

Photoluminescence from Tb nanoparticles embedded into SiO₂ films at high temperature

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Abstract— The present work studied the photoluminescence (PL) emitted from Tb ions implanted from room temperature (RT) up to 350 °C in a SiO₂ matrix, followed by a further anneal process. The ions were implanted with energy of 100 keV and fluence of 3×10^{15} ions/cm². The annealing was performed in O₂ or N₂ atmosphere with temperatures ranging from 500 °C up to 800 °C. The PL measurements were performed at RT and the structural measurements were done via transmission electron microscopy (TEM) and Rutherford backscattering technique (RBS). As a result, we have observed that the PL emission is more intense for samples implanted at high temperature.

Keywords - Ion implantation, Tb nanoparticles, photoluminescence, Transmission Electron Microscopy (TEM)

I. INTRODUCTION

Silicon has been the material of choice for several decades in the microelectronics industry due to its excellent electrical, chemical and mechanical properties. With the increasing miniaturization of the integrated circuits, according to the Moore's Law [1], several difficulties are currently hampering their evolution in terms of processing and transmission speed. Those difficulties arise due to numerous physical factors that become more relevant as the scale of such circuits becomes closer to atomic dimensions [2]. One promising alternative is to replace the way that the signals are transmitted and processed inside the integrated circuits, namely, the use of photons instead of electrons. However, silicon being an indirect band gap semiconductor also makes it a poor photoemitter due to the low probability of radiative recombination.

In the search for the luminescence of silicon-compatible materials, novel elements were used in order to obtain a more intense emission with a wider range of wavelengths. Regarding rare earths

(RE) embedded in SiO₂ matrixes; the first successful result related with PL emission was reported in 1983 by Ennen et al. [3]. In this case, it was observed that a 1.54 μ m emission from Er³⁺ ions that were introduced in a SiO₂ matrix by room temperature ion implantation. In the 90s, the study of the luminescence from RE embedded in Si compatible matrices started to be intensively investigated, [4]. Several works have been published involving other RE's, like Tb and Eu [4]-[7]. In 2007, Prucnal et al. [8] reported an intense electroluminescence (EL) emission with a strong influence of the excitation current on the spectral emission characteristics of the fabricated devices. An extensive review of the subject can be found in Ref. [9].

In all the previous reports where the ion implantation technique was used, it was performed at room temperature (RT). On the other hand, very recently it was proved that implantations performed at high temperatures (hot implants) induce higher PL yields when compared with the ones performed at RT. In fact, when Si [10]-[14] and Ge [15] were hot implanted in a SiO₂ matrix and further annealed, PL yields ten times higher for Si, and three times higher for the Ge were obtained, as compared with the corresponding RT implantations.

Then, in the present work, we have studied the influence of the Tb hot implants into a SiO₂ matrix on the corresponding PL emission. In addition, the influence of the annealing temperature and also the annealing atmosphere were investigated. We have done structural measurements by using transmission electron microscopy (TEM) and the Rutherford backscattering technique (RBS) was used to

determine the implanted ion profiles at each step of the experiment.

II. EXPERIMENTAL DETAILS

The samples consist of a 100 nm thick SiO₂ layer thermally grown on <100> Si wafer. The SiO₂ films were subsequently implanted with Tb ions. The implantations were performed with a fluence of 3×10^{15} ions/cm², at an energy of 100 keV ($R_p = 45$ nm, $\Delta R_p = 9$ nm), resulting in a peak concentration of approximately 1 at%. During the implantations, the samples were kept at a constant temperature, ranging from RT up to 350 °C. Afterwards, the samples were annealed for 1 h in N₂ or O₂ atmosphere, with temperatures ranging from 500 up to 800 °C.

For the PL measurements, the samples were excited with a 266 nm (4.66 eV) solid state laser, with 7 mW of excitation power. The sample's emission was dispersed by a 30 cm monochromator and then detected by a CCD camera. All the spectra were corrected taking into account the system's response.

Rutherford backscattering technique (RBS) and transmission electron microscopy (TEM) were used in the structural characterization. In the first case we have used the 1.2 MeV He⁺ beam provided by a 3 MV Tandetron accelerator and for the second one, a 200 kV Jeol transmission electron microscope was used.

III. RESULTS

A. PL measurements

In Fig. 1(a), a typical PL spectrum of a Tb implanted sample is displayed. The spectrum presents several emission lines which correspond to radiative electronic transitions of the Tb ions, as reported in the literature [16], [17]. The shape of PL line does not change with the implantation or annealing temperatures, neither with the anneal atmosphere, only its intensity is modified. Further, the emission lines maintain their relative intensities. In what follows, we will refer the obtained results only related to the doublet at 542 nm, which is the most intense PL line.

In Fig. 1(b) the 542 nm PL yield as a function of both the implantation and annealing temperatures is displayed. An inspection of the figure shows the following features: The implantation temperature strongly influences the PL yield. With increasing implantation temperatures, there is an increase of the PL emission, being the minimum for the RT and maximum for 350 °C. Concerning the annealing temperature, the maximum is observed at 500 °C regardless of the implantation temperature. However, the maximum PL yield is observed at a combination of a hot implant at 200 °C and anneal at 500 °C. Finally, it should be stated that for temperatures higher than 500 °C, all the samples show a decrease in the PL yield, independent of the implantation temperature.

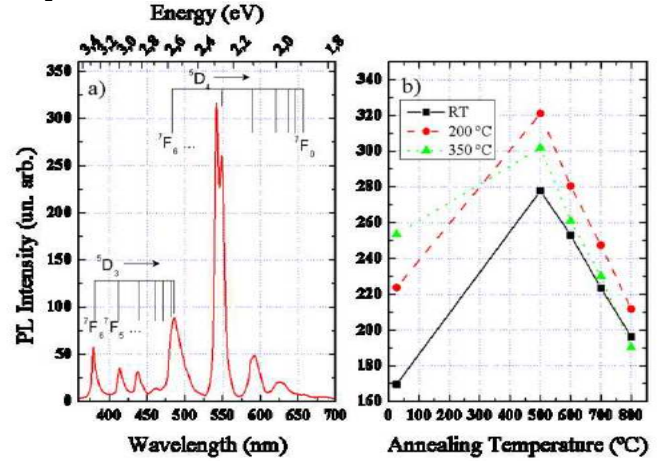


Fig. 1 (a) Typical spectrum of a Tb implanted sample, showing the radiative electronic transitions of the Tb ions. (b) PL intensity of the 542 nm line as function of the annealing temperature for samples implanted at RT, 200 and 350 °C.

B. RBS results

In Fig.2 the results of the RBS measurements performed on the samples implanted at room temperature and at 350 °C, and further annealed at 800 °C are displayed. As can be observed, the Tb depth distribution remains unchanged. However, the total area is 30% smaller as compared with the as implanted profile. Since no Tb penetration into the Si bulk is observed, it should be assumed that the Tb out-diffuses through the surface.

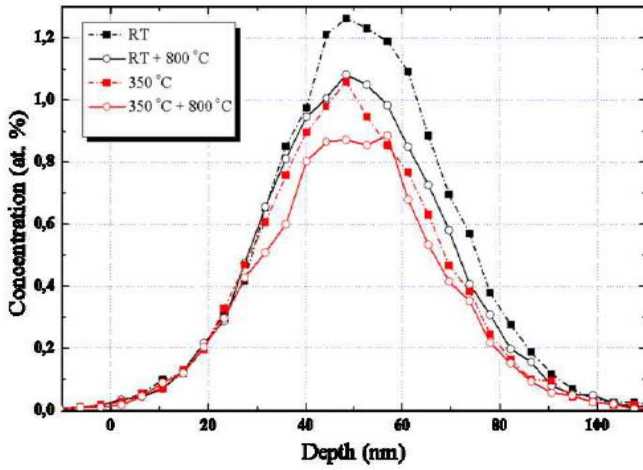


Fig. 2 RBS spectra from Tb implanted samples at RT and 350 °C, before and after an 800 °C, 1 h anneal in a N₂ atmosphere.

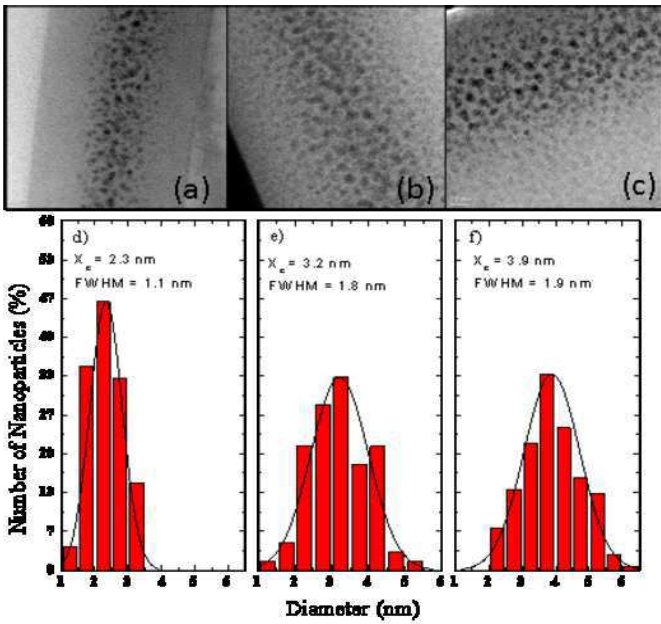


Fig. 3 TEM images for Tb implanted samples: (a) as-implanted at 350 °C, (b) implanted at RT and further annealed at 800 °C and (c) implanted at 350 °C and subsequently annealed at 800 °C. Corresponding histograms are shown in figures (d), (e) and (f).

C. TEM results

The TEM images, shown in a Fig. 3, reveal that implantation performed at 350 °C provides sufficient thermal energy for the precipitation of nanoparticles during the implantation process. Further, from the histograms obtained from the micrographs, the nanoparticles size distributions of the samples were determined – see Fig. 3. For the as-implanted samples at 350 °C, Fig. 3(a), the mean size diameter is of 2.3 nm, for the RT implanted and further annealed at 800 °C, Fig. 3(b), it is of 3.2

nm and for the samples implanted at 350 °C and subsequently annealed at 800 °C, Fig. 3(c), it is of 3.9 nm. Fig. 3(d), (e) and (f) are the corresponding histograms from where the values of the mean size diameters were extracted.

IV. CONCLUSIONS

In this work, the influence of the implantation and annealing temperatures as well the annealing atmosphere on Tb implanted in SiO₂ matrix were investigated.

We have noted that PL emission intensity from the samples studied in the present work as a function of implantation and annealing temperature depends essentially on two conflicting factors. On one hand, the post-implantation anneal favors the nucleation and growth of the nanoparticles, which is not only unnecessary but also unwanted. This is because the PL emission from rare earth oxides is due to electronic transitions of atomic levels of such ions. On the other hand, non-radiative defects present mainly in the as-implanted samples, compete in the capture of excitation photons and even of emitted photons from the RE luminescent centers, hampering the PL emission. A way to maximize the PL emission consists in the passivation of the non-radiative defects generated by the implantation process and, at the same time, trying to avoid the growth of the precipitates. The hot implantation partially eliminates the non-radiative defects created during the implantation process, which is why the PL intensity of the as-implanted samples is always higher for the hot implanted samples as compared to the RT ones.

In conclusion, the optimal compromise was obtained for samples implanted at 200 °C and annealed afterwards at 500 °C. The annealing atmosphere did not play a significant role on the shape or intensity of the PL emission. TEM images revealed that the mean diameter of the nanoparticles distribution increases with the implantation temperature and, more significantly, with the annealing one. Further, RBS spectra show that samples annealed at 800 °C had an accentuated out-diffusion of Tb atoms, causing a loss of 30% of the implanted Tb concentration. However, the shape of the implantation profile was preserved. These two

factors explain the strong reduction in the PL intensity of the samples annealed at 800 °C.

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