Influence of the implantation and annealing parameters on the photoluminescence produced by Si hot implantation

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Abstract

We report an investigation on the effect of the fluence and annealing time on the photoluminescence (PL) from Si nanocrystals produced by hot implantation of Si into a SiO_2 matrix followed by thermal treatment in nitrogen. We have varied the implantation fluence in a wide range, from 0.35×10^{17} to 4×10^{17} Si/cm^2. In addition, the PL evolution with the annealing time (1 up to 15 h) was studied for the samples implanted with fluences between 1×10^{17} and 4×10^{17} Si/cm^2. After annealing the spectra present two PL bands: one centered at 780 nm and a second one around 1000 nm. The influence of the studied parameters on the PL behavior of both bands suggests different origins for their emission. The results are discussed in terms of current models.

Keywords: Silicon nanocrystals; Photoluminescence; Hot implantation

1. Introduction

Since the discovery of intense light emission in porous Si [1] and in Si nanocrystallytes [2,3] an intense research activity has been developed in studying Si nanostructures due to their promising applications in optoelectronics and photonic devices [4–6]. The investigation of structures consisting of Si nanocrystals (Si NCs) has mostly devoted to improve their quantum efficiency for photoluminescence (PL) as well to understand their light absorption and emission processes. Although the exact mechanism for light emission remains controversial, nowadays it is well established that basically the emission energy is dependent on either the NCs size [7–9] or radiative processes at the Si NCs/matrix interface [9–12].

Si NCs embedded in SiO_2 matrix have been extensively studied as a function of the implantation fluence, annealing temperature and annealing time [10,13–15]. However, in all the previous works the implantations were performed at room temperature (RT) and only one PL band centered at around $\lambda \cong 780$ nm was observed. More recently, we have taken another experimental approach [16]. The Si implantations into SiO_2 matrix were performed at high temperatures (basically between 400 and 800 °C), at a fluence of 1×10^{17} Si/cm^2, being the spectra obtained in a linear excitation regime (power density of 20 mW/cm^2). As a consequence two PL bands were observed, one with lower intensity at $\lambda \cong 780$ nm and the other with higher intensity at λ around 1000 nm. Transmission electron microscopy analyses (TEM) of the hot implanted samples have revealed that the NCs size distribution was broader with a larger mean size as compared to RT implantations.

Since hot implantations of Si into SiO_2 produce a new PL line shape composed by two bands, when measured in a linear excitation regime, it should be interesting to study

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its origin. With this aim we have undertaken the present experiment where we study the PL behavior as a function of the Si implantation fluence. In addition, we have also investigated the influence of the high-temperature annealing time on the behavior of both PL bands. It should be mentioned that several studies have given contradictory results concerning the effect of the annealing time on samples implanted at RT [17–20].

2. Experimental

A 480 nm-thick layer thermally grown onto a Si(100) wafer was implanted, keeping the substrate at 600 °C, with 170 keV Si ions at fluences of (0.35, 0.5, 1, 2, 3 and 4) $\times 10^{17}$ Si/cm^2 resulting Si concentrations in a range between 3 and 40 at.%. Samples were further annealed at 1100 °C for 1 h under N_2 atmosphere in a conventional furnace in order to nucleate and grow the Si precipitates. To investigate the effect of the annealing time on the PL emission, samples implanted with fluences of 1×10^{17} to 4×10^{17} Si/cm^2 were annealed from 1 to 15 h. PL measurements were performed at RT using a Xe lamp with a monochromator, in order to get a wavelength of 488 nm (2.54 eV) as an excitation source. The emission was dispersed by a 0.3 m single-grating spectrometer and collected with a visible near-infrared Si detector and an InGaAs cooled one. All spectra were obtained under the same conditions and corrected for the system response. In order to characterize the morphology of the samples, TEM measurements were performed using a 200 keV JEOL microscope.

3. Results

3.1. PL as a function of the implantation fluence

In Fig. 1 are shown the PL spectra of samples implanted between 0.35×10^{17} and 4×10^{17} Si/cm^2 and post-annealed at 1100 °C. The inset of this figure illustrates details of the PL region corresponding to the wavelength interval between 650 and 950 nm. An inspection of the figure shows several interesting features. First, for the lowest implantation fluence only the band centered at 780 nm appears. Second, the shape of the PL spectra noticeably changes with increasing implanted Si fluence. From 0.5×10^{17} Si/cm^2, it can be clearly distinguished two PL bands: one centered at 780 nm and a new one at around 1000 nm. The first band increases its intensity with the fluence up to $\Phi = 0.5 \times 10^{17}$ Si/cm^2 and then decreases, without shifting its position – see inset. On the other hand, the second PL band ($\lambda \sim 1000$ nm) increases its PL signal continuously up to $\Phi = 3 \times 10^{17}$ Si/cm^2 and then decreases by almost 30%, showing a strong redshift with the increasing implanted fluence.

In order to quantify the intensities of both PL bands and their positions, we have fitted the PL spectra with two Gaussians, following the same procedure applied in [16]. The results presented in Fig. 2 show that the peak centered

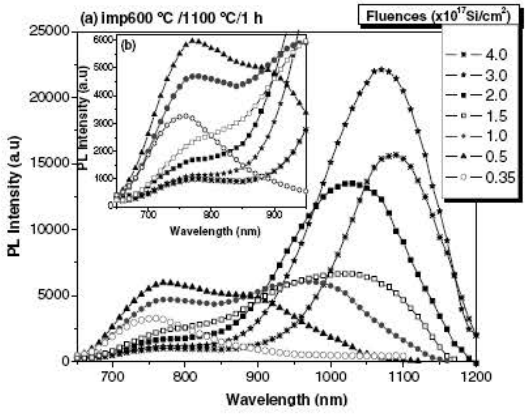

Fig. 1. (a) Typical PL spectra of samples implanted at 600 °C with different fluences and subsequently annealed at 1100 °C for 1 h and (b) insert corresponds to the spectra shown in (a) expanded in the wavelength region of 650–950 nm.

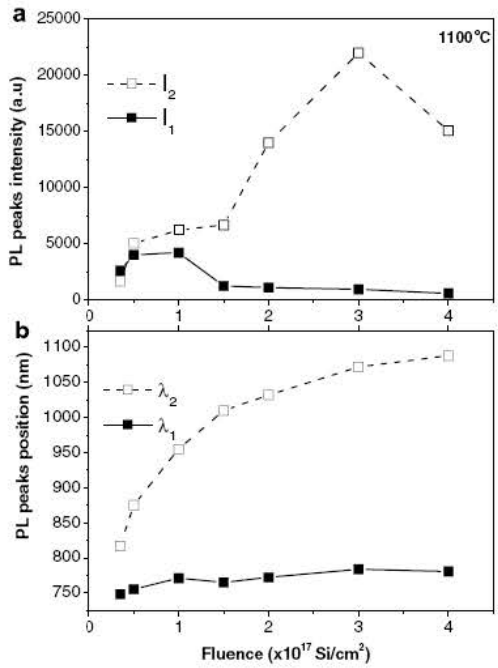

Fig. 2. (a) PL peak intensities and (b) positions as a function of the fluence for samples implanted at 600 °C and annealed at 1100 °C for 1 h. I_1 and I_2 represent the peak intensities for the short and the long wavelength PL bands centered at the positions λ_1 and λ_2, respectively.

at $\lambda = 780$ nm, slightly changes the intensity (I_1) with its position (λ_1) remaining almost constant with the implantation fluence. Therefore, in what follows, we will concen-

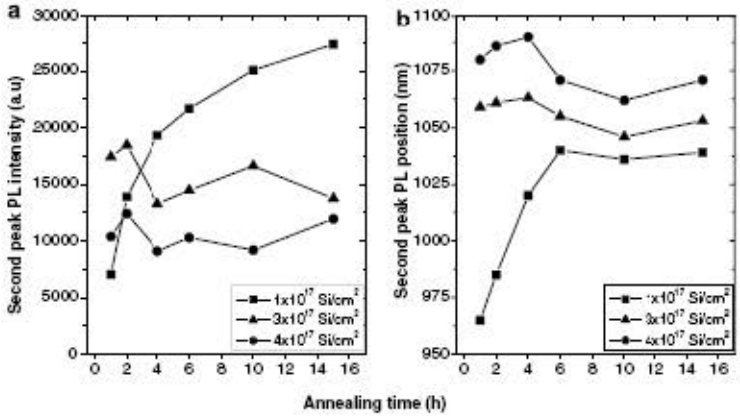

Fig. 3. (a) Second peak PL intensity and (b) position as a function of the annealing time performed at 1100 °C for samples implanted at 600 °C with different fluences.

trate our attention on the behavior of the long wavelength band. In Fig. 2(a) is displayed the evolution of the PL peak intensity (I_2) of this band as a function of the implanted fluence. As quoted above it increases its intensity with the fluence reaching a maximum at $\Phi = 3 \times 10^{17}$ Si/cm^2. Concerning the PL peak position (λ_2), it suffers a noticeable redshift with the fluence, changing from 850 to 1100 nm – see Fig. 2(b).

3.2. PL as a function of the annealing time

In this section we report the results of the PL evolution with the annealing time for samples implanted at 600 °C with different fluences from $\Phi = 1 \times 10^{17}$ to 4×10^{17} Si/cm^2 and post-annealed at 1100 °C. In Fig. 3(a) one can observe that for the sample implanted at 1×10^{17} Si/cm^2 the PL intensity increases with the annealing time, but after 6 h it shows a tendency to saturation. On the other hand, the sample implanted with 3×10^{17} Si/cm^2 presents an initially more intense PL signal, which after 2 h of post-annealing decreases and remains almost constant for longer annealing times. The same behavior is observed for the two other implanted fluences, but with a lower PL signal ($\Phi = 2 \times 10^{17}$ Si/cm^2 is not shown). In Fig. 3(b) are plotted the respective peak positions as a function of the annealing time. For the 1×10^{17} Si/cm^2 fluence, the PL peak position evolution shows a redshift followed by a tendency of saturation after 6 h, which is the same kind of behavior as the one observed in Fig. 3(a). However, for the other fluences one can observe a slightly redshift up to 4 h followed by a fluctuation in the PL peak position for the longer annealing times.

Regarding the TEM analyses, the as-implanted samples have shown no indication of NCs formation, even for implantation temperatures as high as 800 °C. In agreement with TEM observations, no PL signal was obtained in this case.

In Fig. 4(a) and (b) are displayed the results of histograms obtained from TEM analyses corresponding to RT

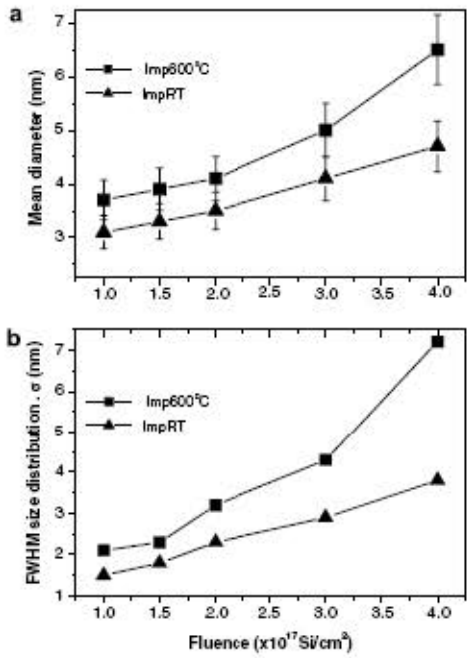

Fig. 4. TEM analyses results for samples implanted at RT (▲) and at 600 °C (■), annealed at 1150 °C. (a) Mean diameter of the Si NCs and (b) size distribution as a function of the implantation fluence. The error bar in (a) is of 10%.

and 600 °C implantations for samples annealed for 1 h. In this figure are represented the mean size diameter and the NCs size distribution as a function of the implantation fluence. It is observed that hot implanted samples present larger nanocrystals with a broader size distribution as compared with those produced by RT implantations.

4. Discussion and conclusions

The results of the present study, performed by Si implantations with the SiO_2 substrate kept at 600 °C, are at variance with was previously published in the literature for RT implantations. For the lowest implantation fluence, we have observed mainly one PL band centered at 780 nm. This feature could be attributed to the low excess Si in the matrix (3.5 at.%). However, for fluences higher than $\Phi = 0.5 \times 10^{17}$ at/cm^2, clearly appears a second PL band, with higher intensity and centered at around 1000 nm which was never observed before. Regarding the behavior of the 780 nm PL band, it was observed that its intensity changes with the implantation fluence, but its position is almost independent of the Si excess concentration. In general, previous works on Si NCs produced by RT Si implantations in SiO_2 matrix have only observed one PL band around 780 nm. The absence of a PL redshift for this band with increasing fluences was reported in [3] in contrast with the results of [10,13], which demonstrate a PL redshift with the fluence. Our results are clearly in agreement with those of [3], since no change in the 780 nm PL position was observed. These contradictory results could be due to non-linear effects in the PL emission produced by the use of high laser excitation power densities on the samples as demonstrated in [16]. Thus, concerning the 780 nm (~1.6 eV) band, its origin can be attributed to radiative states at the Si/SiO_2 interface. This assumption is due to the fact its PL peak position is not affected by changes in the Si NCs size produced by the different hot implanted fluences or annealing times.

The 780 nm PL band behavior can be explained on the following basis. There are in the literature *ab initio* calculations [21,22] indicating that oxygen atoms at the interface Si/SiO_2 can act as charge trapping centers by shrinking the band gap below the Si NCs one. Then, radiative recombination of electrons, holes and excitons could take place in this region. This effect has been shown more pronounced for Si NCs with smaller diameters (<2 nm) [23]. All carriers that could recombine radiatively with emitting energies above 1.6 eV are captured in these centers and their emission appears at the same energy of the interface state. We assume that the PL intensity reduction of this short wavelength band with the implantation fluence starts to occur when the recombination energies of carriers are lower than the energy of the radiative interface state.

Concerning the PL band located at the long wavelength side, the PL peak redshift by increasing the implantation fluence indicates that its origin is related to quantum confinement effects. In fact, by TEM analyses we have observed that the mean size and the dispersion of the Si NCs increase with the implantation fluence as well as the annealing time. Hot implantations create precursors (prenucleation centers) for the nanocrystals allowing them, when submitted at higher temperatures, to nucleate forming, consequently, larger and more dispersed NCs when compared to RT implantations, as illustrated by Fig. 4.

The PL intensity reduction observed for the highest implantation fluence, Fig. 2(a), and for the fluences higher than 1×10^{17} Si/cm^2 after 2 h of annealing time, Fig. 3(a), could be explained by the following argument. The PL cross section for absorption came from the product of the oscillator strength of the transitions and the electronic density of states [24]. This product is a function of the size of the NCs and both terms works in opposite direction as the nanoparticles size changes. Consequently, there is an optimum size for which the emitted PL has a maximum. Then, it is very likely that after certain fluence or annealing time the optimum size of the distribution overcomes and, consequently, the resulting PL intensity decreases. In addition, we cannot disregard the influence of the Si NCs radiative lifetime, which depends on the nanoparticle size and its interface quality. Larger Si NCs having longer radiative lifetimes [24] are also more likely to contain non-radiative recombination centers [14].

Concerning the shift with the annealing time of this PL band, as shown in Fig. 3(b) the only case where it can be observed a clear trend is for the sample implanted at 1×10^{17} Si/cm^2 which shows a significant PL peak redshift with increasing annealing time up to 6 h, followed by saturation. According to quantum confinement effects this behavior is in agreement to the Si NCs growth with the annealing time. However, for the higher fluences the PL peak evolution shows fluctuations without a definite tendency. We can assume that the nanoparticles placed in the center of the matrix , where is the Si highest excess, could rise above a critical size for which there is the possibility for non-assisted phonon transitions. Simultaneously, smaller nanoparticles will grow and will emit at different wavelengths, remaining optically actives. Since the size distribution of the nanoparticles is not uniform (Gaussian), the PL emission spectrum will change its maximum and this behavior could be responsible for the fluctuations in the second PL peak intensity and position after the first hours of annealing for the higher fluences as observed in Fig. 3.

In summary, we have investigated the fluence and annealing time effect on the Si NCs PL produced by hot implantations into SiO_2. Such approach induces the formation of larger Si NCs with broader size distributions as compared to those formed by RT implants. We have shown the PL spectra are composed by two PL bands, which are strongly influenced by the studied parameters. The main conclusion of this work is that while the short wavelength PL band has its origin related to radiative interface states, the longer one is due to recombination via quantum confinement effects.

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