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# Red–green–blue light emission and energy transfer processes in amorphous SiN films doped with Sm and Tb

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## Abstract

Amorphous silicon–nitrogen (a-SiN) thin films have been independently doped with Sm, Tb, and Sm + Tb. The films were prepared by reactive cosputtering and characterized by energy dispersive x-ray analysis, optical transmission, and photo- and cathodoluminescence techniques. All films display room-temperature visible luminescence after excitation with either photon or electron sources. The present results indicate that the luminescence intensity is highly susceptible to thermal annealing treatments as well as to the combination of rare-earth ions. In fact, an improvement of about 500% was achieved in the overall optical emission after annealing the films up to 1050 °C for 15 min. Also, the presence of Tb<sup>3+</sup> ions in the Sm + Tb-doped a-SiN films enhanced the Sm<sup>3+</sup>-related emission, and spectrally sharp optical transitions could be verified at 485, 545, and 650 nm. The likely mechanisms behind the optical activation of the Sm<sup>3+</sup> and Tb<sup>3+</sup> ions and the energy transfer processes between these ions and the amorphous SiN matrix, are presented and discussed. In order to improve the blue light emission of the present samples, one a-SiN film simultaneously doped with Sm + Tb + Tm has also been prepared and investigated in detail.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Most of the technological applications expected in the field of rare-earth (RE) doped silicon-based compounds take into account the possibility of combining the electronic properties of Si with the optical characteristics of RE<sup>3+</sup> ions [1]. In the former case, Si presents an unrivaled processing technology that is responsible for a large amount of the actual industrial (micro-) electronic devices. RE<sup>3+</sup> ions, on the other hand, exhibit sharp and well-defined optical transitions that are almost insensitive to temperature and to the characteristics of the host

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matrix. Based on these aspects, devices based on the Si + RE technology could give rise to a new optoelectronics era, where the main objective is to substitute electrons for infrared photons in the (*on-chip* or *chip-to-chip*) transit of information. In the case of Si-based wide-bandgap materials, it is also possible to anticipate hybrid Si + RE light-emitting devices operating in the visible spectral range in the form of displays, see for example [2].

While it is true that the spectral characteristics of RE<sup>3+</sup> ions are weakly affected by temperature and by the matrix details, the energy transfer processes involved in the excitation-recombination of the RE<sup>3+</sup> ions are not [3]. In fact, much of the present research effort in the field of RE-doped compounds focuses on the systematic investigation of the spectroscopic properties of RE<sup>3+</sup> ions (or a combination of them) when inserted in different solid hosts [4, 5].

Motivated by the above scenario, the present contribution contains a comprehensive study of amorphous silicon–nitrogen thin films doped with Sm and Tb species. The simultaneous incorporation of Sm<sup>3+</sup> and Tb<sup>3+</sup> ions into the amorphous SiN matrix was also investigated to achieve light emission in the red–green–blue spectral range as well as to explore the energy transfer mechanisms between these two ions. Finally, and in order to improve the blue light emission of the present samples, one a-SiN film doped with Sm + Tb + Tm was also prepared and investigated following the same experimental approach.

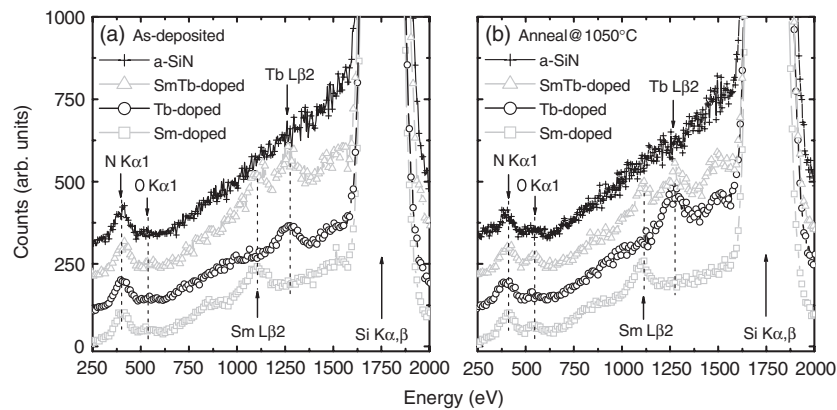
## 2. Experimental details

RE-doped amorphous SiN (a-SiN) films were prepared by radio frequency (13.56 MHz) sputtering of a target of polycrystalline silicon (99.999% pure) partially covered at random with small pieces of Sm and/or Tb metal (99.9% pure). The films were deposited under high-vacuum conditions (base pressure  $<3 \times 10^{-6}$  Torr) in an atmosphere of high-purity nitrogen ( $2 \times 10^{-3}$  Torr). The films, 0.5  $\mu\text{m}$  thick, were simultaneously deposited on crystalline silicon (c-Si) and quartz substrates at  $(175 \pm 25)$  °C. Except for standard cleaning procedures, none of the substrates have received especial treatment. All depositions were preceded by a 1 h long sputtering with pure argon in order to remove contaminants on the surface of the Si + RE target. After deposition, the films were thermally annealed for cumulative periods of 15 min at 300, 450, 600, 750, 900, and 1050 °C in an atmosphere of argon.

The experimental characterization of the films included compositional, optical, and electronic analyses: energy dispersive x-ray (EDX) spectrometry, optical transmission in the ultraviolet–visible (UV–vis) regions, and photo-(PL) and cathodoluminescence (CL) spectroscopy in the 400–850 nm wavelength range. Both PL and CL experiments were carried out at room-temperature on films deposited on c-Si substrates. In the former case, the films were excited with 488.0 nm photons in a micro-Raman setup (typical spot size 1  $\mu\text{m}^2$  and laser power 3 mW). During the CL measurements, an electron beam of 10 keV and 1 mA was adopted, rendering analysed circular areas of approximately 7 mm<sup>2</sup>.

## 3. Results

The study of the present RE-doped amorphous SiN films also included the investigation of one undoped a-SiN sample, prepared under the same deposition conditions and subjected to identical thermal treatments. According to this analysis, and based on the results provided by Raman scattering spectroscopy and x-ray diffraction measurements, it is possible to state that the insertion of Sm, Tb, and Sm + Tb species did not induce any significant change on the atomic structure of the studied a-SiN films, i.e. the films are essentially amorphous even after thermal annealing at 1000 °C [6]. Actually, RE species at the present doping level concentrations are responsible just for the development of characteristic optical emission, as



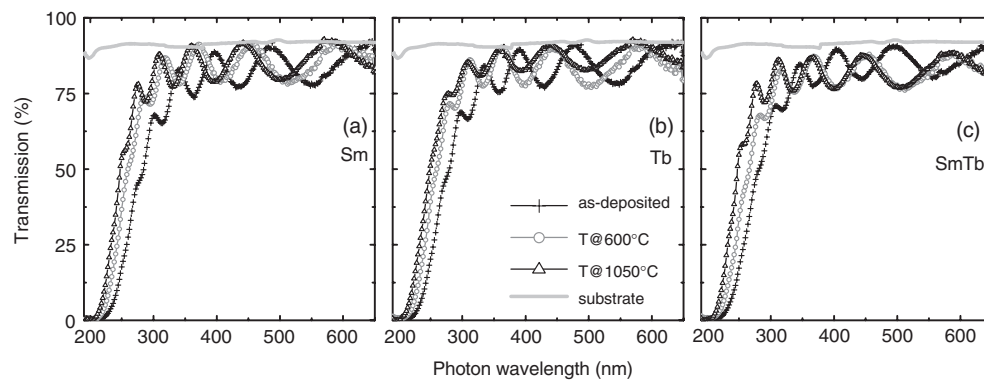
**Figure 1.** Energy dispersive x-ray measurements of amorphous SiN films: (a) as-deposited and (b) after thermal annealing at 1050 °C. The spectra correspond to a-SiN films undoped and doped with Sm, Tb, and Sm + Tb as shown in the figures. Some of the main x-ray emission lines are also indicated in the figures. The analysed films were deposited on c-Si substrates and the spectra have been vertically shifted for comparison purposes.

will be shown below. Also, the present amorphous SiN films are almost stoichiometric with rare-earth contents below 1 at.%, as indicated by an extended investigation including ion beam (Rutherford backscattering and nuclear reaction analysis) and x-ray photoelectron spectroscopy experiments on very similar a-SiN films [7].

Because of the characteristics of the deposition method and due to the amorphous nature of the films, their atomic composition can easily be changed and depends basically on the following experimental conditions: nitrogen partial pressure, relative RE-to-Si target area, and respective sputtering yields. In order to test the atomic composition of the samples considered in this study, all a-SiN films were submitted to energy dispersive x-ray (EDX) measurements.

Figure 1 shows the EDX curves obtained from the samples as-deposited and after thermal annealing at 1050 °C. The presence of Sm and Tb (as well as their combination) in the a-SiN films is evident from the figure. At this point it is convenient to mention that these EDX analyses are only qualitative; most of the concentrations of the films have been determined by the deposition conditions and from a previous compositional study [7]. Except for some increase in the oxygen concentration, the EDX measurements indicate that the atomic content of all films remains almost unchanged (within  $\sim 0.3$  at.%), even after thermal annealing. The relative intensity of all the peaks are consistent with that exhibited by the signal due to Si, and any observed spectral change is within the experimental sensitivity of our instruments. Since the samples have been prepared following exactly the same deposition conditions adopted in [7], we have: [Sm] = 0.8 at.% and [Tb] = 0.7 at.%. Also, it is not clear if the oxygen detected by EDX originates mainly from the films or from the unintentional oxide layer present between the a-SiN films and the crystalline Si substrate.

Whereas the thermal treatments do not have great influence on the thickness, composition, and structure of the a-SiN films, they induce considerable changes on the optical properties of the samples. Figure 2, for example, displays the optical transmission spectra of RE-doped a-SiN films as-deposited and after annealing at 600 and 1050 °C. The fringe pattern in all spectra refers to interference effects between the film and the quartz substrate [8]. It is also important to remark that, except for small experimental deviations (up to  $\sim 15\%$  when compared with the as-deposited samples), all films present practically the same thickness as the thermal annealing treatments advance.



**Figure 2.** Optical transmission spectra of amorphous SiN films doped with (a) Sm, (b) Tb, and (c) Sm + Tb. The spectra correspond to films as-deposited and after thermal annealing at 600 and 1050 °C. The optical transmission of the crystalline quartz substrate is also shown in the figures. Notice the increased transmission and steepness of the absorption edge at short wavelengths as the films are annealed at higher temperatures. The fringe pattern originates from light interference effects between the film and the quartz substrate. For the present films, the thickness of all films remains almost the same as the thermal annealing treatments advance. The legends in (b) apply for all figures.

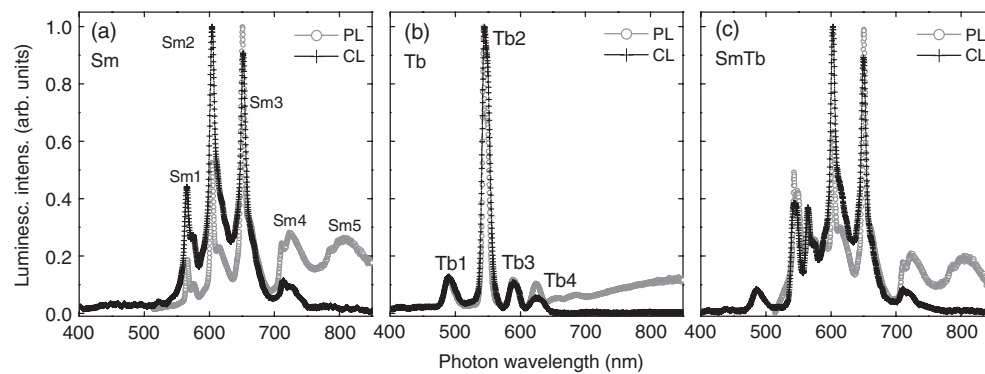
According to figure 2, the films annealed at higher temperatures exhibit a small blue shift and some reduction in the density of tail states, as suggested by the increased transmission and steepness of the spectra at low wavelengths, respectively. It is worth noting that the undoped a-SiN film presents exactly the same behavior (not shown) as do other RE-doped amorphous films [6, 9]. Typically, the optical bandgap of these films stays between 5.5 eV (as-deposited) and ~6 eV (after annealing at 1050 °C) [6].

In fact, thermal treatments affect not only the optical transmission (and optical absorption edge) of the present RE-doped a-SiN samples, but also their luminescence properties. Except for the undoped film, which does not display efficient light emission, all as-deposited RE-doped samples present visible luminescence. The observed emission lines are due to the presence of RE<sup>3+</sup> ions and their intensity is considerably improved after thermal annealing up to 1050 °C. As already mentioned, our luminescence experiments were carried out by exciting the samples with either photon (488 nm) or electron (10 keV) energy sources. Some of the photo- (PL) and cathodoluminescence (CL) spectra of the samples investigated in this work are shown in figure 3. The spectra were obtained at room-temperature from films annealed at 1050 °C.

Most of the luminescence features present in the 400–850 nm wavelength range (figure 3) correspond to optical transitions due to the Sm<sup>3+</sup> and Tb<sup>3+</sup> ions [10]: Sm1 at ~565 nm (<sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>5/2</sub>), Sm2 at ~605 nm (<sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>7/2</sub>), Sm3 at ~650 nm (<sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>9/2</sub>), Tb1 at ~485 nm (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6</sub>), Tb2 at ~545 nm (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub>), Tb3 at ~590 nm (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>4</sub>), and Tb4 at ~625 nm (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>3</sub>). In addition to these, we also observe the Sm4 light emission at ~725 nm (<sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>11/2</sub>), which is associated with the superposition of the <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>11/2</sub> transition due to Sm<sup>3+</sup> ions and the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub>, and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transitions of Sm<sup>2+</sup> ions. The infrared contribution Sm5 at ~810 nm corresponds to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>4</sub> transition and is exclusively due to Sm<sup>2+</sup> ions [10].

#### 4. Discussion

It is evident that thermal annealing treatments induced either the diffusion of light atomic species or some structural reordering (not necessarily crystallization) in the a-SiN films.

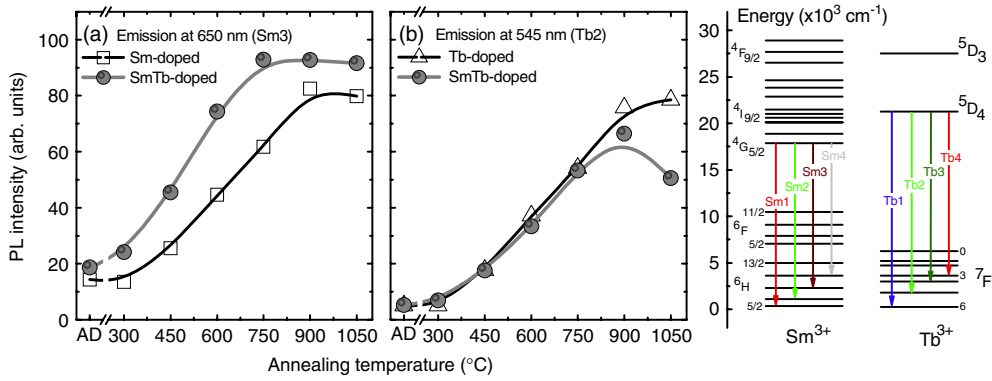


**Figure 3.** Room-temperature PL and CL spectra of a-SiN films doped with (a) Sm, (b) Tb, and (c) Sm + Tb. The measurements were obtained from samples deposited on c-Si substrates and annealed up to 1050 °C for 15 min. The spectra have been normalized for comparison purposes and the optical transitions due to the  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions are indicated in the figure.

Actually, it is well established that both atomic diffusion and structural reordering have great influence on the electronic states of amorphous semiconductors; the former passivating dangling or broken bonds, and the latter promoting atomic rearrangements [11, 12]. As a result of these changes, a decrease in the density of deep and/or tail defects takes place (figure 2) and, as a consequence, a substantial suppression of the nonradiative processes is expected [11]. In fact, this reasoning is consistent with the improvement verified in the PL intensity of all RE-related transitions as the films are annealed at higher temperatures. A similar dependence has been observed in the CL intensity too. However, due to the small number (and simplicity) of the RE-related energy levels involved, and confidence in the intensity values, we decided to discuss this effect based only on the PL results. In that manner, we can also investigate in detail the excitation mechanisms and the likely interaction involving the  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions.

The photoluminescence intensity associated with the light emission due to  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions is represented in figure 4. This figure contains the PL intensity, as a function of different annealing temperatures, of a-SiN films doped with Sm, Tb, and with Sm + Tb.

It is interesting to notice the enhancement that thermal annealing causes in the PL intensity of the a-SiN films; a factor of  $\sim 5$  in the case of the Sm-related transitions (at  $\sim 650$  nm), and more than one order of magnitude for the Tb-related transitions (at  $\sim 545$  nm). As already said, much of this improvement occurs because of a reduction in the number of nonradiative transitions, always present in amorphous semiconductors. It is also possible that the presence of oxygen atoms, even at very small concentrations, has some influence on the observed PL enhancement. Just like nitrogen atoms in the a-SiN matrix, the presence of oxygen species can be responsible for some changes in the local crystal field around the  $\text{Sm}^{3+}$  and/or  $\text{Tb}^{3+}$  ions [13]. Under these conditions, both the photon excitation efficiency and the radiative transition probability of the  $\text{RE}^{3+}$  ions increase. That seems to be the case, especially if we take into account the fact that most of the photon excitation of the  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions is quasi-resonant. In other words, during the PL experiments most of the excitation takes place at the  $^4\text{I}_{9/2}$  and  $^5\text{D}_4$  energy levels of the  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions, respectively (see figure 4), which matches almost perfectly the energy provided by the 488.0 nm photons. Actually, such a mechanism of quasi-resonant excitation of  $\text{RE}^{3+}$  ions has been verified in other wide-bandgap materials [6, 14]. The quasi-resonant excitation mechanism does not imply that the role played by the a-SiN matrix is of minor importance in the optical activation of  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions.



**Figure 4.** Room-temperature PL intensity of some RE-doped a-SiN films as a function of the annealing temperature. (a) PL intensity of the light emission at  $\sim 650$  nm due to the  $\text{Sm}^{3+}$  ions present in Sm- and Sm + Tb-doped a-SiN films. (b) PL intensity of the light emission at  $\sim 545$  nm due to  $\text{Tb}^{3+}$  in Tb- and Sm + Tb-doped a-SiN films. A diagram illustrating the energy levels of  $\text{Sm}^{3+}$  and  $\text{Tb}^{3+}$  ions is also shown on the right side of the figure. Some of the optical transitions typically observed in the present RE-doped a-SiN films were depicted in the energy level diagram using downward arrows.

On the contrary, the amorphous SiN host is fundamental in determining the local environment of the  $\text{RE}^{3+}$  ions as well as their effective recombination in the form of light emission.

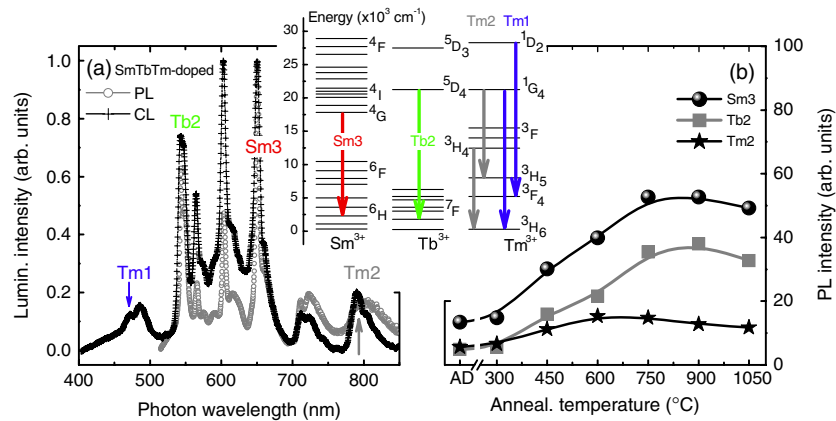
While the above discussion accounts for the effects of thermal treatments on the overall RE-related PL intensity, it is opportune to analyse the Sm + Tb combination individually. According to the experimental data of figure 4(b), it seems that the Sm + Tb codoping has no great effect on the PL intensity of the  $\text{Tb}^{3+}$  ions. The Sm + Tb combination, in contrast, induces an appreciable increase in the light emission intensity due to the  $\text{Sm}^{3+}$  ions (figure 4(a)). Taking into account that the concentrations of Sm and Tb are very similar (0.8 and 0.7 at.%, respectively), such a behavior has to be associated with the energy level disposition of both ions (figure 4). Again, most of the excitation of the  $\text{RE}^{3+}$  ions originates at the  $4\text{I}_{9/2}$  and  $5\text{D}_4$  energy levels, which energy coincides with that of 488 nm photons. One of the first consequences of the Sm + Tb mixture is an augmented probability of optical absorption at  $\sim 488$  nm. Part of the photons absorbed by the  $\text{Tb}^{3+}$  ions (or  $5\text{D}_4$  energy levels) gives rise to the light emission at  $\sim 545$  nm. The 488 nm photons are also absorbed by the  $4\text{I}_{9/2}$  energy level of  $\text{Sm}^{3+}$  ions rendering luminescence at  $\sim 650$  nm. Contrary to  $\text{Tb}^{3+}$ , however, the  $\text{Sm}^{3+}$  ions present additional states between the  $4\text{I}_{5/2}$  (where the excitation takes place) and  $4\text{G}_{5/2}$  energy levels (from where most of the Sm-related optical transitions originates). The presence of these states increases the probability of energy transfer from  $\text{Tb}^{3+}$  ( $5\text{D}_4$  level) to  $\text{Sm}^{3+}$  and, as a consequence, the Sm-related transitions are improved in a-SiN films codoped with Sm and Tb.

In order to further explore the possibility of enhancing the blue light emission of our samples, we also have investigated one a-SiN film simultaneously doped with Sm + Tb + Tm species. For comparison purposes the Sm + Tb + Tm-doped a-SiN film was prepared following exactly the same deposition procedure described in section 2. The main results of this effort will be briefly discussed.

Figure 5 shows the PL and CL spectra of a Sm + Tb + Tm-doped a-SiN sample, their corresponding luminescence intensity as a function of the annealing temperature, and the energy levels of all three  $\text{RE}^{3+}$  ions.

It is evident from the spectra of figure 5 that, at least, two new transitions developed in the RE-doped a-SiN films [10]: Tm1 (at  $\sim 470$  nm) corresponding to the  $1\text{D}_2 \rightarrow 3\text{F}_4$





**Figure 5.** (a) Room-temperature PL and CL spectra of one amorphous SiN thin film doped with Sm + Tb + Tm and annealed up to 1050 °C. (b) PL intensity of the Sm3 (at ~650 nm), Tb2 (at ~545 nm), and Tm2 (at ~790 nm) light emissions as a function of the annealing temperature. For comparison purposes, the PL intensity presented in (b) is exactly the same as in figure 4. The inset contains an energy level diagram indicating some of the main optical transitions observed in the luminescence spectra.

and/or  $^1G_4 \rightarrow ^3H_6$  transitions, and Tm2 (at ~790 nm) associated with the  $^1G_4 \rightarrow ^3H_5$  and/or  $^3H_4 \rightarrow ^3H_6$  transitions. Other Tm-related emissions ( $^1G_4 \rightarrow ^3F_4$  and  $^1D_2 \rightarrow ^3H_4$  transitions) should also be present in the ~650–690 nm wavelength range, but they are not clearly seen in the spectra of figure 5. In addition to the appearance of two new transitions, the data of figure 5 indicate that: (1) consistently with our previous discussion about the suppression of nonradiative processes with annealing, the luminescence of the Sm + Tb + Tm-doped a-SiN film also increases after thermal treatments at higher temperatures, (2) compared to the Sm + Tb-doped films (figures 4(a) and (b)), the present ones exhibit a rather small PL intensity, and (3) the green emission due to  $Tb^{3+}$  ions has been considerably improved in the Sm + Tb + Tm-doped films.

To some extent, it is reasonable to assume that the relative PL intensity of the RE-related light emissions depends on the concentration of  $RE^{3+}$  ions as well as on the characteristics of their energy levels. Actually, we believe that most of the observed decrease in the overall PL intensity (figure 5(b)) occurs because of a total RE concentration around 3 at.%. While this concentration enhances the absorption of 488 nm photons, there is also an increased probability that self-quenching processes take place [15]. This is particularly true for the  $Tm^{3+}$  ions the concentration of which stays at ~1.5 at.%. Moreover, the  $Tm^{3+}$  ions could be at the origin of the partial suppression of the transitions due to  $Sm^{3+}$ , following an energy transfer mechanism similar to that presented by the  $Tb^{3+}$  and  $Sm^{3+}$  ions in the Sm + Tb-doped samples. According to this reasoning, part of the electrons at the  $^4G_{5/2}$  energy level of  $Sm^{3+}$  can recombine radiatively (giving rise to the Sm1, Sm2, etc, emissions) or they can transfer their energy to the  $^3F_2$  state of  $Tm^{3+}$ . In order to determine the real causes of the decrease in the PL intensity of the Sm + Tb + Tm-doped a-SiN films, however, we should prepare and characterize new samples with a lower Tm concentration.

## 5. Concluding remarks

The present work reports the preparation and spectroscopic study of amorphous SiN thin films doped with Sm, Tb, and Sm + Tb species. The whole sample preparation and processing are



based on standard methods which are totally compatible with the actual low-temperature micro-electronics technology. Our main findings can be summarized as follows:

- (1) all films display visible photo- and cathodoluminescence at room-temperature,
- (2) cumulative thermal annealing of the films induces a considerable enhancement of the luminescence signal, which is attributed to a suppression of nonradiative processes in the amorphous matrix,
- (3) the presence of  $Tb^{3+}$  ions in the Sm + Tb-doped a-SiN films also improves the  $Sm^{3+}$ -related light emission, rendering spectrally sharp red–green–blue light emission,
- (4) the likely energy transfer processes between the  $Sm^{3+}$  and  $Tb^{3+}$  ions depend on the ion concentration and, especially, on the characteristics of their electronic levels, and
- (5) we made some attempts to improve the blue emission of the present a-SiN films by simultaneously doping them with Sm, Tb, and Tm species.

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