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Optical activation of Er ions by Si nanocrystals in films synthesized by sol–gel chemistry and ion implantation

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The sensitization of the infrared luminescence of Er ions by Si clusters is studied in oxide films derived from tetraethoxysilane and triethoxysilane gels, doped chemically or by ion implantation with Er and/or Si. No quenching of the luminescence by impurities and structural defects is observed with respect to ion-implanted silica, and a maximum enhancement is observed in the $SiO_{1.5}$ suboxide formed from triethoxysilane. The segregation of erbium silicide or oxide, depending on the synthesis procedure, deactivates the Er ions when their concentration exceeds 1 at % or the temperature of annealing is above 1050 °C.
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1. Introduction

Recently, active research has been devoted to the optical properties of rare earth (RE) ions in films of semiconductors or oxides, because of their potential applications in optoelectronic devices on silicon. They can be excited through the recombination of photogenerated carriers confined in semiconductor crystals and subsequent energy transfer to the RE ions in or near the crystals. This process is more efficient than the direct optical activation of the ions in oxide matrices (in which intra-4f transitions are allowed by the perturbation of the ligand field). However, the solubility of RE in semiconducting matrices is much more limited. Additionally, in the particular case of Si, excitons are not annihilated instantaneously by a coupling with phonons only when the crystals have a nanometric size. Therefore, in most studies of the RE optical sensitization by Si excitons, the used matrix was a suboxide obtained by evaporation, sputtering or Si implantation in silica, and containing Si clusters after subsequent annealing [1–3]. One of the most interesting RE ions is Er^{3+}, because the $^4I_{13/2}$–$^4I_{15/2}$ radiative transition of this ion matches one of the standard wavelengths of infrared telecommunications. Moreover, the excitation energy from the ground state to the $^4I_{9/2}$ level corresponds to that of excitons in Si nanocrystals with a diameter around 3 nm (and in many other semiconducting nanocrystals of similar size).

The purpose of the present paper is to study the same effect in SiO_x films synthesized by sol–gel chemistry, because this technique permits one to tune more easily than other processes the composition of the oxide matrix, in order to optimize the Er solubility and the refractive index of a waveguide. A few studies indicate that the emission of Er is not quenched by the residual content of C, H or the porosity inherent to oxides derived from gels, when they are properly prepared [4]. On the other hand, other authors could not observe a luminescence of Si clusters of a suitable size for emission in the red, formed in silica-gel by implantation followed by annealing [5]. Thus, the first step of a study of the Er sensitization in complex glasses derived from gels consisted of checking if the luminescence of Si clusters obtained by Si implantation in silica-gel (from tetraethoxysilane, TEOS) is unavoidably quenched, or could be used for enhancing the emission of Er, introduced by co-implantation or by wet chemistry. A gel of silicon suboxide, derived from another alkoxide (triethoxysilane, TH), is particularly interesting for this type of optical application. This is because a recent study has shown that it is converted into a composite of silica embedding Si nanocrystals, by heat treatment or irradiation with ions of any type at low fluences [6, 7]. This gel was doped by wet chemistry or implantation as in the case of TEOS. The optical properties of Si clusters and Er ions in suboxides formed from gels are compared to those in evaporated films of SiO_x and pure silica.

2. Experimental details

TEOS (chemical formula $Si[OC_2H_5]_4$) in ethanolic solution was hydrolyzed by the addition of 0.01 mole HCl and 2.5 moles H_2O per mole of alkoxide. Equal volumes of TH ($SiH[OC_2H_5]_3$) and ethanol were mixed and stirred for 1 h, in order to permit the hydrolysis of the ethoxide by the ambient moisture. Analysis of gel films by means of Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) shows that the addition of water to the solution is not necessary, contrary to the case of TEOS, for hydrolyzing the $Si–O–C_2H_5$ bonds. The hydroxide obtained from TH has the stoichiometry $SiO_{1.4}H_{1.1}$ and contains less than 2 at % C. TEOS : Er and TH : Er sols with different Er/Si molar ratios were synthesized by the addition of $Er(NO_3)_3.5H_2O$ in ethanolic solution. The values of the Er concentrations measured by RBS were 0.2, 0.4, 0.75, and 1.50 at % in the four TH films after heat treatment, and 0.35, 0.70 at % in the TEOS : Er films (gels and oxides obtained after heat treatment are referred to with the same abbreviation, for the sake of simplicity). The gels were deposited by spinning on Si substrates at a speed of 3000 r.p.m. in order to obtain, after annealing, oxide films free of cracks, i.e., with a thickness of 300 to 400 nm. The heat treatments were performed under a vacuum of 1.3×10^{-4} Pa, generally for 1 h at 1050 °C when not otherwise stated in the text below. SiO was evaporated under an oxygen pressure of 1.3×10^{-3} Pa, at rates of the order of 0.01 nm s^{-1}, in order to obtain suboxide films with stoichiometries in the range $x = 1.5$–1.7. This is close to that of annealed TH ($SiO_{1.5}$) and was suitable for expecting the formation of clusters 2–5 nm in diameter according to the literature [8]. Some silica and TEOS samples were implanted sequentially with Si then Er, after an intermediate annealing at 1050 °C. The energies of these implantations were, respectively, 100 and 350 keV, and the fluences were 10^{17} Si, 10^{16} Er. TH films were implanted with various Er fluences between 10^{14} and 10^{16} cm^{-2}.

Photoluminescence (PL) measurements were performed at room temperature under excitation with the 488-nm line of an Ar^+ laser, at a power density of 400 mW mm^{-2} for most of the experiments. A single grating monochromator (of focal length 250 mm) with a wavelength resolution of 2.5 nm and a liquid-nitrogen-cooled Ge detector for the wavelength range 0.8 to 1.8 μm or an EMI 9659 QB photomultiplier for the visible range, were used. The luminescence decay was analyzed with a lock-in amplifier and a digital oscilloscope.

3. Results and discussion

The depth profiles of implanted Er ions, as measured by RBS, were found to be in perfect agreement with TRIM calculations, with a maximum at a depth of 120 nm and a range straggling of 305 nm. Those of implanted Si exhibited the width predicted by calculations, but were shifted by 55 nm toward the surface because of the noticeable sputtering that occurred for a fluence of 10^{17} ions cm^{-2}. Therefore, the depth distributions of Si and Er overlapped by only 30% (in area) in samples implanted sequentially with Si then Er. TEM imaging, together with the identifications of phases by means of electron diffraction and electron energy loss spectroscopy, established the presence of different types of precipitations in films annealed at 1050 °C:

(1) Si clusters with a maximum diameter of 10 nm at the mean range of ions in SiO_2 and TEOS implanted films,
(2) Si and Er_5Si_3 clusters with a similar size in the TEOS : Er film containing 0.7% Er and implanted with Si,
(3) Er_2O_3 amorphous clusters in all films containing more than 1% Er,
(4) Si clusters with a mean size of the order of 1 nm in TH and of 2 nm in evaporated SiO_x for $x = 1.7$.

The visible luminescence of all the films (except silica and TEOS films that were not implanted with Si ions) consisted of a broad band centered at 1.6 to 1.9 eV, as shown in Fig. 1. In the case of TH and SiO_x samples, a preliminary study of the luminescence as a function of the annealing temperature, T, showed that films annealed at T below 900 °C already exhibited an emission ascribed to defects shifting from 1.7 to 2.1 eV with increasing T. This was replaced at around 950 °C by a more intense emission from clusters, centered at 1.75 eV. The position of this band shifted from 1.75 to 1.65 eV in the T range 950–1100 °C, and its magnitude increased almost linearly with T (for isochronal annealings of 30 min or 1 h). It is worth noting that the intensity of the PL related to various defects (E′ centers, C impurities) in SiO_2 and TEOS films that were not implanted with Si ions was 10–20 times less intense than that related to Si clusters in the other films, and that its energy position was around 2.1 eV (plot 3 in Fig. 1). The energy of the red emission ascribed to excitons in Si clusters does not correspond in any of the studied films to that predicted by models for the sizes of the clusters observed in TEM [9, 10]. It

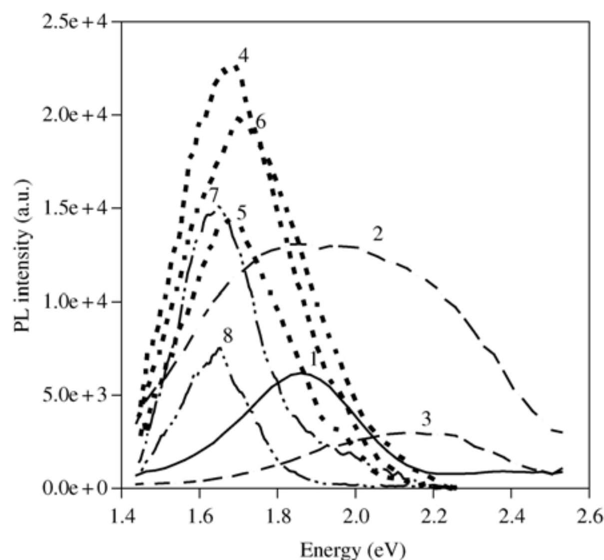

Figure 1 PL spectra in the visible range, for films annealed for 1 h at 1050 °C: (1) $SiO_2 + 10^{17}$ Si ions cm^{-2} + 10^{16} Er ions cm^{-2}; (2) TEOS : Er0.7% + 10^{17} Si; (3) TEOS : Er0.7% unimplanted; (4) TH unimplanted; (5) TH + 10^{16} Er; (6) TH : Er0.2%; (7) $SiO_{1.6}$ evaporated; (8) $SiO_{1.6}$ + 10^{16} Er. All the films except film 3 contained an excess of 10^{17} Si atoms cm^{-2} with respect to silica films of the same thickness.

should, for instance, be 2.0 eV for the very small clusters formed in TH and in evaporated suboxides with a stoichiometry around 1.5–1.7. This discrepancy has often been noted in other types of film, including porous silicon, and has been attributed to a transfer of the exciton energy to interface states associated with dangling bonds. The most straightforward evidence of a transfer of the exciton energy to Er ions was the linear decrease in the intensity of the red band with increasing Er concentration in TH implanted films (TH-I). In other cases, a decrease of the red PL was also observed with respect to reference films free of Er. However, this was not in proportion to the Er concentration in TH : Er samples. The component of the luminescence issuing from the implanted region, of estimated thickness approximately equal to the FWHM of the Er profile, was completely quenched for an Er fluence equal to 10 times the number of Si clusters in the same range of depth in TH-I films (given by the stoichiometry and the size of the clusters observed in TEM). Thus, it seems that only the Er atoms located within 1–2 interatomic distances of the clusters can be excited.

The infrared emission in all films containing Er was split into two components at 1.533 and 1.550 μm. This is typical of the Er^{3+} $^4I_{13/2}$–$^4I_{15/2}$ intra 4f transition, and its lifetime was of the same order of magnitude as that for Er in silica and silica-gel. In TH : Er films, this lifetime increased monotonically with annealing temperature in the range 900 to 1100 °C. Also in both types of TH films containing Er, it decreased with the Er concentration (by about a factor 2). The intensity of the emission in TH : Er films (height and integral) went through a maximum at 1000–1050 °C for all Er concentrations up to 1.5 at %. At the optimal annealing temperature for the PL, a maximum emission was recorded from the TH : Er film containing 0.4 at % Er (Fig. 2). The PL enhancement with respect to TEOS films, with the same Er content and thickness but without Si clusters, was comparable to that reported for silica samples implanted sequentially with 10^{17} Si ions of energy 80 keV and 10^{15} Er ions of energy 300 keV (at a similar pump power) [2]. In the TH-implanted samples, a logarithmic increase in the luminescence yield was observed up to a concentration of 1 at % (maximum concentration at the mean range of ions), as shown in Fig. 3. This sub-linear increase is ascribed to processes of up-conversion and migration of excited states toward defects. Indeed, a sublinear increase in the intensity of the infrared PL was also observed as a function of the pump power, while that of the red PL increased linearly (a decrease of the excitation efficiency per incident photon and per cluster is not implicated).

The Er luminescence in a TH sample implanted with 1.2×10^{16} Er ions cm^{-2} was 10 times more intense than in a silica sample implanted and annealed under the same conditions. Taking the Er concentration of implanted samples as the maximum concentration, the luminescence yield (peak height or integral, which are proportional to each other) of a TH-I film was stronger than that of a TH : Er film with the same Er concentration. When normalizing the yields in TH : Er films to those for a film of thickness 75 nm containing the maximum Er concentration in TH-I samples, the difference was still stronger (Fig. 3). This effect is most probably due to a less-efficient excitation by the Si clusters. Indeed, in the case of TH : Er films, Er ions remain preferentially in the solvent until its total evaporation (as indicated by a surface enrichment in films with mean Er concentrations above 0.5%) and a noticeable fraction of them tend to be concentrated in porosities after thermal conversion of the gel into oxide. In contrast, in implanted samples they are distributed at random.

The emission of Er in TEOS : Er films implanted with Si was also enhanced by a factor of the order of 10 with respect to unimplanted reference samples with the same Er concentrations. This factor tended to decrease with the Er concentration, because of the precipitation of a

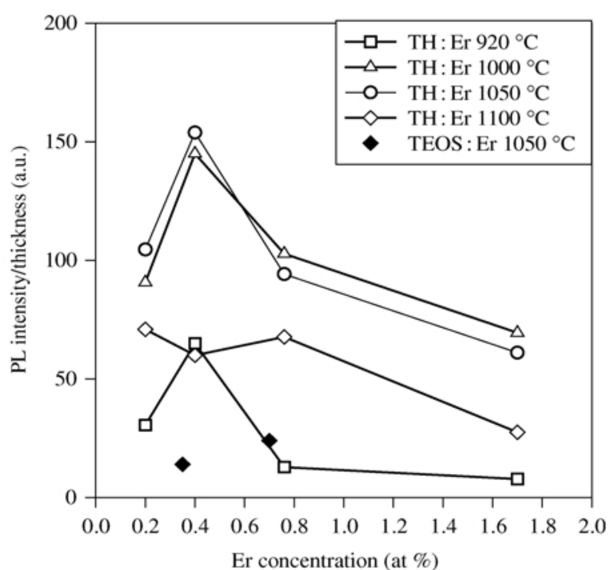

Figure 2 Variation of the infrared PL intensity (normalized to a constant thickness) with the Er concentration and temperature in TH : Er and TEOS : Er films (not implanted with Si).

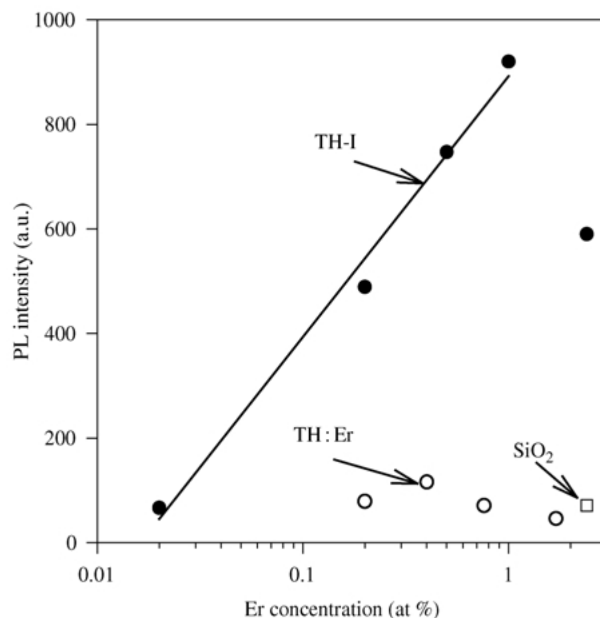

Figure 3 Comparison of the intensities of infrared PL in Er-implanted TH (TH-I), Er-implanted SiO_2 and TH : Er films, all annealed at 1050 °C.

silicide. Another type of segregation, that of Er oxide, was responsible for the quenching of the Er PL in TH implanted with 2% Er at 1050 °C (Fig. 3) and in all TH : Er films annealed at 1100 °C (Fig. 2). Little sensitization of the Er ions by Si clusters was observed in SiO_2 and TEOS films implanted sequentially with 10^{17} Si then 10^{16} Er with respect to SiO_2 implanted only with Er (intensity multiplied by a factor 2 instead of 10 for SiO_2 samples annealed at 900 °C after the Er implantation in Franzo *et al.* [2]). This was due to this segregation of Er oxide and to the insufficient overlap of the implantation profiles.

4. Conclusions

At the present stage of investigations, silica-gel films appear to be as good as pure silica as hosts for Er ions, despite their defective structure and the residual traces of C and H. Films of suboxide derived from triethoxysilane exhibit the most promising properties. Implanting Si in a gel already containing Er in solution, or Er in a gel of suboxide (TH), is more efficient than a dual implantation for enhancing the luminescence of Er ions by a coupling with excitons in Si clusters. The Er concentration in TEOS films doped by the sol–gel route must be limited, as also probably must be the concentration of implanted Si atoms, to avoid their optical neutralization by the formation of a silicide. The concentration of Er implanted in TEOS and TH must also be limited to less than 2%, or the annealing temperature must be kept lower than 1050 °C. Otherwise, the infrared emission is reduced by the segregation of erbium oxide. A similar segregation probably occurs in TH : Er films annealed at 1100 °C for Er concentrations as low as 0.2%, taking into account the decrease of PL intensity. However, annealing treatments at 1000 to 1050 °C are suitable for obtaining crystalline Si particles and an optimal sensitization.

The determination of the optimal conditions for Er sensitization is easier in the case of gel films already containing either Er atoms or Si clusters than in films submitted to dual implantations. Due to their better homogeneity, the study of TH-implanted samples enables one to establish more clearly the transfer of the energy of excitons in Si nanocrystals to Er ions in the matrix than in the case of TH films doped chemically.

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