

Absorption cross-sections and lifetimes as a function of size in Si nanocrystals embedded in SiO₂

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Abstract

The photoluminescence (PL) emission yield of Si nanocrystals embedded in SiO₂ depends on their size and on Si–SiO₂ interface passivation. In this work we aim at clarifying the relative importance of both contributions by studying lifetimes and absorption cross-sections as a function of size, for samples with and without passivation in forming gas. We find that while the PL lifetime increases steadily (quasi-linear dependence), the radiative lifetime increases exponentially with the nanocrystal size. Thus, as expected, radiative oscillator strengths are much smaller for large nanocrystals, but this reduction is partially compensated by a less effective quenching at interfacial non-radiative states. The absorption cross-section per nanocrystal rises as the nanocrystal size decreases, for all excitation wavelengths, implying that the variation of oscillator strength dominates over the reduction of the density of states. Passivation processes do not affect the emission mechanism and increase the emission yield while reducing the density of non-radiative recombination centers at the Si–SiO₂ interface (P_b centers).

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PACS: 78.66J; 78.55; 81.65

Keywords: Photoluminescence; Silicon; Nanocrystals; Absorption cross-section; Lifetime

1. Introduction

Structures containing Si nanocrystals embedded in SiO₂ are candidates for optoelectronic and photonic applications due to their intense visible emission at room temperature, high thermal and chemical stability and compatibility with CMOS technology. Extensive investigations have demonstrated strong tunable

photo- and electroluminescence, and even optical amplification [1–5].

The opening of the band gap when the nanocrystal size shrinks is nowadays an unquestionable fact that arises as a consequence of quantum confinement of carriers in the potential well of the nanocrystal. The photon absorption process in a typical photoluminescence (PL) experiment takes place in the core of the nanocrystal, while the PL emission is shifted to the red (Stokes shift) and consists of an intense and wide emission peaking in the near-infrared or visible spectrum. The contribution to the emission due to direct band to band recombination is important depending

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on size [6], but there is a consensus in that the Si–SiO₂ interface plays a dominant role in the emission mechanism. This is so either through interfacial radiative states and/or vibronic interactions of excitons with localized vibrational modes at the interface (Si–O) [7,8].

We clarify in this work the relative importance of both size and passivation on the PL yield by extensively studying lifetimes, either radiative and non-radiative, and absorption cross-sections for different excitation wavelengths. This has been done previously for porous silicon [9] and scarcely for Si nanocrystals embedded in SiO₂ [10]. Radiative oscillator strengths (OSs) are much smaller for large nanocrystals, but this reduction is partially compensated by a less-effective quenching at interfacial non-radiative states. The absorption cross-section per nanocrystal rises as the nanocrystal size decreases and the variation of the OS dominates over the reduction of the density of states. We demonstrate in this work that the passivation by H of the non-radiative interfacial centers (P_b like) is essential to increase the PL emission yield. Furthermore, the passivation process does not interfere with the emission mechanism/s.

2. Experimental details

The samples studied in this work were produced by ion-implantation of Si into thermally grown 800 nm-thick SiO₂. The doses of implantation ranged from 10¹⁷ to 3 × 10¹⁷ ions/cm² (10–30% Si excess at the maximum), while the energy of implantation was kept at 150 keV. At this energy, the projected range of the implantation is situated at a depth of 200 nm. The samples were annealed in a N₂ atmosphere at different temperatures (1100°C, 1150°C and 1200°C) from 4 to 8 h, conditions for which all the Si has precipitated [11].

The experiments include frequency and time resolved PL for measuring lifetimes and absorption cross-sections of Si nanocrystals. The PL spectra were obtained by exciting the samples with either an Ar or a He–Cd laser, in the visible (457, 488 and 514 nm lines) and UV ranges (325 nm). A Ge detector and a GaAs photomultiplier were used as detectors. For the lifetime measurements in the visible range, an acoustic–optic modulator was used to chop the laser

signal, and the photomultiplier was connected to a fast storing digital oscilloscope. The time response of the whole system is of the order of few microseconds.

The size distribution of the nanocrystals has previously been estimated by means of high-resolution transmission electron microscopy (HREM), and the concentration of P_b centers by electron spin resonance (ESR), the details of which can be found elsewhere [11,12].

3. Results and discussion

3.1. Transient behavior

An excited nanocrystal can return to its ground state through either radiative or non-radiative processes. These can, respectively, be described by the corresponding recombination rates 1/τ_{RAD} and 1/τ_{NRAD}. The PL lifetime, τ_{PL}, is given by the inverse of the sum of both contributions. Considering the nanocrystals as a quasi-two-level system, the equation that describes the PL emission in steady state at a given wavelength, λ, is

$$I_{\text{PL}}(\lambda) = N(\lambda) \frac{\tau_{\text{PL}}(\lambda)}{\tau_{\text{RAD}}(\lambda)} \frac{\phi(\lambda_{\text{p}})}{\phi(\lambda_{\text{p}}) + 1/\sigma(\lambda, \lambda_{\text{p}})\tau_{\text{PL}}(\lambda)}, \quad (1)$$

where $N(\lambda)$ is the number of nanocrystals emitting at the wavelength λ, τ_{PL} is the PL lifetime, φ(λ_p) is the pumping flux of photons, and σ(λ, λ_p) is the absorption cross-section of those nanocrystals emitting at λ, for the pump wavelength λ_p. It is well known that the PL of the nanocrystals presents a non-exponential decay that is best fitted by a stretched-exponential function [13]

$$I_{\text{PL}}(t) = I_0 + I_1 \exp \left[- \left(\frac{t - t_0}{\tau_{\text{PL}}} \right)^\beta \right]. \quad (2)$$

The β factor has been related to disorder and energy transfer between nanocrystals [10]. We have used the stretched-exponential equation and observed that by taking β equal to 0.76 it was possible to fit quite well all the spectra, having then comparable results for τ_{PL}. This value for β is very close to that obtained by other authors with similar samples [7].

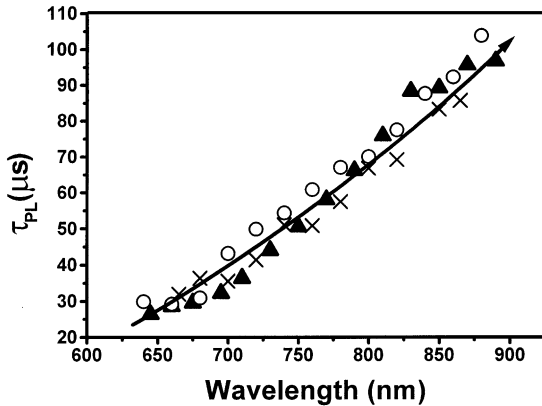


Fig. 1. PL lifetime of the 10% sample, as a function of the emission wavelength, obtained for excitations wavelengths of 457 nm (▲), 488 nm (○) and 514 nm (×).

We have measured the τ_{PL} in two different ways in order to check consistency with the quantum confinement model for the emission. In Fig. 1 we have represented the PL lifetimes at different excitation wavelengths by selecting a very narrow spectral window of detection; τ_{PL} is then plotted as a function of the λ of emission. If we consider that nanocrystals with different sizes would emit at different λ , then this representation is equivalent to giving τ_{PL} as a function of the size of the emitting nanocrystals. This representation is independent of the pumping wavelength and is almost identical for all the samples irrespectively of the average nanocrystal size of the ensemble, being thus a first indication of the validity of assuming a direct relationship between λ of emission and size. We have represented in Fig. 2 the τ_{PL} at the maximum wavelength of emission, as a function of the average nanocrystal size measured by HREM (for samples with Si excess from 10% to 30%). Moreover, we have plotted again in Fig. 2 the best fit of the previous Fig. 1, converting the x -axis from wavelength to average size by using the results of the band gap versus size calculations reported by Lannoo et al. [14]. The agreement of the two sets of results is remarkable, confirming the validity of the quantum confinement theory in this case.

The τ_{PL} increases almost linearly from 50 to 200 μs as the average nanocrystal size increases from 3 to 7 nm and the emission becomes less efficient for large nanocrystal sizes. The radiative lifetime τ_{RAD} cannot

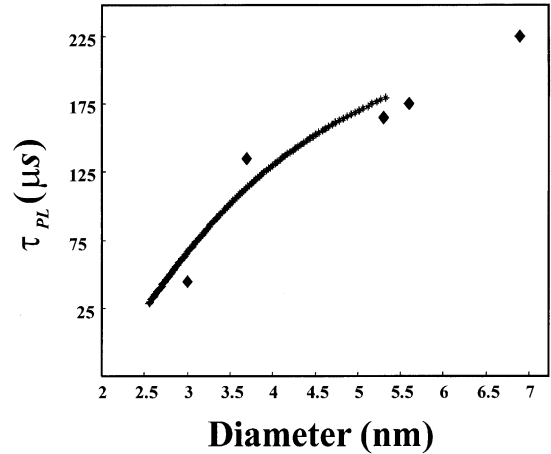


Fig. 2. Evolution of the PL lifetime as a function of the diameter of the nanocrystals. The continuous line is obtained by converting the fit of the results of Fig. 1 to its dependence on the diameter. Scattered points (◆) were measured at the peak of emission of samples with different size distributions.

be extracted by using only the τ_{PL} measurements, since τ_{PL} includes the non-radiative recombination lifetime τ_{NRAD} and its variation is unknown to us. Nevertheless, if we increase the excitation power up to the saturation of PL, Eq. (1) can be written as

$$I_{\text{sat}}(\lambda) = N(\lambda) \frac{\tau_{\text{PL}}(\lambda)}{\tau_{\text{RAD}}(\lambda)}. \quad (3)$$

Then, the evolution of τ_{RAD} versus size can be readily obtained from I_{sat} and τ_{PL} and the results are shown in Fig. 3. The τ_{RAD} increases exponentially as the diameter increases, spanning over more than two orders of magnitude in the measured ranged. This trend agrees remarkably well with the theoretical calculations [15] also represented in Fig. 3. The loss of confinement, and hereby the reinstatement of the momentum conservation rule, translates in a strong decrease of radiative recombinations. It has a similar effect on absorption and further mention of it will be done below.

In order to establish a relationship between the emission yield and the passivation of the Si–SiO₂ interface, some of the samples underwent a post-annealing step at 450°C in forming gas (FG) for up to 2 h. We find that, although there is an important intensity increase with the duration of the anneal, the shape of the PL peak does not change at all [12]. This

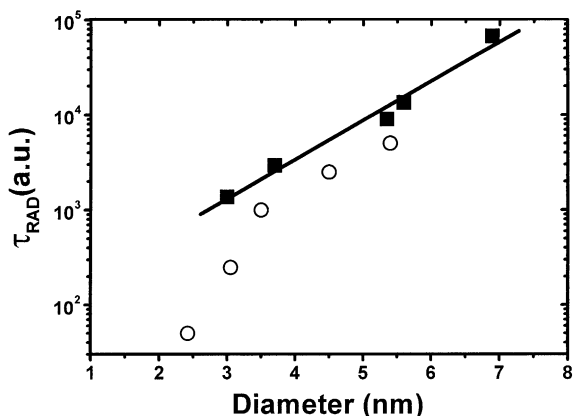


Fig. 3. Radiative lifetime as a function of the nanocrystal diameter, as extracted from our results (■), and as calculated theoretically by Lanoo et al. (○). Our results, which were originally in arbitrary units have been rescaled in order to simplify the comparison of both trends.

means that passivating the interface does not have any direct influence on the mechanisms of absorption and emission. ESR measurements were performed on the same samples to evaluate the decrease in the density of dangling bonds (P_b centers) due to the FG treatment. There is an almost perfect inverse correlation between the PL intensity and the amount of P_b centers at the Si–SiO₂ interfaces, as has been recently reported by us [12].

Regarding the PL lifetime evolution with the annealing in FG, Fig. 4 depicts the most outstanding results. The τ_{PL} increases proportionally to the PL intensity (see inset) and from Eq. (3) it is then clear that τ_{RAD} remains unaffected by the annealing in FG. This is a further confirmation that annealing in FG does not influence the emission process.

3.2. Absorption cross-sections

Since τ_{PL} has already been directly measured, the cross-section and its dependence versus pumping wavelength can be extracted from the fit of the power law of Eq. (1). The fits were done for several samples but the trends are very similar for all of them. The main results are illustrated in Fig. 5. Since we are using relatively low-energy excitations, the smallest nanocrystals are inefficiently excited and this appears under the form of an absorption edge, which is located

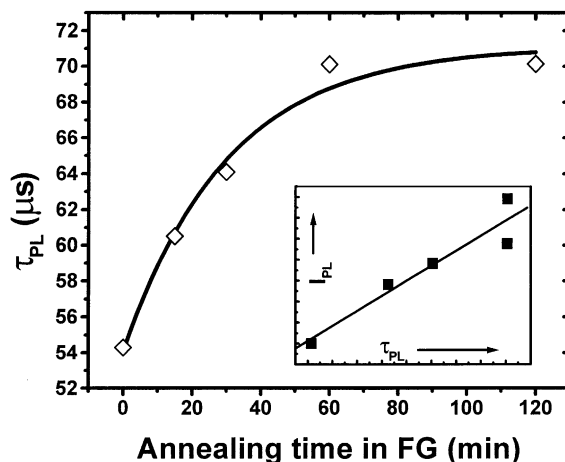


Fig. 4. PL lifetime represented as a function of the duration of the anneal in FG. The inset shows the data plotted as I_{PL} versus τ_{PL} .

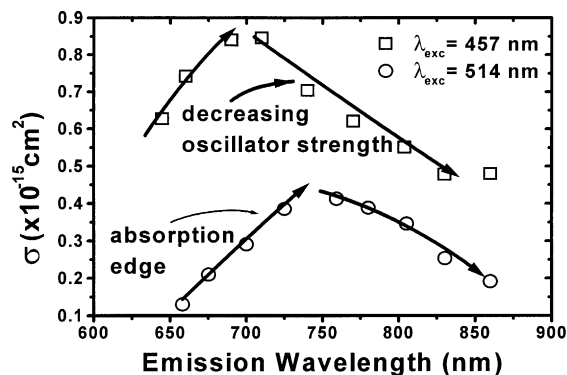


Fig. 5. Absorption cross-section of the 20% sample for two different wavelengths of excitation, 457 and 488 nm.

at different emission wavelengths, i.e. nanocrystal sizes, depending on the excitation wavelength. The absorption process is strongly influenced by the extent of the overlap between the electron and hole wave functions and the density of electronic states available. The cross-section is given by relation [16] $\sigma(E) = g(E)f(E)$, where $g(E)$ is the density of states and $f(E)$ is the OS of the transition. The increase of the overlap that arises from quantum confinement modifies the OS in such a way that the OS can be described as a function of the size by a relation of the type $f(d) = F/d^\gamma$, where some authors take a value for γ between 2 and 6 [3,17]. The increase of the transition probability as the nanocrystals become

smaller is compensated by an equally strong decrease in the number of electronic states available in the structure. These opposite contributions make the absorption cross-section per nanocrystal rather smooth, although the dominant effect in our case seems to be the increase of the OS. Our results differ significantly from those presented by Kovalev et al. [9] for porous silicon. We believe that the differences arise because of the different nature of the samples.

4. Conclusions

The PL lifetime increases linearly while the radiative lifetime increases exponentially with the nanocrystal size. Thus, radiative OSs are much smaller for large nanocrystals, but this reduction is partially compensated by a less-effective quenching at interfacial non-radiative states. The value of the absorption cross-section per nanocrystal varies from 10^{-16} to 10^{-15} cm², for the excitation energies used in this work. It decreases slowly as the diameter of the nanocrystal increases as a consequence of the compensation of OS and density of states variation. The behavior of the lifetime and absorption cross-section as a function of size confirms that both the emission and absorption are modulated by quantum confinement effects. The passivation by H of interfacial centers (P_b like) is essential to increase the PL emission yield and the passivation process does not interfere with the emission mechanism.

Acknowledgements

The authors thank Drs. Manel López and Stephanie Cheylan for their help. We also want to acknowledge

the financial support of the IST-2000-29650 SINERGIA contract.

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