$ , whereas the



**Figure 2.** PL spectra for Nd-doped in the indicative matrix (a)  $\text{SiO}_2$ , (b)  $\text{Si}_3\text{N}_4$ , (c) SRSON prepared with  $r_N = 10.5\%$ , and (d) Si-rich Si oxynitride with different  $r_N$  ranging from 7.0% to 13.3%; in (d) the inset shows the integrated 920 nm peak intensity versus  $r_N$  and the right depicts the origin of 920 nm peak from  ${}^4\text{F}_{3/2}$ - ${}^4\text{I}_{9/2}$  transition in the  $\text{Nd}^{3+}$  ions.

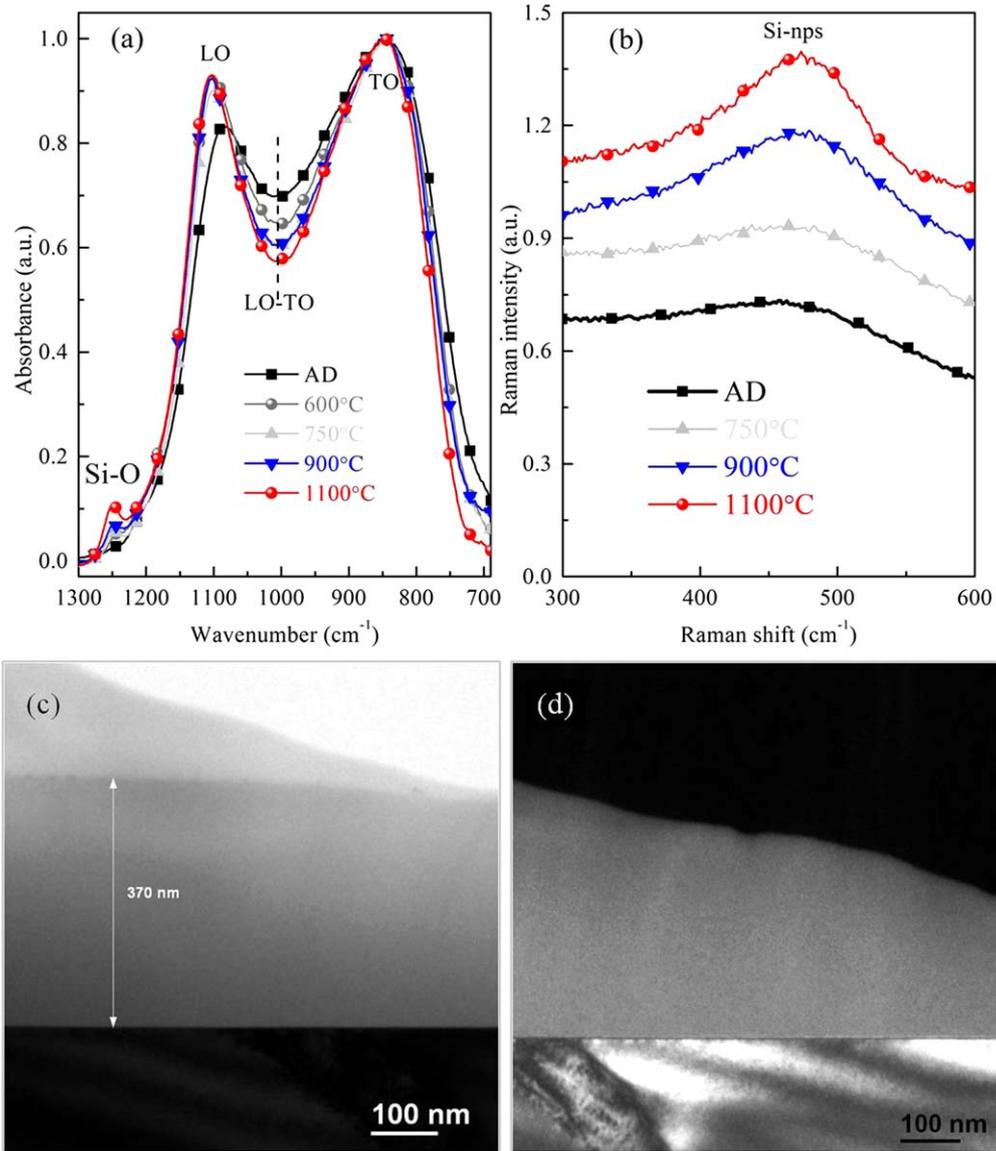
evolutions of  $LO_{\text{Si-N}}$  position and intensity are more pronounced. The  $LO_{\text{Si-N}}$  peak position, obtained by fitting with Gaussian formula, is displayed in figure 1(b). Thus, a significant blue-shift of  $LO_{\text{Si-N}}$  peak position and a concomitant increase of its intensity with  $r_N$  can be noticed. Such behavior is ascribed to a remarkable increase of Si-N bonds and thus confirms an enhancement of N content in the host matrix [29]. As presented in figure 1(c), each value of the absorption coefficient is lower than  $10^3 \text{ cm}^{-1}$  in the 1.0–1.5 eV range. For higher energies from 1.5 to 4.5 eV, it can reach some tens of  $10^4 \text{ cm}^{-1}$ . As noticed, all these curves are between those of amorphous  $\text{Si}_3\text{N}_4$  and Si materials. The absorption coefficient curve for the sample with  $r_N = 13.3\%$  is close to that of amorphous  $\text{Si}_3\text{N}_4$ , while with decreasing  $r_N$  the absorption coefficient increases towards the value of amorphous Si. Moreover, the refractive index shown in figure 1(d) decreases with  $r_N$  which demonstrates that the increase of the nitrogen content in the plasma diminishes the Si incorporation in the  $\text{Si}_3\text{N}_4$  matrix. This evolution is in agreement with the FTIR results confirming that  $r_N$  is an effective parameter to carefully tune the layer composition, i.e. the Si/N ratio.

Figures 2(a)–(c) present the PL spectra for Nd-doped in stoichiometric  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , and SRSON matrices. No PL signal was observed from the former two matrices, while the latter exhibits a remarkable peak at about 920 nm. This suggests an excess of Si in the matrix is required to achieve PL signal. Thereafter, the PL spectra dependence on nitrogen rate  $r_N$  used to prepare the samples are shown in figure 2(d). To note that, all these spectra come from the samples with annealing at 750 °C, which corresponds to an optimal temperature as described below. No emission is seen from 500 to 800 nm for any  $r_N$  value. However, one can clearly observe a PL peak centered at 920 nm ascribed to the  ${}^4\text{F}_{3/2}$ - ${}^4\text{I}_{9/2}$  transition in the  $\text{Nd}^{3+}$  ions [30]. Such an emission achieved with a non-resonant excitation wavelength (488 nm) for the  $\text{Nd}^{3+}$  ions confirms the presence of sensitizers towards this RE ions in the host matrix. The integrated PL intensity of  $\text{Nd}^{3+}$  (inset of figure 2(d)) gradually increases with the  $r_N$  increases from 7.0% to 10.5%, then falls down for higher  $r_N$

values (from 11.1 to 13.3%). The Nd content is assumed to remain constant since the applied power density on the  $\text{Nd}_2\text{O}_3$  cathode was the same for all these samples. Thus, the evolution of  $\text{Nd}^{3+}$  PL intensity is probably determined by the Si/N ratio. As estimated by XPS measurements, the optimized sample (for  $r_N = 10.5\%$ ) was found to contain 47.4, 46.2, 5.7, 0.8 at% for Si, N, O, Nd element, respectively. The Si concentration is excessive comparing to those in  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$ , thus the sample is called Nd-doped Si-rich Si oxynitride (Nd-SRSON).

#### Effect of microstructure

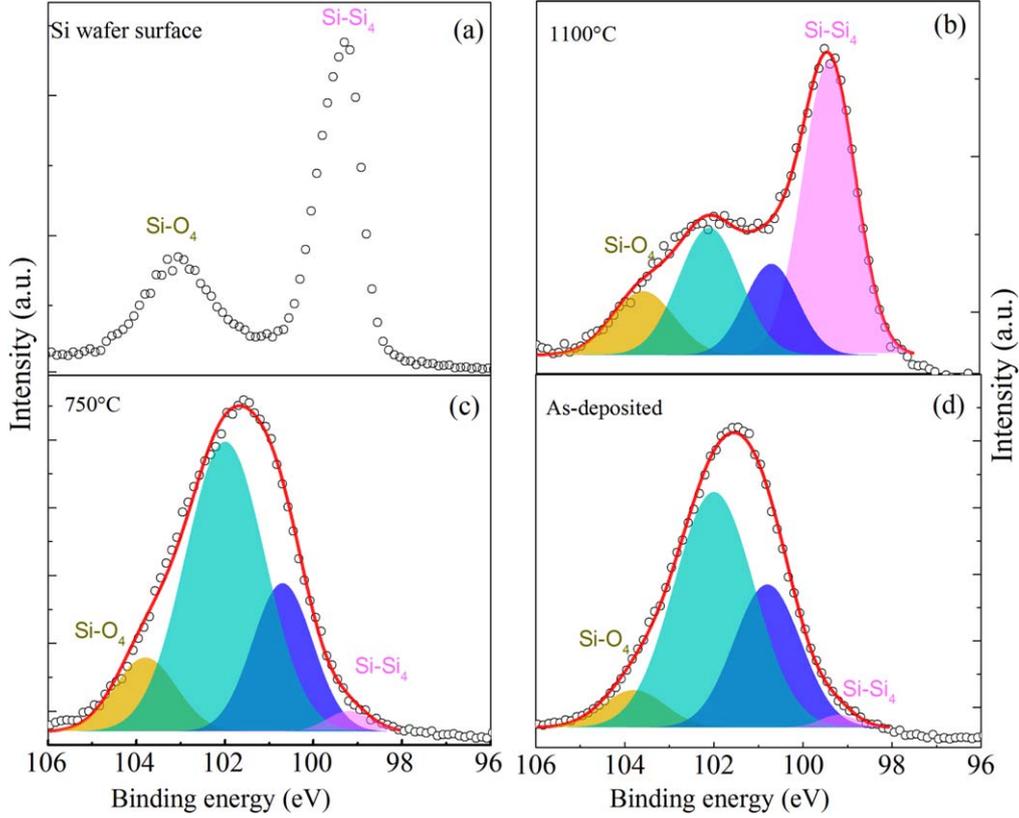
To further understand the PL dependence, it is important to investigate the effect of microstructure influenced by thermal annealing conditions. The optimized layer ( $r_N = 10.5\%$ ) has been studied by FTIR and Raman spectroscopes, TEM and XPS experiments. Figure 3(a) shows the layer microstructure evolution for different annealing temperatures ranging from 600 °C to 1100 °C using FTIR experiments. All spectra are normalized to the  $TO_{\text{Si-N}}$  band intensity. In contrast to the as-deposited sample, the  $LO_{\text{Si-N}}$  peak intensity increases and shifts towards higher wavenumbers for annealed samples. For the former, such a behavior means that the number of Si-N bonds increases due to annealing. This implies the presence of some N dangling bonds in the as-deposited matrix, which recombine with Si atoms upon annealing. Moreover, the  $LO_{\text{Si-N}}$  peak intensity approaches near saturation after annealing at 600 °C. This suggests that an achievement of the recombination of N dangling bonds with Si to form Si-N bond does not require higher temperatures such as 1100 °C. By the way, the intensity of  $LO_{\text{Si-N}}$ - $TO_{\text{Si-N}}$  bands overlapping at about  $1010 \text{ cm}^{-1}$  is gradually attenuated with increasing temperature. This behavior suggests that the host matrix becomes more ordered by the atomic rearrangement. The peak centered at  $1250 \text{ cm}^{-1}$  is attributed to a Si-O bond. Such a peak appears after annealing and its intensity increases with temperature. This is probably due to a phase separation within the matrix induced by the thermal treatment.



**Figure 3.** (a) FTIR spectra recorded with an incidence angle of  $65^\circ$  and (b) Raman spectra for the optimal Nd-SRSON layer as-deposited (AD) and annealed at the indicated temperatures, TEM pictures for  $1100^\circ\text{C}$ -annealed film taken in bright (c) and dark (d) field modes.

Figure 3(b) reports the Raman experiments performed on corresponding as-deposited,  $750^\circ\text{C}$ -,  $900^\circ\text{C}$ - and  $1100^\circ\text{C}$ -annealed samples. Both as-deposited and  $750^\circ\text{C}$ -annealed samples present a weak band at about  $480\text{ cm}^{-1}$ . This suggests that the Si-nps density is very low for these two thin films. With  $T_A$  increase especially at  $1100^\circ\text{C}$ , the spectra show a remarkable peak. It attests the increase of amorphous Si-nps number within the host matrix [31]. It also confirms a structural rearrangement of the matrix and/or a phase separation in the Nd-SRSON materials under such a high annealing temperature. The absence of a peak at about  $521\text{ cm}^{-1}$  indicates that no crystalline Si-nps have been formed upon  $1100^\circ\text{C}$ -annealing temperature process. The TEM results are shown in figures 3(c) and (d). The observations exclude the presence of crystal in the film annealed at  $1100^\circ\text{C}$ . This agrees well with the Raman experiments and strongly confirms that the Si atoms assemble during annealing as amorphous species.

The XPS spectra can provide the chemical surrounding, i.e. atomic binding condition in the samples. For the Si element, according to the random bonding model, each Si atom coordinates to four atoms in the SRSON matrix and forms tetrahedral units  $\text{Si-Si}_k\text{N}_x\text{O}_y$  ( $k + x + y = 4$ ;  $k, x, y = 0, 1, 2, 3, 4$ ). Figure 4 shows the Si  $2p$  XPS spectra and components peaks for the optimal sample as-deposited (figure 4(b)) and annealed at the indicated temperature (figures 4(c), (d)). The Si  $2p$  XPS spectrum of Si wafer used as substrate is also added for comparison (figure 4(a)). Four component peaks were obtained after a de-convolution process. Two peaks centered at  $103.8$  and  $99.2\text{ eV}$  have been experimentally observed and respectively attributed to  $\text{Si-O}_4$  and  $\text{Si-Si}_4$  species [32–34]. For the former, the peak intensity is quite low for the as-deposited layer and shows an enhancement upon annealing. This suggests the O atoms in as-deposited layers are located in a metastable state, rearrange locally and thus form Si-O bonds during annealing. For the later, the



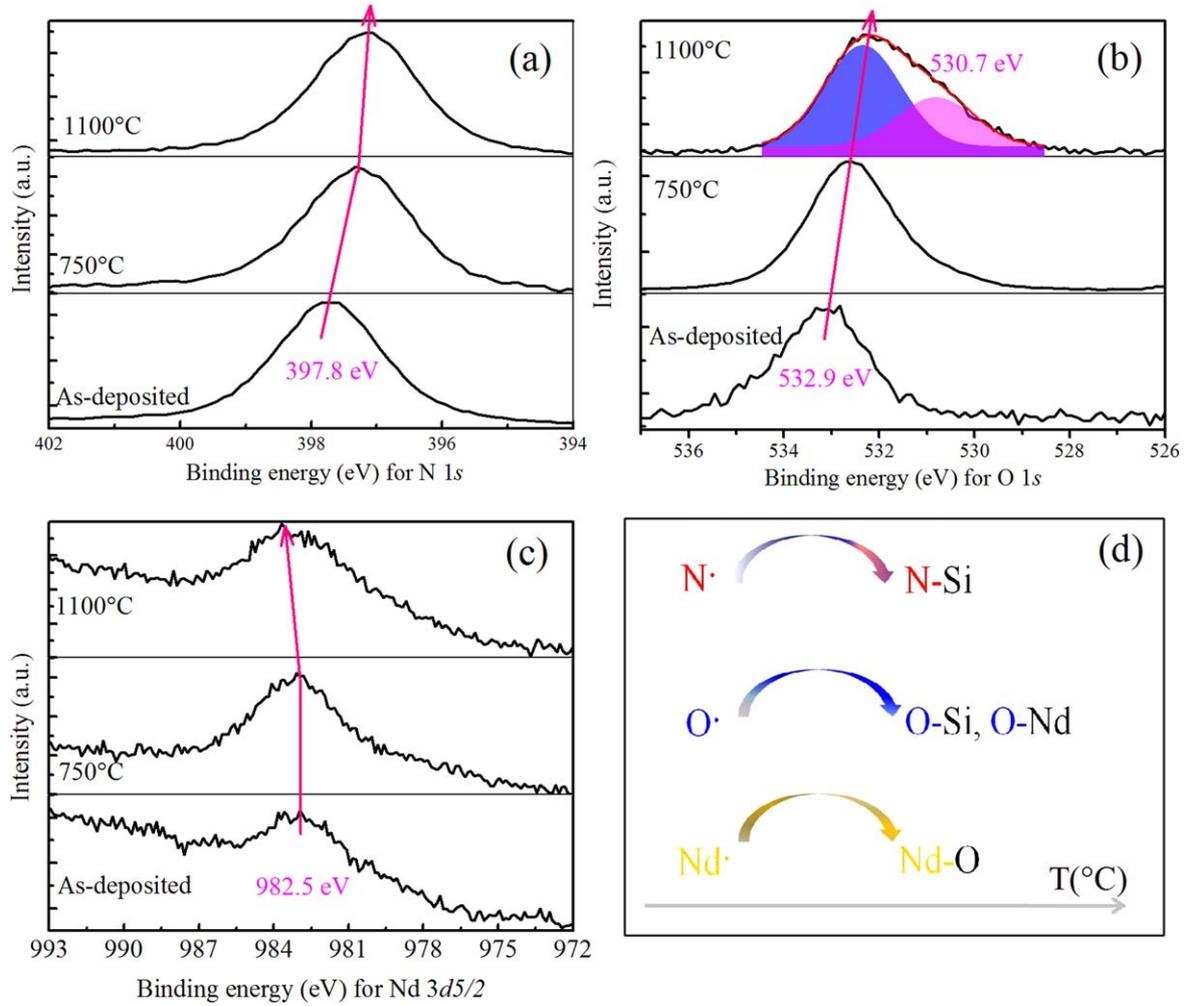
**Figure 4.** The raw Si 2p<sub>3/2</sub> spectra data (open circles) and component peaks (filled area) obtained from the fit of the high-resolution XPS spectra in the Si 2p<sub>3/2</sub> region for the optimized sample (for  $r_N = 10.5\%$ ) annealed at the indicated temperature ((b-d)) and Si wafer (a).

peak intensity is rather low for the as-deposited film. It is slightly enhanced by annealing at 750 °C, while it significantly increases at 1100 °C. This agrees well with Raman results and again evidences that a phase separation occurred after high temperature annealing. In case of the other two components peaking at 101.9 and 100.8 eV, they are assigned to the tetrahedrons containing Si-Si bonds, i.e.  $k'=1, 2$ , or 3 in Si-Si<sub>k</sub>N<sub>x</sub>O<sub>y</sub> formula ( $k' + x + y = 4$ ;  $x, y = 0, 1, 2, 3$ ) according to the calculation by Cova *et al* [35]. In comparison with the case of  $k = 0$ , such Si-Si<sub>k</sub>N<sub>x</sub>O<sub>y</sub> species are named in this paper as Si-rich tetrahedrons. The tetrahedron corresponded to 100.8 eV has a higher  $k'$  value than that for 101.9 eV. As noticed, these two components from Si-rich tetrahedrons mainly occupy the Si 2p peak area for the as-deposited sample. Their intensities relative to Si-Si<sub>4</sub> species show a little decrease after a 750 °C annealing treatment and a remarkable decrease at 1100 °C one. For this later case it indicates the decomposition of Si-rich tetrahedrons and thus the formation of Si-Si<sub>4</sub> species.

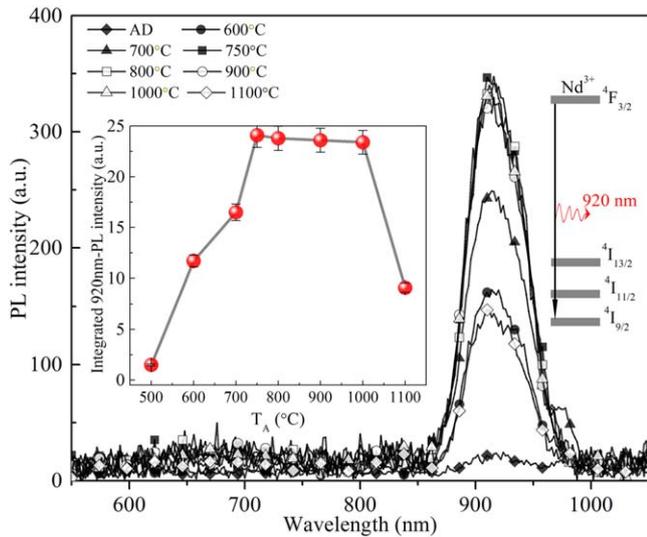
In case of N 1s binding energy region (figure 5(a)), the peak centered at 397.8 eV is observed for the as-deposited sample and presents a red shift for annealed ones. This shift means that the N oxidation state decreases after annealing [36, 37]. Since the oxidation state is dependent on the coordination number in the system, which mainly contains N and Si atoms, one would thus infer the existence of an N-SiN<sub>x</sub> ( $x < 3$ ) species with dangling bonds in the as-deposited sample. During annealing, the N-SiN<sub>x</sub> ( $x < 3$ ) species

converts to an N-Si<sub>3</sub> leading to a passivation of the N' dangling bond [38]. In case of O 1s binding energy region (figure 5(b)), the peak locates at about 532.9 eV for the as-deposited sample and gradually shifts to lower binding energy upon annealing. Note that the 1100 °C-annealed sample shows a broader band that can be fitted into two components peaking at 532.5 and 530.7 eV. The shift of the former component from 532.9 to 532.5 eV is explained by the conversion from O-Si species into O-Si<sub>2</sub> species [39, 40]. This leads to an enhancement of Si-O bond number with annealing temperature, which is consistent with FTIR results (figure 3). The other component at 530.7 eV is assigned to an O-Nd bond [41]. It indicates the change of Nd surroundings under high temperature annealing. As displayed in figure 5(c) for Nd 3d<sub>5/2</sub> binding energy region, the 1100 °C-annealed sample shows a higher energy peak in contrast to both as-deposited and 750 °C-annealed samples. This peak is attributed to Nd-O bond, while the shift is interpreted by the increase of Nd oxidation state [42]. Figure 5(d), as a conclusion for 5(a)-(c), schematically depicts the evolution of chemical surrounding for N, O, and Nd. It illustrates the passivation of dangling bond upon thermal annealing.

The PL spectra are displayed in figure 6 for as-deposited and annealed films. The Nd<sup>3+</sup> emission was recorded and its intensity versus  $T_A$  is shown in the inset. In contrast to the as-deposited sample, the annealing treatment significantly enhances Nd<sup>3+</sup> PL intensity even at low  $T_A = 600$  °C. When increasing  $T_A$ , the PL intensity is improved by a factor of



**Figure 5.** High-resolution XPS spectra for (a) N 1s, (b) O 1s, and (c) Nd 3d5/2 binding energy region for the optimized sample ( $r_N = 10.5\%$ ) annealed at the indicated temperature, (d) drawing of evolution of chemical surrounding for N, O, and Nd elements.

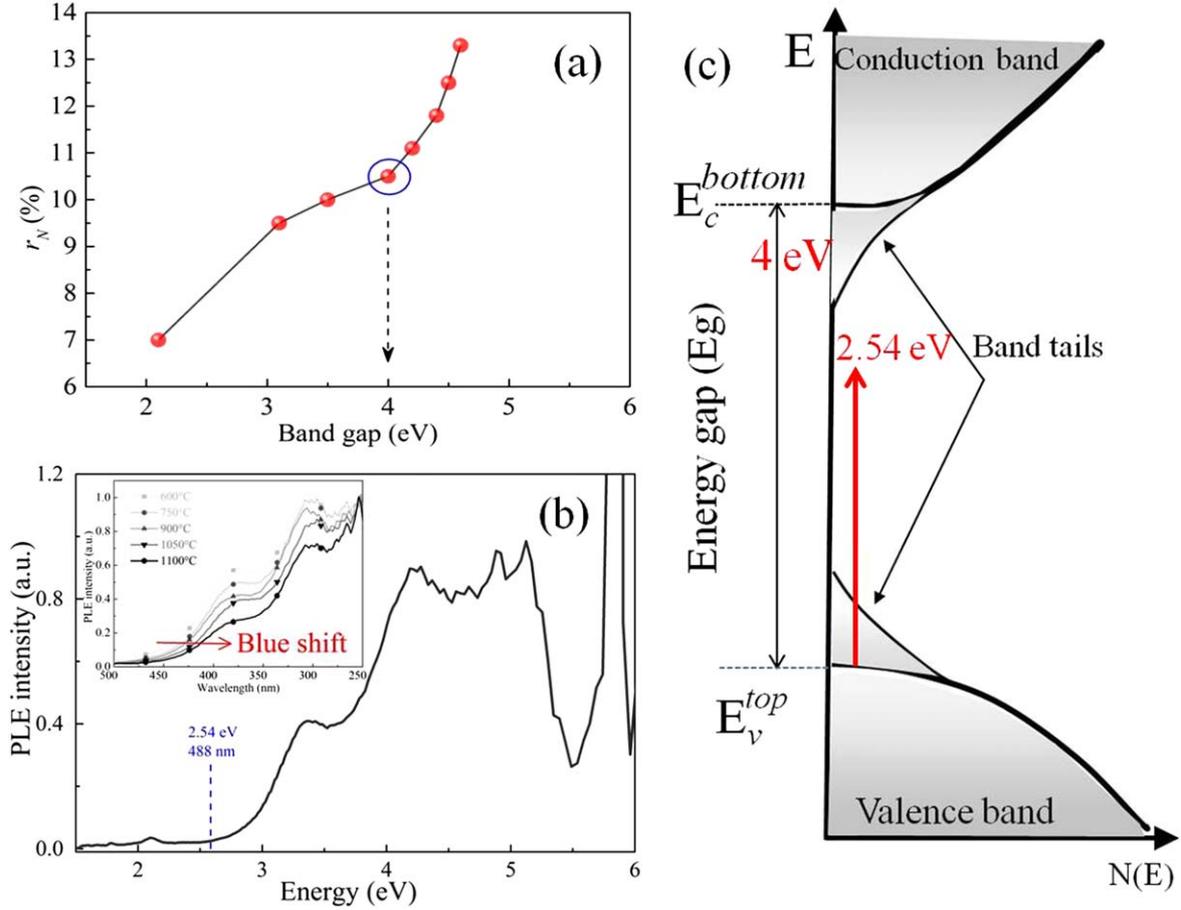


**Figure 6.** PL spectra of as-deposited (AD) and annealed samples (at indicated  $T_A$ , annealing temperature). The left inset shows the integrated PL intensity for 920 nm peak versus temperature and the right one depicts the origin of 920 nm peak from  ${}^4F_{3/2}$ - ${}^4I_{9/2}$  transition in the  $Nd^{3+}$  ions.

more than 10 before collapsing at 1100 °C. This behavior corresponds to the evolutions of matrix microstructure and chemical surrounding for  $Nd^{3+}$  ions, which determine the fraction of efficient coupling between sensitizers and  $Nd^{3+}$  ions. The samples show a high  $Nd^{3+}$  PL intensity in a quite wide range of moderate annealing temperatures ranging from 750 °C to 1000 °C. This is obtained by a concomitant effect of the recovering of non-radiative defects, the evolution of sensitizers' number and optically active  $Nd^{3+}$  density.

#### ET mechanisms

From ellipsometry data analyzed by means of new amorphous dispersion model, the energy band gap was estimated for various  $r_N$  in this study. The band gap energy, as shown in figure 7(a), varies from 2.1 to 4.6 eV with  $r_N$  varying from 7% to 13.3%. Such band gap enlargement is related to less Si incorporation in the  $Si_3N_4$  matrix. This causes the matrix to become more ordered and the band-tails concomitantly shrink [43]. For  $r_N = 10.5\%$  the band gap energy was found equal to about 4.0 eV, which is much higher than the excitation energy at 2.54 eV. Furthermore, PL excitation (PLE) measurement collected at 920 nm was carried out on the optimized sample



**Figure 7.** (a)  $r_N$  used to prepared samples versus band gap estimated by the new amorphous dispersion model, the 750 °C-annealed optimized samples ( $r_N = 10.5\%$ ) corresponds to a band gap of 4.0 eV; (b) *PLE* spectra detected at 920 nm for optimized samples ( $r_N = 10.5\%$ ) annealed at 750 °C. The inset shows the *PLE* spectra evolution for indicative values of  $T_A$ ; (c) schematic illustration of the excitation photon with 2.54 eV compared to the matrix band gap and tails.

annealed at 750 °C and the obtained spectrum is shown in figure 7(b). As seen, the *PLE* intensity is weak for energy lower than 2.8 eV by comparison with the higher energy range (2.8–4.0 eV) where the *PLE* intensity increases with a slope shape. Such shape is a characteristic of band-tails to band-tails absorption mechanism in an amorphous silicon oxynitride matrix [25]. These spectra present a blue-shift with  $T_A$  increase. This shift is related to the passivation of defect density as well as to the shrinking of band-tails in the matrix. The matrix band gap and tails are schematically illustrated in figure 7(c). As seen, the excitation energy 2.54 eV used in this work does not reach the conduction band. Therefore, the sensitization of  $\text{Nd}^{3+}$  ions is not directly due to an *ET* occurring from exciton generated between conduction and valence band.

As discussed on figures 1 and 2, excessive Si in the matrix is required to form Si agglomerates and thus achieve  $\text{Nd}^{3+}$ -emission under a non-resonant excitation (488 nm) [44, 45]. These agglomerates, according to the *TEM*, Raman, and *XPS* experimental results, are amorphous and small for the optimized sample. This agrees well with our previous work demonstrating that a few Si atoms are enough to act as *RE* sensitizer [16]. Furthermore, the Si agglomerates at atomic scale, as observed by Salh *et al*, are optically active and

display green–yellow emission [46]. The exciton emitting green–yellow light is likely to couple with the nearby  $\text{Nd}^{3+}$  ion [47]. Indeed, the visible emission was not observed in our case for the  $\text{Nd}^{3+}$  doped layers while a clear *PL* peak at 920 nm was present via a non-resonant wavelength excitation. This infrared *PL* at the expense of visible emission suggests the occurrence of efficient *ET* from atomic scale Si agglomerates to  $\text{Nd}^{3+}$  ions.

Following the discussion on the nature of the sensitizer, the correlation between the composition, microstructure, and emission properties are described here. Excess Si atoms are needed to create the atomic scale Si agglomerates. However, high Si/N ratio would result in a formation of large Si agglomerates. These latter are ineffective to transfer energy to  $\text{Nd}^{3+}$  ions [48]. Therefore, the  $\text{Nd}^{3+}$ -*PL* intensity shows a maximum value at a moderate Si/N ratio. Moreover, the non-radiative defects such as N and O should be recovered to achieve a high *PL* intensity. Annealing treatment shows a good approach to promote N $\cdot$  and O $\cdot$  recombination with Si, as evidenced by both *XPS* and *FTIR* results. Whereas, annealing at high temperature 1100 °C, too large Si agglomerates are grown by a decomposition of Si-rich tetrahedrons species. It would also result in the clustering of Nd ions, which favors an energy cross-relaxation process. This will

reduce the effective sensitizers and/or emitter centers. Such behaviors demonstrate the importance of controlling deposition parameter and annealing temperature to optimize sample composition and microstructure in order to (i) favor the generation of effective sensitizers, (ii) recover the non-radiative defects, (iii) promote the highest coupling number between sensitizers and lanthanide ions.

## Conclusion

The correlation between the composition, microstructure, and emission properties of Nd-SRSON films have been studied in detail. The maximum *PL* intensity of Nd<sup>3+</sup> ions was obtained from the films (i) deposited by reactive magnetron co-sputtering of pure Si and Nd<sub>2</sub>O<sub>3</sub> cathodes under mixed (N<sub>2</sub>/Ar = 10.5%) plasmas, and (ii) post-annealed at 750°C–1000 °C. This, as demonstrated above, corresponds to the best environment for the achievement of dense effective sensitizers and for a passivation of non-radiative defects such as N· and O· dangling bonds. The optical measurements confirm that the excitation process of Nd<sup>3+</sup> ions did not involve the valence-conduction band but the excitation rate is enhanced by atomic scale Si agglomerations. The overall analysis involves six types of optical measurements. This seems an effective methodology to monitor the evolution of composition and microstructure, such as Si agglomerations and non-radiative defects. This approach exhibits a great advantage to study atomic sensitizers towards *RE* ions and thus achieve favorable emission.

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