Structural and emission properties of Tb$^{3+}$-doped nitrogen-rich silicon oxynitride films

This content has been downloaded from IOPscience. Please scroll down to see the full text.
2017 Nanotechnology 28 115710
(http://iopscience.iop.org/0957-4484/28/11/115710)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 156.17.68.46
This content was downloaded on 20/02/2017 at 16:12

Please note that terms and conditions apply.

You may also be interested in:

Green light emission from terbium doped silicon rich silicon oxide films obtained by plasma enhanced chemical vapor deposition
A Podhorodecki, G Zatryb, J Misiewicz et al.

Amorphous sub-nanometre Tb-doped SiOxNy/SiO2 superlattices for optoelectronics
Joan Manel Ramírez, Jacek Wojcik, Yonder Berencén et al.

Nanocrystals for silicon-based light-emitting and memory devices
S K Ray, S Maikap, W Banerjee et al.

Analysis of the luminescent centers in silicon rich silicon nitride light-emitting capacitors
S A Cabañas-Tay, L Palacios-Huerta, J A Luna-López et al.

Effect of thermal annealing treatments on the optical activation of Tb3+-doped amorphous SiC:H thin films
J A Guerra, F De Zela, K Tucto et al.

Structural analysis of the interface of silicon nanocrystals embedded in a Si3N4 matrix
J Barbé, K Makasheva, S Perraud et al.

The evolution of the fraction of Er ions sensitized by Si nanostructures in silicon-rich siliconoxide thin films
P Noé, H Okuno, J-B Jager et al.

Role of Li+ on white light emission from Sm3+, Tb3+ co-doped Y2O3 nano-phosphor
R S Yadav, R V Yadav, A Bahadur et al.
Structural and emission properties of Tb\textsuperscript{3+}-doped nitrogen-rich silicon oxynitride films

C Labbé\textsuperscript{1}, Y-T An\textsuperscript{1}, G Zatryb\textsuperscript{2}, X Portier\textsuperscript{1}, A Podhorodecki\textsuperscript{2}, P Marie\textsuperscript{1}, C Frilay\textsuperscript{1}, J Cardin\textsuperscript{1} and F Gourbilleau\textsuperscript{1}

\textsuperscript{1} CIMAP, Normandie Univ, ENSICAEN, UNICAEN, CEA, CNRS, 6 Boulevard Maréchal Juin 14050 Caen Cedex 4, France
\textsuperscript{2} Department of Experimental Physics, Wrocław University of Technology, 50-370 Wrocław, Poland

E-mail: christophe.labbe@ensicaen.fr

Received 1 June 2016, revised 8 October 2016
Accepted for publication 30 November 2016
Published 17 February 2017

Abstract

Terbium doped silicon oxynitride host matrix is suitable for various applications such as light emitters compatible with CMOS technology or frequency converter systems for photovoltaic cells. In this study, amorphous Tb\textsuperscript{3+} ion doped nitrogen-rich silicon oxynitride (NRSON) thin films were fabricated using a reactive magnetron co-sputtering method, with various N\textsubscript{2} flows and annealing conditions, in order to study their structural and emission properties. Rutherford backscattering (RBS) measurements and refractive index values confirmed the silicon oxynitride nature of the films. An electron microscopy analysis conducted for different annealing temperatures (T\textsubscript{A}) was also performed up to 1200 \degree C. Transmission electron microscopy (TEM) images revealed two different sublayers. The top layer showed porosities coming from a degassing of oxygen during deposition and annealing, while in the region close to the substrate, a multilayer-like structure of SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} phases appeared, involving a spinodal decomposition. Upon a 1200 \degree C annealing treatment, a significant density of Tb clusters was detected, indicating a higher thermal threshold of rare earth (RE) clusterization in comparison to the silicon oxide matrix. With an opposite variation of the N\textsubscript{2} flow during the deposition, the nitrogen excess parameter (N\textsubscript{ex}) estimated by RBS measurements was introduced to investigate the Fourier transform infrared (FTIR) spectrum behavior and emission properties. Different vibration modes of the Si–N and Si–O bonds have been carefully identified from the FTIR spectra characterizing such host matrices, especially the ‘out-of-phase’ stretching vibration mode of the Si–O bond. The highest Tb\textsuperscript{3+} photoluminescence (PL) intensity was obtained by optimizing the N incorporation and the annealing conditions. In addition, according to these conditions, the integrated PL intensity variation confirmed that the silicon nitride-based host matrix had a higher thermal threshold of rare earth clusterization than its silicon oxide counterpart. Analysis of time-resolved PL intensity versus T\textsubscript{A} showed the impact of Tb clustering on decay times, in agreement with the TEM observations. Finally, PL and PL excitation (PLE) experiments and comparison of the related spectra between undoped and Tb-doped samples were carried out to investigate the impact of the band tails on the excitation mechanism of Tb\textsuperscript{3+} ions.

Supplementary material for this article is available online

Keywords: terbium, silicon, nitride, thin film, rare earth, photoluminescence, vibration mode

(Some figures may appear in colour only in the online journal)
deposition techniques used to form such rare earth (RE) doped thin films to implantation, molecular beam epitaxy (MBE), magnetron sputtering and plasma-enhanced chemical vapor deposition (PECVD), the most common host matrix for Tb$^{3+}$ ions is SiO$_2$ [1–4]. Some works in the literature have made a step forward by fabricating various devices based on this matrix [4–7]. Some investigations have also been carried out on Tb$^{3+}$:SiC(N) materials [8–10], as well as on silicon-rich silicon oxide films (Tb$^{3+}$:SRSO) [11] with CMOS devices [12]. However, the incorporation of excess silicon into SRSO, contributing to the formation of Si nanoclusters, significantly reduced the emission intensity of lanthanide ions as a result of a strong non-radiative recombination [13–15].

For this reason, some researchers have focused their work on silicon (oxy)nitride thin films with the aim of finding efficient light sources directly integrable on optical chips [16]. Indeed, the silicon oxynitride host is an attractive choice because of its relatively small band gap (4 ~ 5 eV), which may play an important role in the energy transfer from matrix to RE ions with an efficient electrical injection [17]. Moreover, this matrix should have much higher RE ion solubility in comparison to its silicon oxide counterpart, and thus prevent clustering of RE ions [18]. Furthermore, Si rich silicon nitride (SRSN) has been investigated, since excess Si can form clusters which act as luminescence centers to enhance RE emission [19]. In contrast to this, various studies mention the role played by the localized states in the band tails (BTs) of the amorphous matrix acting as sensitizers for RE emission [16, 20–22]. As underlined by Yerci et al the addition of N atoms introduces more disorder than in the case of SRSO matrices [16]. In this case, in contrast to excess Si, the excess N (N$_{ex}$) would introduce many defects, leading to the appearance of BTs. For this reason, one can expect an efficient sensitization of RE ions in nitrogen-rich silicon (oxy) nitride (NRS(O)N) films [17, 23]. Indeed, for such matrices an intense Tb$^{3+}$ photoluminescence (PL) signal was observed by Jeong et al [24], Yuan et al [25] and by our group [26], even for non-resonant excitation. From these results, two significant applications have been demonstrated using a Si-based host matrix: a CMOS device based on a Tb$^{3+}$:SiO$_x$N$_{1-x}$/SiO$_2$ superlattice [27] and a photovoltaic application based on a down converter system [28, 29]. Therefore, the Tb$^{3+}$ excitation mechanism in NRSON requires further investigation in order to fully understand this key process.

In this study, we have investigated the structural and optical properties of Tb-doped NRSON films. These films were fabricated by reactive magnetron co-sputtering method for varying reactive nitrogen flows and annealing temperatures ($T_A$). Rutherford backscattering (RBS), transmission electron microscopy (TEM) and energy-filtered TEM (EFTEM) measurements have been performed to analyze the composition and structure of these samples. An investigation of different vibration modes of the Si-N and Si-O bonds was conducted using Fourier transform infrared (FTIR) spectrometry. Taking into account both the reactive flux and the annealing effect, we report here the optimal conditions for preparation of highly luminescent samples and discuss the Tb-clusterization effect. Finally, the energy transfer mechanisms between the NRSON host matrix and the Tb$^{3+}$ ions were considered.

2. Experimental details

In this work, Tb-doped NRSON films were deposited onto p-type 250 μm-thick (100)-oriented Si wafers by reactive radio frequency magnetron co-sputtering of a pure Si target topped with 5 Tb$_4$O$_7$ pellets under pure nitrogen plasma. The N gas flux was varied from 3 to 9 sccm, while the plasma total power was concomitantly changed over the range of 4–28 μWbar. The deposition temperature ($T_d$) and RF power density were fixed at 200 °C and 1.23 W.cm$^{-2}$ respectively. Annealing was carried out under a given N flow, at temperatures ($T_A$) varying from 500 °C to 1200 °C over 1 h.

The chemical composition of the layers was obtained by RBS measurements using a 1.5 MeV $^4$He$^+$ ion beam with a normal incidence and a scattering angle of 165°, revealing the relative atomic concentrations (% at.) of the various elements. TEM was used to observe the evolution of the structure of the samples upon annealing. For these observations, cross-sectional thin foils were prepared by means of a FEI HELIOS Nanolab 660 focused ion beam until electron transparency was achieved. The samples were then investigated using a double corrected JEOL ARM200 operated at 200 keV, equipped with a cold field emission gun, and a GATAN imaging filter (GIF) (QUANTUM 965ER spectrometer). The chemical analyses were performed by EFTEM, using the image mode of the GIF to analyze the compositional variation of the layers. The digitized images were processed by the commercial GATAN software DIGITAL-MICROGRAPH. The microscope was also equipped with an Energy Dispersive x-ray (EDX) spectrometer for chemical analysis.

The FTIR spectra were recorded across the range of 500–4000 cm$^{-1}$ using a Nicolet Nexus spectrometer under normal and Brewster’s (65°) incidence angles. The optical properties of the layers have been characterized using Ellipsometry and Photoluminescence spectroscopy measurements. The former were conducted by means of a UVISEL Jobin-Yvon ellipsometer with an incident angle of 66.2°. The experimental spectra were recorded over a 1.5–5 eV range with 0.01 eV resolution. The refractive indices, given at 1.95 eV, as well as the thicknesses, were deduced from the experimental data by a dispersion law derived from the Forouhi–Bloomer model for amorphous semiconductors, using DeltaPsi2 software [30]. The thickness and refractive index uncertainties were ±10 nm and ±0.01 respectively. Finally, measurements of photoluminescence (PL) and PL excitation (PLE) spectra were performed at room temperature by means of a Jobin-Yvon Fluorolog spectrophotometer, using a 450 W Xe lamp as excitation source with a spectral resolution lower than 5 nm. The PL lifetime was obtained by means of an optical parametric oscillator with 5 ns pulse at full width at half maximum (FWHM) and 10 Hz repetition rate for 244 nm wavelength excitation. The spot diameter was 500 μm with an average energy of 15 mJ.
3. Elemental composition analysis

Elemental compositions of the as-deposited (AD) samples were determined by RBS measurements. Figure 1(a) shows RBS spectra ranging from 0.20 up to 1.10 keV for the samples obtained with different N flows. The backscattering signals from N and O atoms can be seen in figure 1(a), along with that from Si coming from both thin film and substrate as reported in previous works [14, 27]. Note that the oxygen content in the films originates from the Tb4O7 chips. The slight change in the curve shape indicates a small variation of the composition of these films (figure 1(a)). Figure 1(b) shows RBS spectra in the 1.15–1.40 keV range, which corresponds to the backscattering from Tb\(^{3+}\) ions. The width of the Tb-related band changes from sample to sample due to their different thicknesses (230–280 nm), coming from the different N gas flux. The band intensities (RBS yields) are very similar, indicating that the Tb content is almost the same for all the films. Moreover, Tb spatial distribution in each sample is quite uniform across the film thickness.

By fitting RBS spectra as shown in figure 1, the film compositions were obtained (see figure 2(a)). The fits require the use of two layers: one at the top of the film (so called ‘top layer’) in contact with air and another one at the interface near the substrate (so called ‘interface layer’). The ratio between the resulting top and interface layers’ thicknesses varied from three (190 nm/60 nm) to one third (60 nm/190 nm). Atomic concentrations are calculated considering the weight of the interface and top layers thicknesses. As can be seen in figure 2(a), the Tb concentration is constant in all of the investigated films and equal to 0.73 ± 0.05 at.%. The fact that Tb has a homogeneous distribution across the whole film for the AD samples differs from Tb-doped SRSO layers. Indeed, for SRSO host matrices, it has been shown that Tb ions tend to agglomerate and form clusters close to the film/substrate and film/air interfaces, even at low concentration (0.1 at.%) [14]. As expected, the nitride matrix seems to prevent such an agglomeration process even for seven times...
higher Tb concentrations. This issue is discussed further in section 7. Regarding the other elements, the O content varies between 13 at.% and 17 at.%, while the Si content increases from 29 at.% up to 36 at.%. Surprisingly, a slight decrease of the N concentration of almost 5 at.% is observed with increasing N flow.

To further the investigation, N excess (N_{ex}) was deduced using the following relation:

\[
N_{ex}(\%) = \frac{\left[ N \right] - \frac{4}{3} \left[ Si \right] + \frac{2}{3} \left[ O \right] - \frac{7}{6} \left[ Tb \right]}{\left[ N \right] + \left[ O \right] + \left[ Si \right] + \left[ Tb \right]} \times 100
\]

where the term [element] represents the atomic concentration (at.%) of the element (see supplementary data). This ratio gives the deviation from a perfect SiO_{2} and Si_{3}N_{4} mixture [28, 31] and highlights the importance of N compared to the other elements. Excess N evolution as a function of N flow is displayed in figure 2(b). Clearly, N_{ex} decreases with N flow, having values from 24.4%, 17.9%, 14.9%, 14.7%, to 9.4% (see the left scale of figure 2(b)) which correspond to samples named S_{24}, S_{18}, S_{15}, S_{14}, and S_{9} respectively. Such behavior seems to be linked with the layer deposition rate (right scale of figure 2(b)), which gradually decreases as the N_{2} flow increases. A similar result has been obtained by Xu et al [32], who suggested that, from target to substrate, the ejected species collide and/or react with N_{2}, leading to the modification of the mean free path. Thus, some species do not have enough energy to reach the substrate. Consequently, one can assume that a high N_{2} flow is unfavorable to the incorporation of N atoms and to the deposition rate of the growing film.

4. Refractive index analysis

The refractive index was also investigated. The bilayer model used to estimate the refractive index by fitting with DeltaPsi software is consistent with the bilayer model used in RBS analysis. The refractive index increases from 1.54 up to 1.79 with N content. These low index values are between those of nanotechnology 28 (2017) 115710 N content. These low index values are between those of nanotechnology 28 (2017) 115710 materials, confirming that we have fabricated an oxynitride matrix [17, 33, 34].

5. Microscopic analysis of the annealing temperature effect

In this section, we present different TEM images of the S_{9} sample in a cross-section configuration for different T_{A} values. These images were obtained for the AD sample and for samples annealed at 700 °C, 1000 °C and 1200 °C, for 1 h under N flow (figures 3–5).

According to these observations, the deposited thin films remain amorphous (without diffracting particles) whatever the post annealing treatment applied. The AD S_{9} sample presents porosities coming from almost the middle of the film (dashed horizontal line in figure 3(a)) and forming vertical tortuous columns of nanoscale diameter in the direction of the top surface (figure 3(a), zoom inset), using a slight defocus condition. These hollow columns are more visible upon 700 °C annealing (figure 3(b), zoom inset) which is probably related to the degassing of light elements from the film (O and/or N) during annealing. But the deposition process itself—lasting almost two hours at a substrate temperature of 200 °C—seems to have the same effect, since a similar microstructure is observed for the AD sample. Apparently, this degassing process—coming from almost the middle of the film—results in a two-layer structure. These results confirm our previous assumption with two modeled layers, named top and interface layers, used for the RBS and refractive index modeling. Note that the limit between these layers can change without apparent logic between one quarter to three-quarters of the full thickness. The same kind of degassing has also been confirmed via TEM observations on other samples (not shown here).

To investigate this issue in more detail, the S_{9} sample has been annealed at higher temperature (T_{A} = 1000 °C) and EFTEM images (figure 4(a)), displaying O and N maps, have been recorded for the whole thickness of this film, by using their respective K edges at 532 eV and 401 eV. Unfortunately, the rare earth element concentration remains too low to be imaged by this technique. Notably, the silicon profile map (not shown) has a homogeneous distribution in the film, by contrast with the O and N profiles shown in figures 4(b)–(e). Indeed, concerning the interface layer, O is highly concentrated both on the top and on the bottom (figure 4(b)), whereas N is concentrated mostly in the middle (figure 4(c)). Surprisingly, the profiles of these two last elements offer a clear complementary contrast, displaying a kind of multilayer structure. Note that such N, O distributions are also apparent for the AD and all the annealed layers.

Concerning the top layer, the EFTEM maps reveal low O content, while the N is homogeneously distributed as we can see in figure 4(e), where only the bottom of the top layer is visible but the whole top layer has a uniform distribution of these elements. The low O content, confirmed by RBS measurements (0.1 at.%), suggests the degassing of this element. The oxygen may diffuse towards the surface representing the boundary between the top and the interface layer (figures 4(a)–(e)), featuring the possible physical limit for degassing inside a solid phase. This frontier position does not appear to vary significantly with the thermal budget (figures 3(b) and 4(a)), suggesting that this effect appears during deposition (figure 3(a)).

This limit, as well as the separation of the two different elements (figure 4(d)), highlighting an unmixing inside the interface layer, are strictly parallel to the substrate surface. These boundaries could be induced by the stress evolution of the film during the deposition [35]. More precisely, this observation suggests a stress-induced diffusion of N by the Si substrate [36, 37], or at least evidence of the significant role of this interface, leading to a phase separation with a predominant SiO_{2} phase (when O content is significant) or Si_{3}N_{4} phase (when it is weak). Then, the film/substrate interface
could be at the origin of a surface-directed spinodal decomposition (SDSD) \[38\] in the pseudobinary \((\text{SiO}_2)_{x}(\text{Si}_3\text{N}_4)_{1-x}\) alloy system. As a matter of fact, such an unintended multilayer structure has already been observed by Liu et al \[39\] for \((\text{HfO}_2)_{x}(\text{SiO}_2)_{1-x}\) alloy systems near the substrate, and has been attributed to a spinodal decomposition (SD) \[38\].

Another similar effect has been noticed for Si-rich-HfO\(_2\) materials, but in this case coming from the air-film interface with HfO\(_2\) and SiO\(_2\) phases \[40\]. Such a SDSD process has also been shown in ZrO\(_2\)-SiO\(_2\), La\(_2\)O\(_3\)-SiO\(_2\), and Y\(_2\)O\(_3\)-SiO\(_2\) systems \[41\]. The SD is also the process at the origin of the formation of Si nanoclusters in SiO\(_2\) or SiN\(_x\) host matrices due to the high Si content \[42-44\]. In our case, the N\(_{ex}\) could be at the origin of such effect assisted by a stress-induced diffusion. In addition, the deposition occurs at 200 °C which is a relatively high deposition temperature for a magnetron co-sputtering process, providing a degassing affecting also the SDSD. Indeed, usually, such SD effect generates a composition wave which has a 4–5 nm periodicity. In our case, this periodicity is approximately one order of magnitude higher (30–40 nm), impacted by the degassing and the deposition of our thicker film (230–280 nm). In other studies with Si excess reported in the literature, one can again find periodicity with a large thickness of almost 40 nm, similar to our case \[42, 43\].

A TEM image, shown in figure 5, was obtained on the S\(_9\) sample annealed at 1200 °C, to check the thermal budget threshold at which clusterization occurs. The elemental EFTEM map (not shown) is presented in the supplementary data. The TEM image reveals a significant density of clusters with a darker contrast located below the limit between the top/interface layer (dashed line in figure 5), with a size of about 20–40 nm and a lengthening following this boundary. Note that such clusters start to be detected (weakly contrasted) for samples annealed at 700 °C throughout the thickness of the interface layer. These agglomerates at 1200 °C were
identified by EDX measurements as amorphous Tb-rich clusters (inset of figure 5). Similar particles have already been observed and identified as Tb-oxide clusters (TbO₂, Tb₂O₅) in SiO₂ by Nazarov et al. Their presence is due to a more stable thermodynamic state of this phase, and they are located in the center of the film for a $T_a$ of 900 °C and at the air/film and film/substrate interfaces for higher $T_a$ [6]. Due to the fact that our clusters stay amorphous, they should not be in the same stoichiometry as mentioned above. In contrast to this observation, a Tb-doped silicon-rich silicon oxide with 50 at.% Si shows Tb diffusion from both film interfaces towards the middle of the film, becoming uniform across the film depth [13, 14]. In our case, the surprising position of this line of clusters is probably due to separation between the interface and the top layer, offering a stable energy for the formation of Tb clusters. In any case, such Tb clusters are completely formed at 1200 °C, confirming that such a nitride-based host matrix is less favorable to RE clustering than its silicon oxide counterpart, due to slower diffusion of RE [18, 27, 45, 46]. In others words, the silicon oxynitride matrix has a higher thermal threshold of RE clusterization compared to the silicon oxide matrix.

6. Infrared spectroscopic analyses

6.1. Constant nitrogen excess

FTIR spectra were performed on as-deposited $S_0$ (figure 6) and as well as on all NRSON samples (figure 7). The spectra for the $S_0$ sample were measured under a normal incident angle (figure 6(a)) and Brewster angle (figure 6(b)). As can be seen, a broad band ranging from 650 cm⁻¹ up to 1350 cm⁻¹ with no sharp peaks appears.

To identify the different peaks constituting such a broad band, we have fitted the normal incident angle spectrum with five Gaussian peaks (fewer would not be consistent with the literature cited in table 1), revealing the transversal optical modes (TO) (figure 6(a)). However, the Brewster angle spectrum reveals the longitudinal modes (LO) and therefore an additional 6th peak appears (figure 6(b)). The fits, with three parameters for one Gaussian peak (position, amplitude, FWHM), are performed without any constraint.

The various peak positions are displayed in table 1. Focusing on the Si-O absorption bands, a well-known peak under normal incident angle is observed at 1070 cm⁻¹ and attributed to the TO₃ stretching mode, which is also confirmed under Brewster angle at 1076 cm⁻¹ [47–51]. The LO₃ mode is present at 1222 cm⁻¹, compared with 1250 cm⁻¹ and 1254 cm⁻¹ in SiO₂ matrix respectively [47, 49] or 1227 cm⁻¹ and 1250 cm⁻¹ in the case of the SiO₂Nₓ matrix [48, 52].

An important third peak is visible at 1128 cm⁻¹ under normal incidence, which is blue-shifted at 1146 cm⁻¹ under Brewster angle incidence. This peak cannot be ascribed to the TO₄ vibration band usually localized at 1200 cm⁻¹. This is confirmed by the fact that the appearance of the LO₄ mode under Brewster angle involves a red-shifted peak located at 1160–1170 cm⁻¹ [47, 53]. Such a peak is attributed to an ‘out-of-phase’ stretching vibration mode of the Si-O bond. Indeed, Pai et al [50] based on previous results on local density of vibrational states (LDOVS) by Lucovsky et al [54], underline a weak coupling between Si and O atoms, causing this high frequency edge at 1150 cm⁻¹: the same position we noticed. This first result is confirmed by Kirk et al, who did an investigation of the disorder effect on IR absorption spectra in the a–SiO₂ host matrix and found that the interpretation of the IR spectra is somewhat in contradiction to an independent-oscillator model [47]. Indeed, by introducing disorder-induced mechanical coupling between $\text{LO}_2$-$\text{TO}_3$ and $\text{LO}_4$-$\text{TO}_4$, a broad and significant vibration band appears in the range 1076-1256 cm⁻¹, corresponding approximately to our bandwidth. Note that the amorphous character of our samples permits the detection of a low contribution of the LO peaks even under normal incident angle, as reported previously [55]. In addition, the blue shift observed according to the appearance of the LO mode under Brewster angle for our samples, is in agreement with the spectra displayed by Kirk et al [47]. This important shoulder in the 1100–1250 cm⁻¹ range under Brewster angle is also shown in previous works on silicon oxynitride host matrices deposited by PECVD [56–58].

The three last vibration bands are positioned at 867 cm⁻¹, 956 cm⁻¹ and 1024 cm⁻¹ under normal angle (or at 869 cm⁻¹, 953 cm⁻¹ and 1029 cm⁻¹ under Brewster angle) (see table 1). These energies correspond approximately to the positions ($\approx$903 cm⁻¹, 965 cm⁻¹, 1030 cm⁻¹) found by Naiman et al after a dispersion analysis on (reoxidized) nitrided oxides on silicon [59], as well as the ones proposed by Moreno et al [60]. The latter found modes peaking at 896 cm⁻¹, 962 cm⁻¹ and 1026 cm⁻¹ after performing
modelling of silicon nitride system. But these peak positions are not ascribed to a specific vibration mode. Our first peak at 867 cm$^{-1}$ is well known and is originating from the Si-N stretching mode\cite{52, 56, 61–64}. The difference between this first peak position at 867 cm$^{-1}$ and 903 cm$^{-1}$ (or 896 cm$^{-1}$) for the other authors, could suggest that we did not take into account the Si-O TO$_2$-LO$_2$ peaks at 810–820 cm$^{-1}$ (figures 3(a)–(b)) \cite{47, 48}.

As for the two last peaks at 956 cm$^{-1}$ and 1024 cm$^{-1}$, their attribution is more complicated. Focusing on the 956 cm$^{-1}$ peak, this band could be explained by the Si-OH bending mode but our matrix does not contain any hydrogen.
[65]. Another possibility could be the existence of an asymmetric mode Si-O-Tb bonds. But, as mentioned by Ono et al [66], the heavier the element that binds with oxygen atom in Si-O is, the lower the vibrational frequency [66]. Then some authors have observed a vibrational frequency at about 900 cm\(^{-1}\) for a Si-O-Pr [66] or, although Nd is heavier than Pr, around 910-950 cm\(^{-1}\) for Si-O-Nd [67]. Yet, Tb atom is much heavier than the Pr or Nd ones and thus, a vibration at 955 cm\(^{-1}\) for this bond could be excluded. Finally, such a peak at 956 cm\(^{-1}\) was found in a 220 nm-thick SiO\(_2\)N\(_2\) [68] and more precisely at the interface layer with the Si substrate whose thickness was about 2 nm on etched nitrided oxide layer [59]. In a detailed study of Ono et al this peak, positioned exactly at 960 cm\(^{-1}\) but, in 1993, this peak was attributed to the doubly bonded N atoms associated with two Si atoms (≡Si-N-Si≡) with the asymmetric stretching mode [69].

The last peak found at 1024 cm\(^{-1}\) underlined by the dispersion analysis of Naiman et al is ascribed, in their previous study, to the planar trigonal bonded nitrogen (Si\(_3\)≡N\(_3\)) [68]. Nevertheless, some studies assign this peak to a shoulder of the main (Si-N) stretching band at 870 cm\(^{-1}\) [62, 60, 71].

### 6.2. Variable nitrogen excess

The spectra in figure 7(a) show a blue shift of the maximum intensity of about 60 cm\(^{-1}\) towards 1075 cm\(^{-1}\) with decreasing the N\(_2\) flow inside the deposition chamber and so increasing N\(_{ex}\). However, we note (see figure 11(a) in supplementary data) that during this N\(_{ex}\) rise (9.4% to 24.4%), the different peaks positions blue-shifted slightly by only 20 cm\(^{-1}\), except for the Si-N (TO) and Si-O (LO\(_3\)) modes which did not shift at all. Then this refocusing at 1075 cm\(^{-1}\) is not due to a shift of all the peaks positions. Such a variation in shape is due to the decreasing of the out-of-phase peak intensity (see figures 11(b)-(c) in supplementary data). This decrease was already seen for AD films upon N incorporation [57, 58], as well as for annealed samples [56], obtained by PECVD technique.

In the last 2050–2300 cm\(^{-1}\) energy range (figure 7(b)), we note an absorption peak centered at 2202 cm\(^{-1}\). Such a peak originates from Si–H stretching [72] or isocyanate groups (N=C=O) or nitrile (C≡N) bond stretching [73]. But no H or C atoms were detected in our samples. Nevertheless, the intensities of these peaks seem to be sensitive to the N\(_{ex}\) increase. Based on the study of adsorption of N\(_2\), chemisorbed on Rh/SiO\(_2\) samples, an important absorption peak at around 2200 cm\(^{-1}\) at low temperature is explained by the N≡N bond linked to the Rh ion [74]. Consequently, our peak can be ascribed to the azide N≡N stretching mode [75], which gives a (Si-N≡N) resulting bond centered at 2202 cm\(^{-1}\), depending on the N\(_{ex}\) concentration. Such a peak also attests to the N-rich character of our nitride matrix.

### 7. Emission properties

#### 7.1. Photoluminescence properties

Figures 8(a) to (c) show the PL spectra of the samples annealed at different temperatures for one hour in a pure N\(_2\) flow. These samples were excited at room temperature using a 325 nm line from a lamp source. This wavelength is non-resonant with energy levels of the Tb\(^{3+}\) ion. As observed, each sample shows four PL peaks centered at about 490, 545, 590, and 624 nm, which correspond to the intra-4f \(^5\)D\(_4\) → \(^7\)F\(_j\) (j = 6, 5, 4, 3) transitions of Tb\(^{3+}\) ions respectively, as depicted in figure 8(a). These peaks have already been reported in previous studies on Tb:SiN layer obtained by reactive co-sputtering [76] or PECVD deposition techniques [24, 25]. For each spectrum, the strongest peak intensity is located at 545 nm \(^5\)D\(_4\) → \(^7\)F\(_j\)). This band has been selected to investigate the \(T_A\) effect for various N\(_{ex}\). The evolution of its integrated PL intensity with these parameters is shown in figure 8(b) as a function of \(T_A\).

For all samples, the PL intensity increases with \(T_A\), reaches a maximum and starts to decrease for higher \(T_A\) values. The former (increasing) evolution of PL intensity is due to the passivation of non-radiative channels in the host matrix [77], whereas the latter (decreasing) could be assigned to the combination of two effects. Even if the porosities already appear in the AD sample (figure 3(a)), the drop in PL intensity could originate from the rising number of porosities with annealing, offering more surface recombination centers and providing new non-radiative channels [78]. The second possible effect, which seems to be dominant, is the formation of Tb clusters, such as those observed in the TEM image in figure 5 at \(T_A\) = 1200 °C and already detected at \(T_A\) = 700 °C. These clusters have a detrimental effect on PL intensity by the reduction of the number of optically active Tb\(^{3+}\) ions [79]. Such an effect is commonly seen in other rare
earth-doped Si-based matrices, including Nd:SiN\textsubscript{4} [80] and Er:SRSO [36].

It is interesting to note that the maximum PL intensity appears at different \( T_A \) values depending on the \( N_{ex} \). This optimum is reached at \( T_A = 600^\circ \text{C} \) for samples \( S_9 \) and \( S_{14} \)—both having lower \( N_{ex} \) content (9.4\% and 14.7\%), while it appears at \( 800^\circ \text{C} \) for sample \( S_{15} \) and \( 900^\circ \text{C} \) for samples \( S_{18} \) and \( S_{24} \)—containing more \( N_{ex} \). The temperatures corresponding to these maxima seem to be the limiting temperatures below which cluster formation is not the predominant effect. Above this limit, the RE aggregates drive down the PL intensity. Apparently, by introduction of a high N excess, the formation of clusters is delayed. This shift of the \( T_A \) by almost \( 300^\circ \text{C} \) has already been observed for Er ions incorporated in both SiO\textsubscript{2} and SiN\textsubscript{4} [81]. In this study, the maximum intensity was underlined at \( T_A = 800^\circ \text{C} \) for the silicate matrix, while the maximum was not achieved for the SiN\textsubscript{4} matrix with a higher thermal budget. Our results confirm this point and show that the silicon nitride-based host matrix has a higher thermal threshold of RE clusterization than its silicon oxide counterpart [18].

7.2. Time-resolved photoluminescence

Although it is interesting to increase the \( N_{ex} \) in the film in order to prevent the formation of Tb clusters, we have found that the maximum PL intensity is about three times lower with a high \( N_{ex} \) value (figure 8(b)). Indeed, such a strongly non-stoichiometric composition may affect the quality of the host matrix and create many non-radiative defects. For deeper investigations, we conducted time-resolved PL measurements. Figure 9(a) displays the PL decays detected at 545 nm (\( ^5D_4 \rightarrow ^7F_3 \)) wavelength as a function of \( N_{ex} \), obtained for samples annealed at \( T_A = 600^\circ \text{C} \). The decay times deduced from these curves are shown in figure 9(b). Note that the lifetime of BT-related PL (see section 7.3) is usually in the nanoseconds scale, which is too short to be measured by our experimental setup [82].

The decay curves exhibit a non-exponential behavior and for this reason we have calculated the mean decay time (\( \tau_m \)) using the following equation:

\[
\tau_m = \int_0^\infty \frac{I(t)}{I_0} \, dt
\]

where \( I(t) \) is a time dependent peak intensity while \( I_0 \) is the maximum intensity at \( t = 0 \) s [83]. The lifetime obtained for the samples annealed at \( T_A = 600^\circ \text{C} \) (figure 9(b)) for the lowest \( N_{ex} \) amount is in the range of several hundred microseconds, comparable to the values reported by other authors [24]. The decay time increases slightly with \( N_{ex} \) for \( S_{14} \) sample; a gradual decrease is then noticeable for higher \( N_{ex} \) values. The integrated PL intensity displayed in figure 8(b) (dashed line at \( T_A = 600^\circ \text{C} \)) for the same samples, and reported in figure 9(b) (right scale), shows a similar evolution. Therefore, the PL intensity behavior seems to be governed by the non-radiative recombination coming from the increasing population of defects with \( N_{ex} \). This explains why the maximum PL intensity is about three times lower for the highest \( N_{ex} \) (figure 8(b)).

To go further in the study of the annealing effect, we present the dependence of the PL decay time of the optimized sample \( S_{14} \) detected at 545 nm with respect to \( T_A \) (figures 9(c)–(d)). The PL lifetime increases with \( T_A \) up to \( 1000^\circ \text{C} \), followed by a rapid decrease at \( 1100^\circ \text{C} \). This latter, as explained above, can be explained by the large number of Tb-rich clusters formed leading to new non-radiative channels. Up to \( 1000^\circ \text{C} \), a reduction of the non-radiative recombination takes place, due to defect passivation, which causes the increase of the PL lifetime. That being the case, one wonders why the PL intensity behavior has a maximum at \( T_A = 600^\circ \text{C} \) (figure 8(b)), while the lifetime has a maximum shifted for \( 1000^\circ \text{C} \) (figure 9(d)). The long average lifetime measured (530 \( \mu \text{s} \) at \( T_A = 600^\circ \text{C} \)) comes from the locally isolated Tb\textsuperscript{3+} ions. The diffusion of Tb\textsuperscript{3+} ions probably starts at \( 600^\circ \text{C} \) (Tb-rich clusters detected for the \( 700^\circ \text{C} \) annealed sample by TEM observations—see section 5) reducing de facto the
number of optically active Tb$^{3+}$ ions and concomitantly reducing the PL intensity. Consequently, between 600 °C and 1000 °C, the lifetime continues to increase due to the passivation of defects, while we observe a reduction of the PL intensity. Such behavior has been already detected in Er$^{3+}$ ions in silica glass by Polman et al.\cite{84}.

7.3. Excitation mechanisms of Tb$^{3+}$ ions

Figure 10(a) shows the PL spectra for both undoped and Tb-doped NRSON films annealed at 600 °C for 1 h, measured using 380 nm (3.3 eV) excitation line. The undoped sample displays a broad band from about 2.5 to 3.2 eV (500 to 390 nm) originating from the recombination of excitons in BT states\cite{26}. Indeed under such excitation wavelength, the BT has a significant PL intensity compared to the excitation at 325 nm shown in figure 8(a) and described in our previous study\cite{28}. The Tb-doped sample presents the features of the Tb$^{3+}$ ion peaks. The overlap between the Tb$^{3+}$ energy levels and the BT is evident. This spectral overlap is very important, since it allows indirect excitation of Tb$^{3+}$ ions via BT states, leading to the observed $^5D_4 \rightarrow ^7F_j$ transitions. The same behavior has already been observed for undoped\cite{24, 25} and Tb-doped films\cite{24} and is mainly due to the N dangling bond related recombination process.

Aiming at understanding the energy transfer mechanism to the Tb$^{3+}$ ions, PLE experiments were performed for both samples at 3.2 eV (390 nm) detection wavelength related to the BT PL (figure 10(b)) and also at 2.5 eV (490 nm) and 2.3 eV (545 nm), corresponding to the $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_5$ transitions of the Tb$^{3+}$ ion (figure 10(d)). In the case of BT detection, two peaks appear for the undoped film at 3.3 eV and 4.3 eV (figure 10(b)—black arrows). The first one is identified as a N defect state ($N_i^+$)\cite{26}, while the second is correlated to the absorption of the BT just below the gap\cite{28, 29}. It is linked to the Si–N bonds which introduce localized states due to N–2π lone pair electrons at the top of the valence band\cite{85}. The recombination of holes and electrons in localized states associated with Si–N bonds explains the 2.5–3.2 eV peak in PL\cite{77, 86, 87}.

The Tb doping introduces some amount of oxygen, coming from the Tb$_2$O$_3$ chips, which results in an increase of the band gap. This leads to a blue shift of the two peaks of about 0.6 eV (dashed horizontal lines in figure 10(b)), to 3.9 eV and 4.9 eV respectively. In any case, the Tb doping may affect the BT and its structure, because the peak
intensities are not in the same ratio, in addition of their position changing. In the case of detection at Tb$^{3+}$ related peaks at 2.5 eV (490 nm) and 2.3 eV (545 nm) (figure 10(d)), both PLE spectra show an overall increase in PL intensity with increasing excitation energy. Above all, they have two peaks linked to the N defect state ($N^+_i$) and the absorption of the BTs underlined above, showing their active role in Tb$^{3+}$ ion excitation.

A schematic of the different energy levels of the host matrix and the RE is suggested in figure 10(c). According to the previous studies [26, 28], the excitation of Tb$^{3+}$ in such thin films involves two types of excitations. First, when using high excitation energy photons (>4.9 eV), the carrier-mediated excitation transfer occurs from the matrix to the Tb$^{3+}$ related states, such as the $5K_8$ level or the excited electronic interconfiguration 4f$^5$5d. This is followed by a non-radiative relaxation in Tb$^{3+}$ ions towards the $5D_4$ level. Second, when the excitation energy is lower than the band gap of the matrix (<4.9 eV), the excitons trapped in the BT states or N defect states can directly transfer their energy to Tb$^{3+}$ ions.

![Figure 10](image)

**Figure 10.** (a) PL spectra of undoped and Tb-doped films annealed at 600 °C during 1 h (b) the associated PLE spectra detected at 390 nm (3.2 eV) related to the BT (d) 490 nm (2.5 eV) ($^5D_4$ $\rightarrow$ $^7F_6$) and 545 nm (2.3 eV) ($^5D_4$ $\rightarrow$ $^7F_5$) related to the Tb$^{3+}$ transitions and (c) the schematic of the Tb$^{3+}$ energy diagram depicting the energy transfer between electronic energy levels.

### 8. Conclusions

Tb-doped nitrogen-rich silicon oxynitride (NRSON) films were deposited by co-sputtering with variable N$_2$ flows and submitted to different thermal annealing treatments. The films were found to consist of two sublayers: a porous top layer and a bottom, so called interface layer, formed as a result of an unintended phase separation between SiO$_2$ and Si$_3$N$_4$. An explanation of this effect is proposed, involving spinodal decomposition. With a high annealing temperature at 1200 °C, a formation of Tb-rich clusters was detected just below the separation between the interface and the top layer, revealing a higher thermal threshold of rare earth clusterization for the silicon oxynitride matrix in comparison to silicon oxide matrix.

Based on the RBS measurements, the $N_{ex}$ parameter has been introduced and found to vary in the opposite way to the N flow inside the deposition chamber. FTIR analysis with N excess showed several different peaks associated to the silicon oxide or nitride bonds. A classification of all the vibrational modes for such host matrices is proposed and compared

---

**Nanotechnology 28 (2017) 115710**

C Labbé et al
to previous results in the literature. In particular, the ‘out-of-phase’ stretching vibration mode of the Si–O bond at 1146 cm\(^{-1}\), detected under Brewster angle illumination, has been observed. We have found that its impact is reduced for high N excess values, i.e. for a low N\(_2\) flow in the deposition chamber. Another peak, linked to the azide N≡N bond at 2202 cm\(^{-1}\), has also been identified.

The highest Tb\(^{3+}\) PL intensity was obtained by optimizing the N incorporation and the annealing conditions. The PL spectra reveal the well-known peaks of Tb\(^{3+}\) ion at 490 nm (\(^2\)D\(_4\) \(\rightarrow\) \(^2\)F\(_{6}\)) and 545 nm (\(^2\)D\(_4\) \(\rightarrow\) \(^2\)F\(_{5}\)) wavelengths. Finally, we found that the maximum PL intensity of the 545 nm Tb\(^{3+}\) line corresponds to the annealed film at 600 °C with 14.7% N excess, corresponding to 8 sccm N\(_2\) flow. The study in function of \(T_A\) showed the role of Tb clustering in quenching PL intensity. In particular, the analysis underlined that the effect of Tb clustering in silicon oxynitride matrix is significantly reduced, compared to that in silicon oxide matrix, due to a higher thermal threshold of Tb clusterization. From this point of view, and for the same thermal budget, the silicon oxynitride matrix allowed a much higher concentration of optically active Tb\(^{3+}\) ions, which is beneficial for light emitting applications development.

The PL decay curves showed that the decay times of Tb\(^{3+}\) ions are of the order of several hundred microseconds and revealed that the PL intensity was affected by the emergence of non-radiative defects with N excess. Besides, the values of the decay times continued to increase with the annealing temperature, while the PL intensity decreased, revealing the formation of Tb-rich clusters, in agreement with the TEM observations. Finally, the mechanism of the excitation of Tb ions has been explored. PLE spectra of undoped and Tb-doped films have highlighted two main absorption peaks. The first peak was identified as the N defect state (N\(_4^+\)), while the second was ascribed to the absorption of the BTs just below the gap at 4.9 eV for the Tb\(^{3+}\) doped sample. When excitation energy was lower than the band gap (<4.9 eV), the excitons trapped in the BT states or N defect states can directly transfer their energy to Tb\(^{3+}\) ions.

Acknowledgments

This work was financially supported by the French Research National Agency through the GENESE project (No ANR-13-BS09-0020-01), the GENESIS EQUIPEX (ANR-11-EQPX-0020) and the LABEX EMC3 ASAP project. This work was also supported by the CEA/DSM/ENERGY contract (HOFELI Project) and the Chinese Scholarship Council (CSC) program and Polonium Partenariat Hubert Curien (PHC No 27720WC) Program.

The authors would like to thank Dr Sophie Boudin from CRISMAT Laboratory (Caen, France) for the PL and PLE experiments. In Poland, this work was funded by the National Science Centre in the framework of the Project No DEC-2012/05/D/ST7/01121.

References

[14] Podhorodecki A et al 2012 Green light emission from terbium doped silicon rich silicon oxide films obtained by plasma enhanced chemical vapor deposition Nanotechnology 23 475707
[16] Yerci S et al 2010 Visible and 1.54 μm emission from amorphous silicon nitride films by reactive cosputtering IEEE J. Sel. Topics Quantum Electron. 16 114
[20] Li R et al 2009 Temperature dependence of the energy transfer from amorphous silicon nitride to Er ions App. Phys. Lett. 95 041111
[22] Debieu O et al 2013 Structural and optical characterization of pure Si-rich nitride thin films Nanoscale Res. Lett. 8 31
[25] Zhizhong Y et al 2006 Photoluminescence of Tb3+ doped SiNx films grown by plasma-enhanced chemical vapor deposition J. Appl. Phys. 100 083106
[27] Ramirez J M et al 2015 Amorphous sub-nanometre Tb-doped SiOxNy/SiO2 superlattices for optoelectronics Nanotechnology 26 085203
[34] Bãék T 1982 Silicon oxynitride; a material for GRIN optics Appl. Opt. 21 1069–72
[38] Cahn J W 1965 Phase separation by spinodal decomposition in isotropic systems J. Chem. Phys. 42 93–9
[39] Liu J et al 2010 Surface-directed spinodal decomposition in the pseudobinary alloy (HFO2)x(SiO2)1–x J. Appl. Phys. 107 123510
[40] Khomenkova L et al 2014 Spectroscopic and structural investigation of undoped and Er3+ doped hafnium silicate layers Physica B: Condensed Matter 453 100–6
[43] Delachal F et al 2009 Properties of silicon nanoparticles embedded in SiNx deposited by microwave-PECVD Nanotechnology 20 415608
[51] Debieu O et al 2011 Effect of the Nd content on the structural and photoluminescence properties of silicon-rich silicon dioxide thin films Nanoscale Res. Lett. 6 161
[64] Tomar V K et al 2007 Deposition and characterization of SiON films using HMDS for photonics applications Semiconductor, Sci. Technol. 22 43


Huang L et al 1997 Structure and composition studies for silicon nitride thin films deposited by single ion beam sputter deposition Thin Solid Films 299 104–9


Fontaine-Gautrelet C et al 2006 On the clarification of the IR stretching vibration assignment of adsorbed N$_2$ on Rh$^0$ and Rh$^{5+}$ surface atoms of supported Rh crystallites The Journal of Physical Chemistry B 110 10075–81

Maier G et al 2000 Reactions of silicon atoms with nitrogen: a combined matrix spectroscopic and density functional theory study1 Organometalics 19 4775–83

Zanatta A R et al 2007 Red-green-blue light emission and energy transfer processes in amorphous SiN films doped with Sm and Tb J. Phys.-Condens. Matter 19 8


Street R A 1981 Luminescence and recombination in hydrogenated amorphous silicon Adv. Phys. 30 593–676

Steveler E et al 2010 Indirect excitation of Er$^{3+}$ ions in silicon nitride films prepared by reactive evaporation App. Phys. Lett. 97 221902–3

Li R et al 2011 Energy transfer and stimulated emission dynamics at 1100 nm in Nd-doped SiNx Opt. Express 19 5379

Ding W-C et al 2009 A comparison of silicon oxide and nitride as host matrices on the photoluminescence from Er$^{3+}$ ions Chin. Phys. B 18 3044–8

Deshpande S V et al 1995 Optical properties of silicon nitride films deposited by hot filament chemical vapor deposition J. Appl. Phys. 77 6534–41


Polman A et al 1991 Optical doping of vwaveguide materials by MeV Er implantation J. Appl. Phys. 7 3778–84

