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Photoluminescence study of Nd^{3+}-doped Si-rich silica films

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Nd^{3+}-doped silicon-rich silicon oxide thin films have been fabricated by reactive magnetron co-sputtering of a pure silica target topped with Nd_2O_3 chips. The incorporation of silicon excess in the films has been controlled by the hydrogen partial pressure P_{H_2} introduced in the plasma. Photoluminescence experiments have been made at room temperature using a non resonant excitation with Nd^{3+} ions. The influences of Nd^{3+} content and P_{H_2} have been studied to improve the Nd^{3+} emission. Photoluminescence spectra reveal an enhancement of the Nd^{3+} emission at 0.9 μm and 1.1 μm when silicon nanoclusters and Nd^{3+} are embedded in a SiO_2 matrix.

Keywords: Nd, Si, nanoclusters Si, energy transfer.

1. Introduction

The development of telecommunication and the miniaturization in the last years encouraged led the scientific community to get involved in optimization of the emission properties of materials doped with rare earths. The erbium ion, for instance, is used in telecommunication for its very attractive emission around 1.54 μm. However, the weak cross-section ($\sigma_{ex} \sim 10^{-20}$ cm^{-2} [1]) limits its exploitation in miniaturized devices. The recent discovery of efficient sensitizing action of silicon nanoclusters (Si-nc) toward Er^{3+} has opened the field to several applications for integrated optoelectronic devices. In this configuration, the effective absorption cross-section is improved by 3 orders of magnitude. The neodymium ion presents also an interesting emission in the near infrared region. Recently, two studies have evidenced the possible sensitizing role of Si-nc toward Nd^{3+} [2, 3].

Experimental results on the excitation of Nd^{3+} ions embedded in silicon rich silicon oxide (SRSO) thin films are reported. Samples have been produced by reactive magnetron co-sputtering. The investigation of the passive optical properties is presented in the first part. Then photoluminescence (PL) emission of Nd^{3+} has been analysed for different hydrogen partial pressures and annealing treatments to get the best luminescence efficiency.

2. Experimental

Thin films were fabricated by reactive RF magnetron sputtering of a pure silica target (99.99%) topped with Nd_2O_3 chips. The percentage area of the co-sputtered neodymium oxide was maintained around 12%. All the films were deposited on P-doped silicon substrate. The incorporation of a Si excess was monitored by the introduction of H_2 in the Ar plasma, thus reducing the oxygen concentration of the sputtered species. The hydrogen rate r_H has been defined by the ratio of P_{H_2} to the total pressure of the plasma. The films were deposited at a power density of 0.76 W/cm^2 and post-annealed at two different temperatures, 950 and 1100°C, for the time ranging from 5 minutes to 4 hours. Such treatment improves the phase separation between Si and SiO_2 and allows recovering the defects that are detrimental to the PL emission.

The refractive index and thickness were determined by ellipsometry (ES), using a Jobin–Yvon ellipsometer for a probing light scanned between 1.5 and 5.0 eV and an incidence angle of 66.2°.

The absorption spectrum of a 10 μm Nd-doped SiO_2 film was produced using a Perkin–Elmer spectrophotometer to choose a non-resonant wavelength for the PL experiments. The latter was performed using an argon laser, operating at a wavelength of 488 nm to optically excite the Si-nc. The emission was analysed by a single monochromator followed by a cooled Ge detector and a lock-in amplifier.

3. Results and discussion

Figure 1 reports the evolution of the refractive index *n* deduced from ES measurement as a function of P_{H_2} before and after annealing treatment at 950°C for 3 hours. The results show that the introduction of hydrogen in the plasma induces an increase of the refractive index (the dotted lines are just guide for the eyes) supporting the incorporation of Si excess in the layer [4]. For higher hydrogen partial pressure, *n* becomes constant which means that the Si excess remains constant as already noticed in Si-SiO_2-Er system deposited with the same process [1, 5]. Since density and refractive index are linearly correlated [6, 7], the increase of the refractive index after annealing could be the result of the film densification.

To investigate the effect of hydrogen content on the PL properties, the absorption spectrum of a thick Nd-doped SiO_2 layer has been recorded within the range of 400–850 nm (Fig. 2). Six absorption bands were present and centered around 460, 508, 526, 583, 746 and 800 nm. According to the literature, they correspond to the absorption from the ground level $^4I_{9/2}$, to the excited states of Nd^{3+} ions. It can be noticed that the 488 nm Ar^+ laser line which is usually used for the excitation of Si-nc is not resonant with Nd^{3+} ions. Emission spectra of the annealed film are reported on Fig. 3 for different r_H values. When hydrogen is missing during deposition,

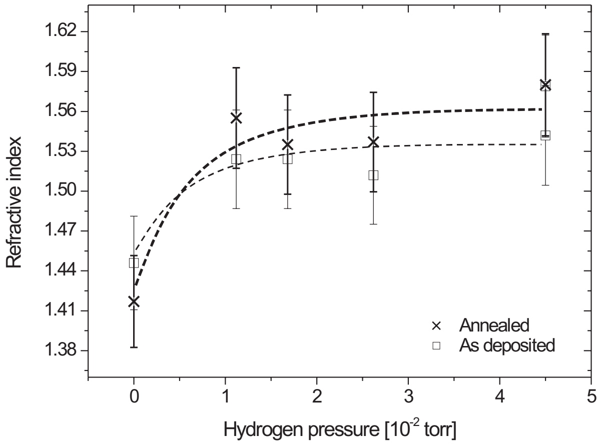

Fig. 1. Evolution of the refractive index measured by ellipsometry with hydrogen pressure in plasma. The dotted lines are just guide for the eyes.

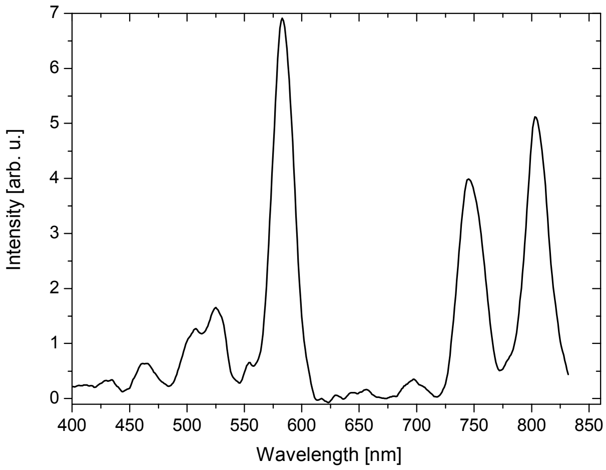

Fig. 2. Absorption spectrum of neodymium ions in SiO_2 thick film (10 μm).

i.e., there is no Si excess incorporated in the film, the PL emission can not be detected. This corroborates the non resonant behavior of the 488 nm Ar^+ laser line used as the excitation source. When r_H reaches 30%, two peaks at 0.9 and 1.1 μm are clearly visible and have been previously described as a signature of Nd^{3+} intra 4*f*-transitions [2, 3]. The comparison between these spectra (r_H = 0% and r_H = 30%) demonstrates the sensitizing role of Si-nc as noticed in the case of Er^{3+} in similar sample [1, 5]. The Si-nc have been excited by the laser and transferred efficiently their energy to

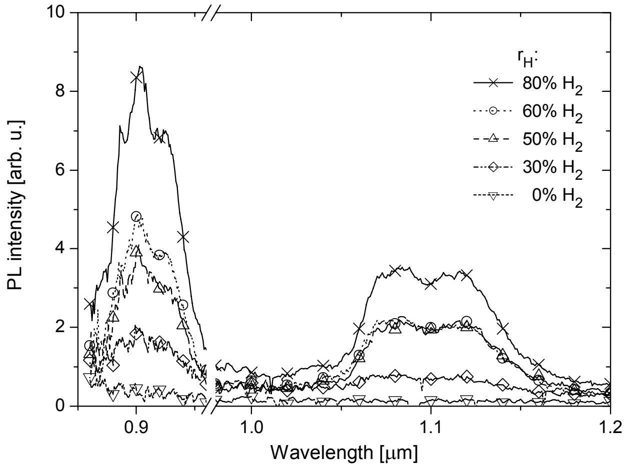

Fig. 3. Room temperature PL intensity as a function of hydrogen ratio after annealing treatment 90 min at 950°C under Ar flow.

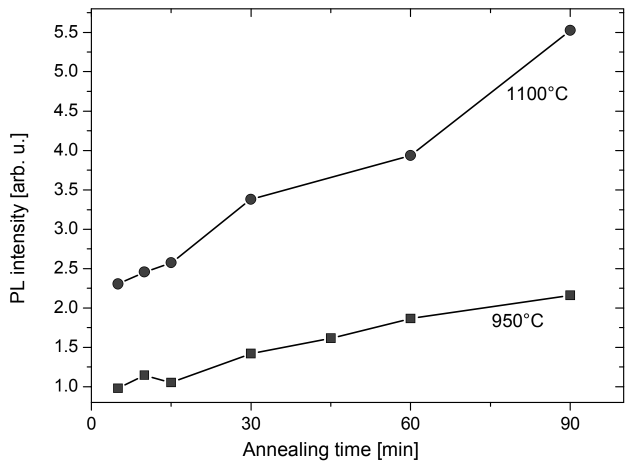

Fig. 4. Evolution of the PL signal at 1.09 μm as a function of the annealing time at 950 and 1100°C.

the rare earth. The PL emission increases with r_H due to a higher number of sensitizer. As far as the result obtained on the refractive index are concerned, we can expect that the increase of the rH favors an increase of the Si nucleation sites in the growing layer due to the competition between deposition and etching of the plasma. The increase of the hydrogen dilution in the plasma is accompanied by an increasing reactive interaction between H-species and the growing surface, which multiplies the nucleation sites and limits the size of the growing grains [5]. Thus, for a same Si excess, the neighboring Nd^{3+} ions being able to be excited through the Si-nc are increased with the concomitant increase of the Si-nc density. This result is also observed in the case of the Si-SiO_2-Er films fabricated under the same conditions [1, 5].

The effect of the annealing time on the PL intensity at 1.09 μm ($I_{1.09}$) for the film fabricated at $r_H = 80\%$ is presented in Fig. 4 for two temperatures 950°C and 1100°C, respectively. After 5 min of annealing treatment, an intense emission has been detected. The $I_{1.09}$ recorded appears to be two times higher for film annealed at 1100°C than at 950°C. For each annealing time a systematic increase of the emission intensity is noticed. The difference of $I_{1.09}$ between the two annealing temperatures increases with the treatment durations. After 90 min, the PL intensity for both annealing temperature becomes three times higher. Such behaviour is a signature of the recovery of the non radiative defects that are detrimental both to the Si-nc/Nd coupling rate and to the Nd^{3+} emission. This recovery needs high annealing temperature. Thereby, the PL intensity at 1.09 nm of the film annealed at 1100°C is always at least two times higher than the one annealed at 950°C. More experiments are in progress to give more insight into the effect of the fabrication parameters to the spectroscopic properties of the Nd^{3+} ions.

4. Conclusions

The Nd^{3+} doped silicon rich silicon oxide thin films have been fabricated by reactive magnetron co-sputtering of a pure silica target topped with Nd_2O_3 chips. The comparison of the PL emissions of the Nd^{3+} ions for films fabricated with different hydrogen rate r_H clearly evidences the role of sensitizing produced by the Si-nc.

The increase of the r_H between 30% and 80% improves the PL by a factor 4, while no signal has been detected for film without Si excess. 90 minutes of annealing time improves the PL intensity at 1.09 μm by a factor 3. The concomitant increase of the temperature has a curative effect on the defects. Further studies are in progress to optimize the Nd^{3+} emission through the appropriate adjustment of the fabrication parameters.

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