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Luminescence efficiency at 1.5 μm of Er-doped thick SiO layers and Er-doped SiO/SiO₂ multilayers

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The luminescence from Er-doped thin films is studied in two different systems. The first one is a SiO single layer. The second one is a SiO/SiO₂ multilayer allowing us to obtain size-controlled silicon nanocrystals. In both systems, the annealing-temperature dependence of the luminescence is investigated. It is shown that the optimal annealing temperatures are equal to 700 and 1050 °C for the single layer and the multilayer, respectively. Moreover the luminescence efficiency at 1.5 μm is one order of magnitude higher in the single Er-doped SiO layer. These results are discussed in relation to the formation of silicon nanoparticles with annealing treatments. © 2006 American Institute of Physics. [DOI: 10.1063/1.2349316]

Er-doped materials have been intensively studied as they are sources of sharp luminescence lines around 1.5 μm due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in the internal 4f shell of the trivalent Er³⁺ ion. This line matches the minimum attenuation coefficient in silica-based fibers used in optical telecommunication systems. Several Si-based materials have been investigated as hosts for Er³⁺ ions. The Er luminescence was then observed in crystalline silicon, amorphous silicon, porous silicon, and silicon dioxide.¹ But dielectric matrices containing silicon nanocrystals (Si-nc) seem more interesting as they give the possibility to get a strong coupling between excitons in the Si-nc and excited states of Er³⁺ ions.² Such systems take advantages of the high excitation cross section allowed by silicon without the detrimental Auger effect with free carriers of crystalline silicon. This coupling yields an enhancement of the photoluminescence (PL) emission of Er³⁺ ions around 1.5 μm .

Silicon nanocrystals can be observed in Si-rich SiO₂ films obtained by implantation of silicon in SiO₂ films³ or by direct preparation of SiO_{x<2} films with techniques such as sputtering, evaporation, or chemical vapor deposition.⁴ In all cases, annealing post-treatments are needed to allow the diffusion of silicon or to lead to the phase separation of SiO_x in Si and SiO₂. The annealing temperature T_a is relatively high, around 1000 °C. A better control of the Si-nc size can be achieved by using SiO/SiO₂ multilayer structures.⁵ The advantage of such systems is to accurately control the thickness of the SiO active layer in which the Si nanocrystals are grown. These layers are separated by SiO₂ barriers whose role is to limit the Si-nc size which is then equal to the SiO barrier thickness. Er doping of such systems was generally made directly during the growth of the films⁶ or by postimplantation.⁷

In this study, we compare the coupling efficiency between Er³⁺ ions and silicon nanoparticles present in thick SiO single layers and in SiO/SiO₂ multilayers. The SiO single layers were prepared by thermal evaporation of SiO powder.⁸ The SiO/SiO₂ multilayers were obtained by successive evaporations of SiO powder and of fused silica glass. The thickness of the SiO active layer is equal to 3 nm,

whereas the SiO₂ barrier thickness is equal to 5 nm. The deposition rate was controlled by a quartz microbalance system and was equal to 1 Å/s. Er evaporation was performed from an effusion cell, allowing us to obtain very low deposition rates. The temperature cell was around 1100 °C. The cell was calibrated by the quartz microbalance allowing us to control the Er³⁺ concentration in the film. For this study, an Er concentration of 0.8 at. % was chosen. The silicon substrates were maintained at 100 °C. For all samples, the total film thickness is equal to 200 nm. The samples were then annealed in a quartz tube under vacuum with a pressure of about 10⁻⁹ Torr. For T_a higher than 950 °C, the furnace used is a molybdenum cavity heated by electron bombardment. The vacuum pressure was better than 10⁻⁶ Torr. The samples were cooled down immediately after reaching the annealing temperature.

The structure of the films was analyzed by Fourier transform infrared (FTIR) spectroscopy and by transmission electron microscopy (TEM) experiments. The FTIR spectroscopy was used to analyze the phase separation in the SiO layer. The spectra were obtained with a resolution of 4 cm⁻¹. The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra. Microstructural observations were performed by TEM at 200 kV on cross-section and on rear-thinned samples, both by the tripod method, without ion milling. The photoluminescence in the range of 600–1000 nm was analyzed by a monochromator equipped with a 150 grooves/mm grating and by a charge-coupled device detector cooled at 140 K. The excitation was obtained by a mercury arc lamp source. The PL in the range of 1400–1800 nm was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. The 355 nm excitation was obtained from a neodymium-doped yttrium aluminum garnet laser. The response of the detection system was precisely calibrated with a tungsten wire calibration source.

The decomposition of SiO into the Si and SiO₂ phases appears during the annealing, leading first to the formation of silicon-rich areas embedded in a SiO_y matrix, with y greater than 1. The stoichiometry of the matrix can be followed by FTIR absorption spectrometry experiments. Indeed, the spectrum of the silicon oxide layers shows a very intense absorp-

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FIG. 1. Infrared absorption spectra of SiO layers annealed at different temperatures T_a .

tion band around 1000 cm^{-1} corresponding to the asymmetric stretching vibration of the oxygen atom in the Si–O–Si group. The evolution of this band is represented in Fig. 1 for different annealing temperatures. This absorption band gives information about the oxidation degree of the matrix since a linear relation exists between the wave number of this mode and the composition y of the SiO_y phase in the samples.⁹ The as-deposited film corresponds to $\text{SiO}_{0.95}$. There is practically no structural change till 500°C . The absorption band starts to shift towards low wave numbers when T_a is equal to 500°C . It finally reaches 1070 cm^{-1} for T_a equal to 950°C , which corresponds to SiO_2 . This band shift is the signature of the appearance of silicon-rich domains. Such an evolution also occurs in the multilayers, although its observation is more difficult since the experimental absorption band contains contributions of the SiO and SiO_2 layers.

For the single layer, no silicon cluster was seen for T_a less than 950°C . At 950°C , silicon clusters with sizes lower than 2 nm are observed on the bright-field image. For T_a equal to 1050°C , the silicon clusters are bigger with clusters as large as 10 nm , as shown in Fig. 2(a). The size dispersion is very large. On the contrary, the SiO/SiO₂ multilayer system is powerful to obtain size-controlled Si nanocrystals, since the SiO₂ barriers limit the maximum Si-nc size given by the SiO layer thickness. In these multilayers, nanocrystals also appear for T_a greater than 950°C . For example, the TEM micrograph of the multilayers after

FIG. 2. Bright-field TEM micrograph of (a) a single SiO layer annealed at 1050°C and (b) a cross-section micrograph of a multilayer annealed at 1050°C .

FIG. 3. PL spectra at 300 K for different SiO/SiO₂ multilayers: (a) undoped and annealed at 1050°C , (b) Er-doped and unannealed, and (c) Er-doped and annealed at 1050°C . The PL spectrum (d) shows the PL of an Er-doped SiO layer annealed at 700°C for comparison.

an annealing at 1050°C is represented in Fig. 2(b). It clearly shows the Si-nc layers between the SiO₂ layers. Both the dark-field view and the high-resolution image of Si nanoparticles showing the Si (111) planes reveal the crystalline character of the Si clusters.¹⁰ The size distribution measured on bright-field TEM images gives a mean diameter of $3.2 \pm 0.7\text{ nm}$, in good agreement with the initial SiO layer thickness. Even at this high annealing temperature, no Si nanocrystals with a size greater than 5 nm were observed.

The energy transfer between the Si nanocrystals and the Er^{3+} ions was demonstrated in the Er-doped multilayers by photoluminescence spectroscopy, as illustrated by the study of different multilayers. An Er-doped multilayer annealed at 1050°C , containing both Si-nc and Er^{3+} ions, was compared to an undoped sample annealed at 1050°C , containing Si-nc, and an as-deposited sample with Er^{3+} ions, but without Si-nc. The PL spectra obtained at room temperature are reported in Fig. 3. For the undoped sample annealed at 1050°C [spectrum (a)], a broad and intense peak visible at 800 nm is attributed to the Si nanocrystals. For the Er-doped as-deposited sample [spectrum (b)], no signal at 800 nm is detected since there is no Si-nc but a small PL band can be seen at 1540 nm . It corresponds to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ intrashell Er^{3+} ion transition. The PL intensity of the Si-nc signal at 800 nm vanishes when Si-nc are coupled to Er^{3+} ions [spectrum (c)], on behalf of the intensity of the Er^{3+} ions signal, which is increased by two orders of magnitude. These points reveal the coupling effect and the energy transfer between the Si-nc and the Er^{3+} ions, yielding a better Er luminescence efficiency, in full agreement with other similar studies.^{2,11} The $1.5\text{ }\mu\text{m}$ PL peak is also obtained in the Er-doped SiO single layer, as shown in Fig. 3 [spectrum (d)]. It must be noticed that the intense luminescence band at 800 nm was not observed in undoped SiO single layers because they do not contain well-confined crystallized Si aggregates. Only a small feature can be seen around 750 nm for this sample after an annealing at 950°C that could be due to silicon nanoclusters.⁸ The very weak signal, compared to that of multilayers, could be explained by the low confinement quality of the matrix. After an annealing at 1050°C , the matrix quality should be better but the silicon clusters are too large to observe a confinement effect. Then, a coupling

FIG. 4. Evolution of the 1.54 μm PL intensity at 300 K as a function of the annealing temperature T_a .

phenomenon between Er^{3+} ions and silicon nanoparticles cannot be seen in the SiO single layer.

The PL intensity at 1.54 μm for both the single SiO layer and the SiO/SiO₂ multilayer is reported in Fig. 4 for different annealing temperatures. It is first observed that the optimal annealing temperatures are equal to 700 and 1050 $^{\circ}\text{C}$ for the single layer and the multilayer, respectively. In these samples, the PL intensity is probably mainly governed by mechanisms such as the formation of Si clusters and the passivation of defects. For the SiO layer, the increase of the intensity for T_a in the range of 500–700 $^{\circ}\text{C}$ could be explained not only by the annihilation of defects which play the role of nonradiative recombination centers but also by the appearance of silicon nanoparticles in the films, as shown by the FTIR and TEM results. It can be supposed that the phase decomposition produces, from 500 $^{\circ}\text{C}$, a great number of silicon aggregates, too small to be detected by TEM, with a high absorption cross section for the excitation wavelength. The absorbed energy is then transferred to the Er^{3+} ions which become luminescent. The number of optically active Er^{3+} ions increases with the appearance of more and more Si clusters. For T_a greater than 700 $^{\circ}\text{C}$, the growth of the Si clusters, due to the Si diffusion and the coalescence phenomenon, induces a decrease of the total number of Si nanoclusters and therefore a decrease of the Er^{3+} luminescence. For the multilayer, the higher optimal annealing temperature is certainly due to the multilayered-structure effect which could delay the dissociation and the coalescence process. A comparable phenomenon was related for Si/SiO₂ and Ge/SiO₂ superlattices by Zacharias and Streitenberger¹² who observed that the crystallization temperature of silicon and germanium was strongly enhanced by the presence of the oxide interfaces.

The second point is that the intensity at the maximum of the luminescence at 1.54 μm is stronger for the monolayer than for the multilayer, even if the signal is normalized to a constant SiO thickness. For T_a equal to 700 $^{\circ}\text{C}$, the PL in-

tensity is one order of magnitude higher for the single layer than for the multilayer. Several reasons could explain the low intensity for the multilayer. Firstly, the distance for coupling the Er^{3+} ions and the silicon clusters was estimated¹³ to be around 1 nm. Therefore a great part of the Er^{3+} ions contained in the SiO₂ layers probably absorbs the light emitted by the Er^{3+} ions located in the SiO layers. Moreover, structural defects probably exist at the SiO/SiO₂ interfaces, with electronic states in the infrared domain that could induce nonradiative recombinations. Our results also suggest that well-defined Si nanocrystals are not necessary to get a good Er^{3+} ion luminescence efficiency and that the key points are certainly the number of silicon nanoparticles and defect centers.

In summary, the luminescence at 1.5 μm was studied in Er-doped SiO single layers and in Er-doped SiO/SiO₂ multilayers, as a function of the annealing temperature. In both samples, the formation of silicon nanoparticles embedded in a silicon oxide matrix was induced by the annealing treatments. The optimal annealing temperatures are equal to 700 and 1050 $^{\circ}\text{C}$ for the single layer and the multilayer, respectively, and the luminescence from the single layer is one order of magnitude higher than that of the multilayer. For this last one, the high optimal annealing temperature and the low PL intensity are due to a strain effect induced by the multilayered structure and to the existence of inactive Er^{3+} ions and defects. Due to the intense luminescence of the single layer and due to the relatively low annealing temperatures needed for obtaining that PL, the Er-doped SiO layer appears to be a promising material for applications.

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