Photoluminescence of undoped and erbium-doped SiO/SiO₂ multilayers

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Abstract - We show the possibility to obtain amorphous SiO/SiO₂ and silicon nanocrystal (Si-nc) superlattices by evaporation. The size of the Si-nc is well controlled. The coupling between the nanocrystals and erbium ions is studied.

I. INTRODUCTION

Erbium (Er)-doped materials have involved an intense research activity because they can emit a sharp luminescence line around 1.54 μm due to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in the internal 4f-shell of the trivalent Er ions. This line matches the minimum attenuation coefficient in silica-based fibers used in optical communications. During last years, several Si-based materials have been investigated as a host for Er ions and luminescence was observed in crystalline silicon, amorphous silicon, and silicon oxide thin films [1]. Other systems containing silicon nanocrystals (Si-nc) in a dielectric matrix seem very interesting because a strong coupling between excitons in Si-nc and excited states of Er ions enhances the photoluminescence (PL) emission around 1.54 μm . Substoichiometric silicon oxide films have particularly been studied because silicon clusters can be generated by annealing post-treatments yielding phase separation into Si and SiO₂. Such films can be prepared by evaporation, chemical vapor deposition, sputtering or Si ions implantation into SiO₂. In particular, our group has prepared amorphous SiO_x films using the evaporation technique either by evaporating a SiO powder [2] or by evaporation of silicon in an oxygen atmosphere [3]. A better control of the maximum Si-nc size can be achieved by using multilayer structures. The advantage of such systems is to accurately control the SiO_x active layer thickness in which the Si-nc are grown. These layers are separated by SiO₂ barriers which role is to limit the Si-nc size. The maximum Si-nc size is then equal to the SiO barrier thickness. Such Er-doped multilayer systems can be prepared by RF sputtering [4], magnetron sputtering of Si in vacuum and Er-doped SiO₂ in an oxygen atmosphere [5], reactive magnetron sputtering of SiO₂ and Er₂O₃ in an hydrogen-argon atmosphere [6] or by evaporation of SiO in an oxygen atmosphere [7,8]. In the last example, Er is introduced by the implantation method.

In this study, Er-doped SiO/SiO₂ multilayers are analyzed. The evolution of the structure of the multilayers with the annealing thermal treatments is followed by infrared absorption spectrometry and by transmission electron microscopy (TEM), in correlation with the evolution of the photoluminescence of the undoped multilayers. The coupling between Si-nc and Er ions is also demonstrated in the Er doped multilayers.

II. SAMPLES ELABORATION AND CHARACTERIZATION

The SiO/SiO₂ multilayers were prepared by successive thermal evaporation of a SiO powder and evaporation of fused silica glass performed by an electron beam gun. The deposition rate was controlled by a quartz microbalance system and was equal to 1 $\text{\AA}/\text{s}$. The thickness of the active layer was equal to 3 nm whereas the SiO₂ barrier thickness was equal to 5 nm. The silicon substrates were maintained at 100 $^{\circ}\text{C}$. The film thickness is 200 nm. For Er doping, the temperature of the effusion cell was 1100 $^{\circ}\text{C}$. After calibration of the cell with the quartz microbalance, the Er concentration in the film was estimated to be equal to 1.8 %. To grow the Si-nc, the samples were then annealed in a quartz tube under vacuum with a pressure of about 10^{-9} Torr. For annealing at temperatures higher than 950 $^{\circ}\text{C}$, the furnace was a molybdenum cavity heated by electrons bombardment. The vacuum pressure was better than 10^{-6} Torr. The samples were cooled down immediately after reaching the annealing temperature.

The Fourier transform infrared spectroscopy (FTIR) 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 transmission electron microscopy (TEM) at 200 kV. TEM analyses were carried out on cross section and on rear-thinned samples, both by the tripod method, without ion milling. For the study of the Er-free samples with annealing temperature, the PL was analyzed by a monochromator equipped with a 150 grooves/mm grating and by a CCD detector cooled at 140 K. The excitation was obtained by a 200 W mercury arc lamp source. To study the coupling between nc-Si and Er ions, the PL 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 YAG:Nd laser. The response of the detection systems was precisely calibrated with a tungsten wire calibration source.

III. RESULTS

Infrared absorption spectroscopy is a powerful technique to show the dissociation process. Indeed, the frequency of the asymmetric absorption band of the Si-O-Si groups is an increasing function of the oxygen content (typically from 1000 to 1080 cm^{-1} for SiO and SiO₂). To obtain the contribution of the SiO active layer, the absorption corresponding to the whole thickness of the SiO₂ barrier was subtracted to the experimental absorption spectra. The resulting absorption bands are represented in Fig. 1. The absorption is located around 1055 and 1068 cm^{-1} for the as-deposited and

annealed at 950 °C samples, respectively. This evolution is indicative of the appearance of a SiO₂ phase in the active layer.

Annealing the films at 1000 °C yields the formation of three dimensionally confined Si-nc, coming from the dissociation of SiO into Si and SiO₂. Fig. 2-a shows a cross-sectional TEM view of the multilayer. The black lines are the

Fig. 1 : Infrared absorption band of the SiO active layer obtained after subtraction of the SiO₂ absorption band to the experimental spectrum.

layers containing Si nanoclusters and the white bands are the SiO₂ layers. These multilayers are very stable since the modulation is still visible after annealing at very high temperatures. In Fig. 2-b, a dark-field plan view of the same sample shows the Si nanoparticles. Both the dark-field view and the HRTEM image of Si nanoparticles showing the Si (111) planes reveal the crystalline character of the Si-nc. The size distribution measured on bright-field TEM images gives a mean diameter of 3.2 nm ± 0.7 nm. This mean size is limited by the SiO₂ layer and controlled by the SiO layer thickness. The good stability of the SiO₂ layer and the phase separation of SiO into Si and SiO₂ allows us to control the Si-nc mean size.

Fig. 2 : TEM images in a) cross-section view and b) dark-field plan view of a multilayer.

Fig. 3 shows PL spectra of the multilayers as-deposited and for different annealing temperatures (Ta). The as-deposited sample shows a weak signal at 540 nm. For Ta = 350 °C, a strong improvement of the PL intensity can be observed. For Ta = 650 °C, the intensity decreases and the peak shifts towards the high wavelengths, at 580 nm. Finally, for Ta = 950 °C, the PL signal has vanished.

Fig. 3 : PL spectra at room temperature of SiO/SiO₂ multilayers for different annealing temperatures.

The position of the PL peak and the evolutions of both the position and the intensity with annealing are comparable to those observed in pure SiO films. Consequently, this luminescence signal can be attributed to the SiO layers. The origin of this luminescence is not clear. Even if a contribution from amorphous silicon can not be excluded, the emission can be explained by silicon oxide defects similar to those that exist in SiO₂. The strong improvement of the PL after an anneal at 350 °C could originate from desorption of water that is well known to create defects in the oxide. The decrease of the luminescence for higher annealing temperatures till 950 °C could then be due to the disappearance of the defects involved by the formation of Si-O-Si bonds and the phase separation process. For the thermal treatments above 950 °C, a new luminescence band around 800 nm appears with a strong intensity. In correlation with the structural study, this luminescence can be attributed to the crystallized silicon nanoclusters which have appeared in the active layer. The PL energy (equal to 1.57 eV) correlated to the Si-nc mean size (3.2

nm) is in good agreement with previous works [9,10]. Moreover to demonstrate that the PL originates from the Si-nc, the size effect on the PL energy was studied. Several SiO layer thicknesses were prepared from 2 to 6 nm. A blueshift of the PL energy was clearly obtained, as predicted by the quantum confinement theory (these results will be published elsewhere).

The electronic coupling between the Si-nc and the Er ions is studied by photoluminescence spectroscopy. Three samples are analyzed. A sample containing both Si-nc and Er ions is compared to two references : a sample with Si-nc and without Er ions, and a sample with Er ions but without Si-nc (without annealing). The PL spectra obtained at room temperature are reported in Fig. 4. In the case of the sample containing only Er ions, there is no signal at 800 nm and a small signal is detected at 1540 nm. It is attributed to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ intra-shell Er ion transition [6-8]. For the sample containing only Si-nc, a peak is visible at 800 nm. The PL intensity of this Si-nc line vanishes when Si-nc are coupled to Er ions, on behalf of the intensity of the Er ions signal, which is increased by two orders of magnitude in this case. These points show the coupling effect and the energy transfer between Er ions and the Si-nc [8].

Fig. 4 : PL spectra at room temperature of samples containing Er ions, Si-nc and Er-coupled Si-nc.

We also notice that the peak of the uncoupled Si-nc is centered around 797 nm, whereas the peak of the Er-coupled Si-nc is centered around 772 nm. Moreover, this last peak seems asymmetric (in comparison with the uncoupled Si-nc peak) with an emission tail on the high-wavelength side of the coupled Si-nc peak. These points may be seen as a PL intensity decrease in the low-energy range of the uncoupled Si-nc peak. It may be linked to a more efficient coupling between the Er ions and the larger Si-nc.

In conclusion, the deposition method used to prepare these Er-doped SiO/SiO₂ multilayers is low cost, compatible with the microelectronics technology, and more simple than high energy implantation. It enables us to get silicon nanocrystals with controlled average size. Those Si-nc can be coupled to Er ions, yielding a better PL efficiency of these ions at 1.54 μ m.

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