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Chuan Hui Liang, Julien Cardin, Larysa Khomenkova, Fabrice Gourbilleau. Effect of rapid thermal annealing on Nd-SiO_x thin film properties. Conference: SPIE Photonics Europe, Apr 2012, Brussels, Belgium. 10.1117/12.922349 . hal-01139857

HAL Id: hal-01139857

<https://hal.science/hal-01139857>

Submitted on 10 Apr 2017

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Effect of rapid thermal annealing on Nd-SiO_x thin film properties

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ABSTRACT

The series of Nd³⁺-doped Si-rich SiO₂ thin films with different excess Si content were deposited by magnetron co-sputtering of three different (SiO₂, Si and Nd₂O₃) targets under a plasma of pure argon at 500 °C. The Si excess content in the samples was monitored via a power applied on Si cathode. The films were submitted to the rapid thermal annealing (RTA) at 900, 1000 and 1100 °C, respectively. It was observed a phase separation and a formation of Si nanoclusters embedded in oxide host. The Si excess, remaining after a RTA-1100 °C annealing, was found to be negligible, confirmed nearly complete phase separation. The Nd³⁺ photoluminescence (PL) property was explored as a function of Si excess and/or annealing temperature. The most efficient Nd³⁺ PL emission was found for the samples with about 4.7% of Si excess. These optimal samples, submitted to RTA-900 °C-1 min treatment and conventional annealing at 900°C for 1 h in nitrogen flow, demonstrated comparable Nd³⁺ PL intensities. This offers future application of RTA treatment to achieve an efficient emission from the materials doped with rare-earth ions.

Keywords: Si-rich SiO₂, neodymium, photoluminescence, rapid thermal annealing

1. INTRODUCTION

Since the discovery of strong visible emission in porous Si observed by Canham¹ at room temperature, Si-based nanostructured materials have been considered as promising candidates for a large number of optoelectronic and photonic applications. Many groups demonstrated that Si nanoclusters (Si-ncs) embedded in SiO₂ host possess visible luminescence. Its peak position is controlled by Si-nc sizes due to the quantum confinement effect². Moreover, these Si-ncs can play a sensitizing role towards rare earth (RE) ions such as Er³⁺ and Nd³⁺, whose effective cross section increases consequently by 3-4 orders of magnitude³. In other words, the interaction of Si-ncs with nearby RE ions allows achieving efficient RE luminescence. Several factors affect Si-ncs-RE ions energy transfer process; they are (i) the size and density of Si-ncs, (ii) a distance between RE ions and Si-nc and (iii) the density of RE ions. The control of all these parameters allowed achieving an optimal RE emission.

Si-ncs embedded in Si-based material have been prepared by many approaches such as sputtering⁴⁻⁵, chemical vapor deposition⁶, molecular beam epitaxy⁷, laser ablation⁸ and ion implantation⁹. The samples fabricated by most of these techniques are in the form of Si-rich material, which should proceed with a post-annealing to allow a phase separation process to obtain Si-ncs. It was found that in Si-rich SiO₂ system, amorphous Si-ncs start to form and grow during the 900 °C-annealing, while the 1100 °C-annealing will lead the Si-nc crystallization¹⁰. During the annealing, there are two competing mechanisms: (i) the growth of existing Si-ncs due to the diffusion of Si atoms in the sample and (ii) the formation and subsequent growth of new Si-ncs at nucleation sites¹¹. Moreover, the annealing may also result in the clusterization of RE ions that causes quenching of the RE emission.

To prevent the further growth of Si-ncs and to obtain small Si-ncs with high density and narrow distribution, a decreasing of the annealing time is expected in the post-annealing¹²⁻¹³. As a consequence, rapid thermal annealing (RTA) is an attractive choice especially in the thin film fabrication process. The RTA can activate dopants, while at the same time it can minimize their diffusion¹⁴. This work aimed at the investigation of the effect of RTA treatment on the properties of Nd³⁺-doped Si-rich SiO₂ (Nd-SiO_x) thin film with different Si excess (Si_{ex}).

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2. EXPERIMENTAL TECHNIQUES

The series of Nd-SiO_x thin films were deposited onto p-type silicon wafers by radio frequency magnetron co-sputtering of three confocal cathodes - Si, SiO₂, and Nd₂O₃ - in a pure argon plasma at a pressure of 3 mTorr. The Si_{ex} was controlled by the monitoring of the Si cathode power density (P_{Si}) from 1.04 to 1.78 W/cm², whereas those for SiO₂ and Nd₂O₃ were fixed at 8.88 and 0.30 W/cm², respectively. The layer thickness was in the 320-360 nm range for all samples investigated. A RTA treatment was performed in a rapid thermal furnace at 900, 1000 or 1100 °C for 30 to 180 s duration under nitrogen gas. However, hereafter the most results will be presented for RTA-1 min treatment. The ramp-up rate to reach annealing temperature was 45 °C/s. The Si_{ex} value was estimated from the Fourier transform infrared (FTIR) spectrum measured at normal incidence of beam light. The photoluminescence spectra were obtained using the 488-nm-line of Ar⁺ laser, which is non-resonant excitation for Nd³⁺ ions.

3. RESULTS AND DISCUSSION

Figure 1 displays the variation of TO₃ peak position of Si-O vibration bond versus P_{Si}, obtained for as-deposited (AD) Nd-SiO_x samples from FTIR spectra measured at normal incidence of excitation beam light.

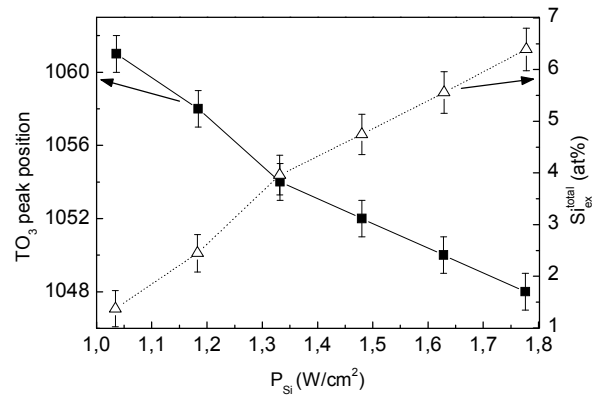


Figure 1. Evolution of TO₃ peak position (left axis) and of estimated Si_{ex}^{total} (at%, right axis) as a function of P_{Si} for as-deposited (AD) samples.

These data allow a rough estimation of a total Si excess, Si_{ex}^{total} . Meanwhile, the obtained data can be underestimated because of the formation of Si agglomerates caused by high deposition temperature (500 °C). It was estimated according to the following two equations¹⁵:

$$x = 0.02 \cdot \nu_{TO_3} - 19.3 \quad (1)$$

and

$$Si_{ex}^{total} (at\%) = \frac{2-x}{2+2x} \cdot 100\%, \quad (2)$$

where ν_{TO_3} and x being the TO₃ peak position and [O]/[Si] ratio, respectively.

Figure 2 represents the evolution of FTIR spectra versus annealing temperature for the samples submitted to RTA treatment.

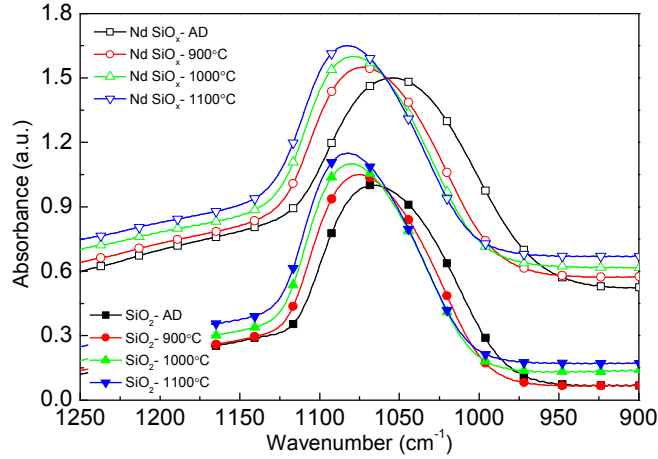
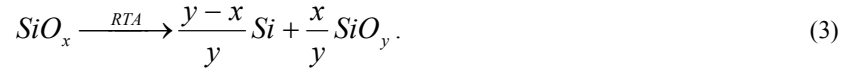


Figure 2. FTIR absorption spectra of typical Nd-SiO_x and SiO₂ films, collected at normal incidence for as-deposited (AD) and RTA-1 min treated samples. The annealing temperature is mentioned in the figure. The spectra for Nd-SiO_x samples are shifted in vertical direction for clarity.

The RTA treatment causes the shift of FTIR spectra towards longer wavenumbers. This is an evidence of the phase separation between Si and SiO_y in Nd-SiO_x samples, which can be considered as a reaction:



The first term in right part represents the formed Si-ncs, while the second term is the SiO_y phase containing the isolated Si atoms. Thus, the excess Si atoms in RTA layer is in two forms, i.e. Si-ncs, Si_{ex}^{Si-nc} , and isolated Si atoms. To obtain the Si_{ex}^{Si-nc} , the y value in Eq.(3) has to be determined. It can be deduced similar to the x estimation above based on the equation (4) ¹⁶:

$$y = 2 \cdot \frac{\nu_{TO_3}^{SiO_x} - \nu_{TO_3}^{Si}}{\nu_{TO_3}^{SiO_2} - \nu_{TO_3}^{Si}}, \quad (4)$$

where $\nu_{TO_3}^{Si}$ value is 965 cm⁻¹ ¹⁷, while the $\nu_{TO_3}^{SiO_x}$ and $\nu_{TO_3}^{SiO_2}$ values correspond to the TO₃ peak for RTA Nd-SiO_x and 320-nm SiO₂ films, respectively. The close values of $\nu_{TO_3}^{SiO_x}$ and $\nu_{TO_3}^{SiO_2}$ peak positions were obtained for the Nd-SiO_x and pure SiO₂ samples submitted to RTA-1100 °C treatment (Fig.2). This could be considered as an evidence of a complete phase separation in Nd-SiO_x samples. However, their FTIR spectra are still broader than that for SiO₂ layers. This means that the excess Si atoms are still present either as isolated ones or as some agglomerates with Nd ions such as Nd-Si-O similar to the case described in our previous work ¹⁸. Furthermore, the Si_{ex}^{Si-nc} was obtained on the basis of equation (5):

$$Si_{ex}^{Si-nc} (at\%) = \frac{y-x}{1+x} \cdot 100\%. \quad (5)$$

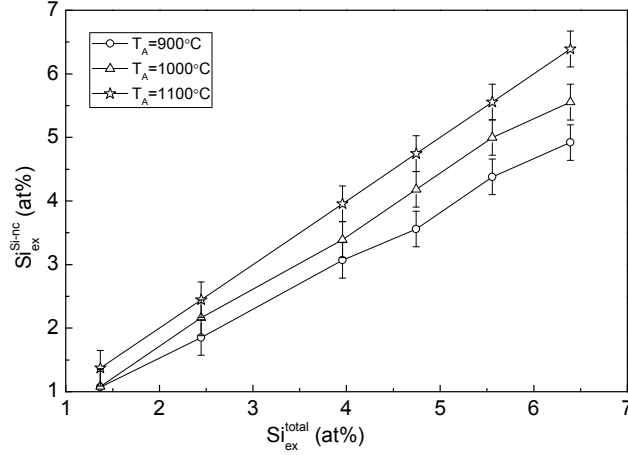


Figure 3. Evolution of Si_{ex}^{Si-nc} as a function of Si_{ex}^{total} for RTA-samples treated at different annealing temperatures (T_A).

The evolution of Si_{ex}^{Si-nc} versus Si_{ex}^{total} for different annealing temperatures is shown in Fig. 3. The ratio of Si_{ex}^{Si-nc} to Si_{ex}^{total} was estimated by the following equation:

$$\eta(\%) = \frac{Si_{ex}^{Si-nc}}{Si_{ex}^{total}} = \frac{2(y-x)}{y(2-x)} \cdot 100\%. \quad (6)$$

It was found to be $\eta \approx 78\%$, 88% and 98% Si_{ex}^{total} to form Si-ncs for samples after annealing at 900, 1000 and 1100 °C, respectively. This behavior can be observed in Fig.3 from the slope of curves that increases with the temperature and approaches the value of about 1 that is an ideal case, when all excess Si atoms are agglomerated into Si-ncs. This indicated that for all the samples (i) the η value depends mainly on annealing temperature; (ii) 1100 °C-annealing can allow a complete phase separation.

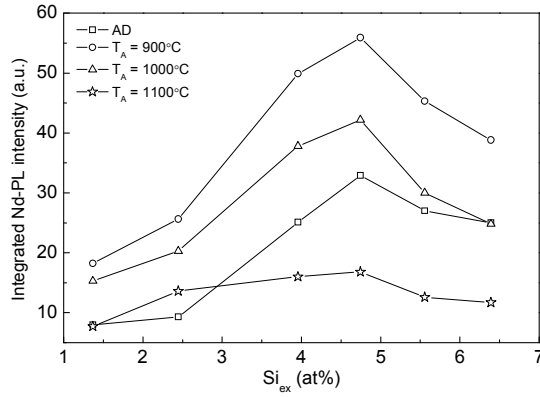


Figure 4. Evolution of the integrated intensity of Nd^{3+} PL for $^4F_{3/2} - ^4I_{9/2}$ transition as a function of Si_{ex}^{total} for AD and RTA-treated samples.

The evolution of the integrated intensity of Nd^{3+} PL was investigated as a function of S_{ex}^{total} for AD and RTA samples and it is presented for ${}^4F_{3/2}$ - ${}^4I_{9/2}$ transition in Fig. 4. Each curve in this figure shows the increase of PL intensity with S_{ex}^{total} from 1.4 to 4.7 at%, and then its decrease with the further rise of S_{ex}^{total} from 5.6 to 6.4 at%. Therefore, the maximum integrated intensity corresponds to the samples with the $S_{ex}^{total} = 4.7$ at% for each curve. This Nd^{3+} PL behavior versus S_{ex}^{total} was explained in the case of $S_{ex}^{total} < 4.7$ at%, by the increase of Si-ncs number as well as higher coupling rate between Si-ncs and Nd^{3+} ions. In the case of $S_{ex}^{total} > 4.7$ at% the larger Si-ncs form at the expense of small size Si-ncs, that causes a decrease of their number and lower coupling rate of larger Si-ncs with Nd^{3+} ions. In addition, comparing different curves in Fig. 4, the integrated PL intensity of RTA-900 °C treated samples exceeds significantly that of the AD samples for each S_{ex}^{total} sample. This indicates that RTA-900 °C annealing at short time (1 min) allowed obtaining the optimal Si-nc density and coupling with Nd^{3+} ions. The decrease of Nd^{3+} PL intensity with the annealing temperature from 900 to 1100 °C is due to enlargement of Si-ncs sizes and improved quality of silicon oxide host (approaching stoichiometric SiO_2) with higher temperatures. This can lead to the formation of SiO_2 shell covered Si-ncs and results in the higher potential barrier for the carriers participating in the energy transfer from Si-ncs towards Nd^{3+} ions. Besides, the formation of Nd^{3+} clusters can occur. This assumption agrees with the following consideration for the samples with $S_{ex}^{total} \leq 4.7$ at%. One can suppose that the Si-nc density in these samples RTA treated at 900 and 1000 °C proportional to S_{ex}^{Si-nc} , i.e. the $S_{ex}^{total} = 4.0$ at% allowed to obtain $S_{ex}^{Si-nc} = 3.4$ at% in RTA-1000 °C, whereas for sample $S_{ex}^{total} = 4.7$ at% after RTA-900 °C treatment the $S_{ex}^{Si-nc} = 3.6$ at%. However, in spite of these close values, corresponding PL intensities differ in about 1.3-1.4 times (Fig.4).

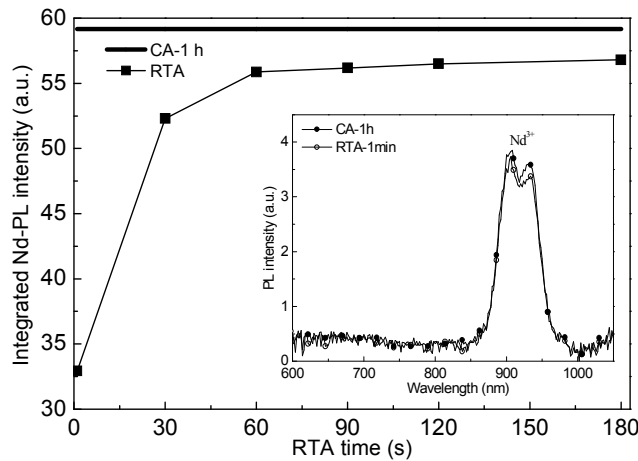


Figure 5. Evolution of the integrated intensity of Nd^{3+} PL for ${}^4F_{3/2}$ - ${}^4I_{9/2}$ transition as a function of annealing time at RTA-900 °C for sample with $S_{ex}^{total} = 4.7$ at%. The solid line on top represent of the level of PL intensity for the same transition obtained for similar sample treated by conventional annealing (CA) at 900 °C for 1 h in nitrogen flow. The inset is the PL spectra for RTA-900 °C-1 min and CA-900 °C -1 h sample, respectively.

Figure 5 shows the evolution of Nd^{3+} PL intensity versus RTA duration at 900 °C for the optimal sample ($S_{ex}^{total} = 4.7$ at%). The PL intensity increased greatly in the first one minute, while it saturates for the longer RTA duration. The level of the Nd^{3+} PL intensity achieved for the samples submitted to a conventional annealing (CA) at 900 °C for 1 h in nitrogen flow is also presented in Fig.5 by solid line. The inset of this figure shows the PL spectra for RTA-900 °C-1 min and CA-900 °C-1 h sample, respectively. One can see that both of them have close PL intensities (the

RTA-900 °C-1 min optimal sample had an integrated intensity of about 95% of that of a sample after a CA-900 °C-1 h). It is seen that only first few minutes transform the sample microstructure and allow reaching high PL intensity of Nd³⁺ ions, whereas further, longer annealing changes Nd³⁺ PL efficiency insignificantly. These results demonstrate that RTA treatment offers a possibility to obtain an efficient emission of Nd³⁺ ions in SiO_x samples comparable with that achieved for CA-treated samples; however some optimization of RTA conditions is still required.

4. CONCLUSIONS

This study supported that the RTA treatment had a significant effect on the microstructure of Nd-SiO_x thin films, and great increase of Nd³⁺ PL intensity was obtained after RTA. Moreover, with the aim to optimize Nd³⁺ PL by RTA, the layers with various S_{ex}^{total} were investigated and the strongest Nd³⁺ PL was obtained for sample with 4.7 at% S_{ex}^{total} annealed at 900 °C. This result may push RTA as an exciting candidate for the thin film fabrication process.

5. ACKNOWLEDGEMENTS

The authors thank the French National Agency (ANR), which supported this work through the Nanoscience and Nanotechnology program (DAPHNES project ANR-08-NANO-005).

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