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Abstract

Nd-doped Si-rich silicon oxide thin films were produced by radio frequency magnetron co-sputtering of three confocal cathodes: Si, SiO₂, and Nd₂O₃, in pure argon plasma at 500°C. The microstructure and optical properties of the films were investigated versus silicon excess and post-deposition annealing treatment by means of ellipsometry and Fourier transform infrared spectrometry as well as by the photoluminescence method. A notable emission from Nd³⁺ ions was obtained for the as-deposited sample, while the films annealed at 900°C showed the highest peak intensity. The maximum emission was observed for the films with 4.7 at.% of Si excess.

Keywords: Si-rich-Silicon oxide, Neodymium, Magnetron sputtering, Refractive index, Infrared absorption, Photoluminescence

PACS:

1. Introduction

During last decade a great research effort has been focused on the development of the Si-based nanostructured materials for photonic application [1-5]. Among them, Si nanoclusters (Si-ncs) embedded in SiO₂ host are widely studied due to an
achievement of room-temperature light emission from the blue to the infrared depending on the Si-ncs size [6-7].

Rare-earth (RE) ions possess narrow emission lines and receive more and more interest from the scientists in the world [8]. RE doped silica is a well-known medium for laser application, but its use requires high-power sources to achieve an efficient emission. Considerable attention was paid to silica co-doped with RE ions and Si-ncs since (i) such nanocomposite materials can be pumped using broadband sources due to the spectrally wide absorption of Si-ncs and (ii) Si-ncs are found to be efficient sensitizers of RE ions.

In this regard, the most studied materials are Er-doped Si-rich silicon oxide (SRSO) due to promising application as a source for optical communication. In previous works [9-15] a significant enhancement of photoluminescence (PL) intensity of the intra-4f shell transition of Er$^{3+}$ due to the energy transfer from Si-ncs to RE ions has been demonstrated. The detailed study of the excitation mechanism of Er$^{3+}$ ions showed that the excitation rate depends on the Si-ncs size and becomes higher for the smaller Si-ncs [16].

In the contrast of well-studied Er-SRSO system, other RE ions are not well-addressed. On the contrary to Er$^{3+}$ ions, the doping of SRSO with Nd$^{3+}$ ions is most promising due to overlapping of 4f-shell absorption transitions with the range of intrinsic Si-ncs PL. Moreover, Nd$^{3+}$ ions offer very important light emission in the infrared spectral range at 1.06 and 1.32 μm in a four-level system configuration which avoid re-absorption of the emitted radiation. The benefits of Si-nc sensitizers towards Nd$^{3+}$ ions was already demonstrated [17-18]. However, its improvement requires a special attention to some critical parameters as the coupling rate between Nd$^{3+}$ ions and Si-ncs as well as the quality of the surrounded host medium aiming significant decrease of the non-radiative channels contribution. In the former case, the coupling rate can be monitored via the Nd$^{3+}$ ions content and the Si excess (Si$_{ex}$) concentration. The latter has a direct influence on the number of Si-ncs embedded in SiO$_2$ as well as on the host quality.
In this study, both the structure and the optical properties of Nd-doped SRSO thin films were investigated versus Si-ex and the annealing treatment in order to obtain high efficient of Nd$^{3+}$ light emission via energy transfer from Si-ncs toward Nd$^{3+}$ ions.

2. Experimental techniques

The samples were deposited onto p-type silicon wafers by radio frequency magnetron co-sputtering of three confocal cathodes: Si, SiO$_2$, and Nd$_2$O$_3$, in a pure argon plasma. The substrate was rotated during the deposition to ensure a high homogeneity of the film. The deposition temperature and the total plasma pressure were kept at 500ºC and 3 mTorr, respectively. The power density applied on the SiO$_2$ and the Nd$_2$O$_3$ cathodes were fixed at 8.88 and 0.30 W/cm$^2$, respectively, whereas the power density applied on the Si cathode, $P_{Si}$, was varied from 0.74 to 2.37 W/cm$^2$. The deposition time was tuned to achieve the film thickness in the 250-300 nm range for avoiding the effect of the film stresses on the optical parameters [19]. An annealing treatment was performed in a conventional furnace at 900 and 1100ºC during 1 hour in a nitrogen flow. Spectroscopic ellipsometry was used to determine the optical constants: thickness and refractive index $n$ of the films. The data were collected by means of a Jobin-Yvon ellipsometer (UVISEL) where the incident light was scanned in the 1.5-4.5 eV range under an incident angle of 66.3°. The fitting of the experimental data was performed using DeltaPsi2 software [20].

The sample’s infrared absorption properties were investigated by means of a Nicolet Nexus Fourier transform infrared (FTIR) spectrometer. The spectra were acquired under normal and Brewster angle incidence (65°). The PL spectra were recorded with a photomultiplier tube Hamamatsu (R5108) after dispersion of the PL signal with a Jobin-Yvon TRIAX 180 monochromator using an Ar+ laser operated at 488 nm which is a non-resonant wavelength for Nd$^{3+}$ excitation. For this study, we focused our PL experiment in the visible-near infrared range (600 ~ 1000 nm) to analyze the unique contribution of the RE ions in the de-excitation process [17].

3. Results and discussion
3.1 The $\text{Si}_{\text{ex}}$ estimation

Figure 1 displays the evolutions of the refractive index $n$ and the TO$_3$ peak position of Si-O vibration bond as a function of $P_{\text{Si}}$ for as-deposited samples. The $n$ value increases from 1.48 to 1.70 with $P_{\text{Si}}$. According to the effective medium approximation (EMA) and using the Bruggeman model theory [21-23], the O/Si ratio ($x$) can be determined from the equation (1):

$$x = \frac{-36n^4 + 691n^2 + 773}{22n^4 + 665n^2 - 472}$$ (1)

To note that the $n$ value is given at 1.95 eV, and during the deducing of equation (1), $n_{\text{a-Si}} = 4.498$ and $n_{\text{SiO2}} = 1.457$ are used.

Furthermore, the peak position of the TO$_3$ mode in Fig. 1 decreases almost linearly with the increased $P_{\text{Si}}$. On the basis of the following equation (2) [24]:

$$x = 0.02\nu - 19.3$$ (2)

$\nu$ is the TO$_3$ peak position of sample SiO$_x$, one can obtain the $x$ value. For this pure SiO$_2$ layer was grown at the same conditions as SRSO-Nd layers and had the same thickness. This approach gives more accurate estimation than the comparison with the TO$_3$ peak position of SiO$_2$ (~ 1080 cm$^{-1}$) published elsewhere [25].

Thereafter, $\text{Si}_{\text{ex}}$ (at.%)) was calculated from $x$ using the equation (3):

$$\text{Si}_{\text{ex}}(\text{at.}) = \frac{2 - x}{2 + 2x} \times 100$$ (3)

And the results of $\text{Si}_{\text{ex}}$ estimated from both FTIR and EMA are shown in Fig. 2. It is worth to note that the $\text{Si}_{\text{ex}}$ values obtained by the two methods are in good agreement within uncertainty.

3.2 Effect of annealing treatment on the microstructure
Figure 3 shows a typical evolution of the FTIR spectra recorded at the Brewster incidence for films (\(P_{\text{Si}} = 1.33\ \text{W/cm}^2\)) as-deposited and annealed at 900 and 1100°C. This film was chosen as a typical one to study for its highest emission from Nd\(^{3+}\) ions discussed later. The spectra are normalized with respect to the TO\(_3\) phonon mode intensity. It is found that the TO\(_3\) peak position shifts from 1050 to 1080 cm\(^{-1}\) with the increasing annealing temperature (\(T_A\)). This great shift is explained by the condensation and agglomeration of the Si\(_{\text{ex}}\) resulting in the formation of Si-ncs \([26]\) at the expense of volumic silica. The evolution of FTIR spectra is a confirmation of the formation of SiO\(_2\) and Si phases via phase separation in the SiO\(_x\) host \([27]\). Moreover, the intensity of the LO\(_3\) peak increases and the intensity of the LO\(_4\) - TO\(_4\) pair mode attenuates with the increase of \(T_A\). The former is a signature of the improvement of the Si/SiO\(_x\) interface \([28]\), whereas the latter indicates a reduction in disorder of the host.

3.3 Photoluminescence properties

The film with \(P_{\text{Si}} = 1.33\ \text{W/cm}^2\) was once more chosen to demonstrate the evolution of light emission properties versus an annealing treatment. The room temperature PL spectra of sample as-deposited and annealed at 900 and 1100°C are shown in Fig. 4. It is seen that the sample annealed at 1100°C emits a broad PL band in the visible domain that can be ascribed to radiative carrier recombination in Si-ncs.

As one can also see from Fig.4, no emission was detected in this range for both as-deposited and 900°C-annealed sample. However, this latter FTIR spectrum (Fig. 3) shows a phase separation process and thus the presence of Si-ncs. We conclude that the visible emission is quenched either due to energy transfer or to defect in the host \([29]\). This assumption is confirmed by the analysis of the Nd\(^{3+}\) PL bands (Fig. 4).

In the infrared domain, there are peaks centered at around 920 nm corresponding to the intra-4f shell transition of Nd\(^{3+}\) ions from the \(^4\text{F}_{3/2}\) to the \(^4\text{I}_{9/2}\) level. The presence of the PL of Nd\(^{3+}\) ions after non-resonant excitation at 488 nm confirms the
sensitizing effect of Si-ncs toward Nd$^{3+}$ ions. Moreover, the most efficient emission is observed for the sample annealed at 900°C which corresponds to the best coupling between Si-ncs and Nd$^{3+}$ ions. It is worth to note that a notable emission from Nd$^{3+}$ ions was obtained for the as-deposited sample and this fact can be explained by either formation of Si-ncs during fabrication process or by energy transfer from host defects towards RE ions [19].

[Figure 4]

In the following part, the effect of Si$_{ex}$ on Nd$^{3+}$ PL properties will be studied as shown in Fig. 5. The Nd$^{3+}$ PL intensity shows first an increase with Si$_{ex}$ for all as-deposited and annealed samples, up to a maximum corresponding to sample with Si$_{ex}$ = 4.7% ($P_{Si} = 1.33$ W/cm$^2$), and then decreases for higher Si$_{ex}$. This behavior may be explained by two reasons. On the one hand, the first increase of Si$_{ex}$ is expected to enhance the density of Si-ncs for an optimized Nd$^{3+}$:Si-ncs interaction. Further increase of Si$_{ex}$ up to 11.5 at.% might lead to increasing the average size of the former Si-ncs at the expense of their density and then of their coupling with Nd$^{3+}$ ions. On the other hand, the Si incorporated into the sample may result in disorder in the host, which will favor the non-radiative channels. Besides in Fig. 5, the samples annealed at 900°C show the highest PL intensity whatever the Si$_{ex}$. This observation may be ascribed to the formation of Nd$_2$O$_3$ clusters [17] for samples after annealing at high temperature ($T_A = 1100\text{°C}$). To note that there is no peak for sample with Si$_{ex}$ = 0.3 at.%, possibly because the emission is too weak to be detected for the low Si$_{ex}$, the Nd$^{3+}$:Si-ncs distance is too high to allow the energy transfer process.

[Figure 5]

4. Conclusion

We have investigated the influences of Si$_{ex}$ and $T_A$ on the structure and optical properties of Nd-doped SRSO thin films fabricated by co-sputtering technique. It has been shown that the increase in Si$_{ex}$ improves the Si-ncs coupling to Nd$^{3+}$ ions, and that, it may raise the disorder in layer resulting in the increase of the number of non-
radiative channels. In addition, it has been evidenced that the post annealing treatment at 900 and 1100°C enhances the layer quality favoring the Nd$^{3+}$ PL emission. However, high temperature annealing leads to a decrease of the Nd$^{3+}$ emission due to the coalescence of Si-ncs and/or the formation of Nd$_2$O$_3$ cluster. Therefore, both moderate $T_A$ and Si$_{ex}$ are very important to be found with aim to optimize the emission from Nd$^{3+}$ ions. In this study, the sample with Si$_{ex} = 4.7$ at.\% ($P_{Si} = 1.33$ W/cm$^2$) shows the highest Nd$^{3+}$ peaks after annealing at 900°C for 1 h.

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References


Figure captions

Fig. 1 Evolution of the refractive index $n$ taken at 1.95 eV energy (left axis) and of the TO$_3$ Si-O peak position (right axis) versus $P_{Si}$ for as-deposited samples. The lines on top and bottom are the TO$_3$ position (1065 cm$^{-1}$) and the refractive index $n$ (1.457) for pure SiO$_2$ grown at the same conditions with the same thickness as SRSO-Nd layers, respectively.

Fig. 2 Evolution of $S_{ex}$ (at.%) as a function of $P_{Si}$ for as-deposited samples.

Fig. 3 Typical evolution of the FTIR spectra measured in Brewster incidence for as-deposited and annealed films.

Fig. 4 Typical evolution of the PL spectra of sample with $P_{Si} = 1.33$ W/cm$^2$ for as-deposited and annealed films.

Fig. 5 Evolution of the Nd$^{3+}$ PL intensity at 920 nm as a function of the $P_{Si}$ for as-deposited and annealed films.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5

- as-deposited
- $T_A=900^\circ C$
- $T_A=1100^\circ C$

PL intensity at 920 nm ($10^5 \text{ W/cm}^2$) vs. Si$_{ex}$ (at.%)