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# Quantum confinement regime in silicon nanocrystals

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ABSTRACT

We study the origin of photoluminescence (PL) in Si nanocrystals embedded in a silicon-rich $SiO_2$ matrix. PL properties as a function of time and temperature were investigated for nanocrystal diameters ($d$) ranging from about 1.5 to 4 nm. All our observations (logarithmic evolution of the timescale as a function of energy, gap associated temperature shift of the PL energy, and logarithmic evolution of size as a function of confinement energy) indicates that PL occurring in small nanocrystals ($d<4$ nm) originates from quantum confinement.



The discovery of visible photoluminescence (PL) from silicon (Si) nanocrystals at room temperature [1] has attracted much attention within the scientific community due to its potential applications in Si-based light-emitting devices. This low-dimensional effect [2–4] in silicon has stimulated extensive research and development of silicon nanostructured materials, such as porous silicon [5], Si nanoparticles [6], Si nanocrystals embedded in Si oxide [1], and $Si/SiO_2$ superlattices [7]. Although the impetus for this research emerged from predictions of quantum confinement effects in indirect gap semiconductors, PL emitted by Si nanocrystals was also found to originate from other mechanisms, such as for example interface states [8,9], luminescent defect states [10] and oxygen vacancy states at the $Si/SiO_2$ interface [11]. Despite the large number of investigations devoted to understand the origin of PL in Si nanocrystal systems, neither experimental nor theoretical studies have clearly demonstrated the dominance of one of these particular processes in observed PL spectra.

However, two mechanisms of radiative recombination in Si nanocrystal systems are known to dominate in PL emission. After the creation of the exciton inside the nanocrystal, radiative recombination can occur either in the nanocrystal (quantum confinement) or outside at an interface state. The relative contribution of each mechanism is not known [8,12,13] and their respective efficiency as a function of nanocrystal size is poorly understood. In this context, the aim of this paper is to experimentally investigate the PL of Si nanocrystals in order to understand the importance of different radiative recombination mechanisms as a function of nanocrystal size.

Among the various Si nanostructured systems, silicon nanocrystals embedded in a Si oxide matrix is considered one of the most promising as it provides excellent control over nanocrystal size, distribution and density. Numerous methods can be employed to fabricate Si nanocrystals [14–18]. In this work, pulsed laser deposition (PLD) was chosen to further investigate the findings reported previously [15]. To understand the nature of the mechanisms governing the PL spectra, we studied the temperature dependence of the PL peak position. Time-resolved PL spectroscopy was used to determine the carrier lifetime as a function of emission energy. Our results indicate that for nanocrystals ranging from 1.5 to 4 nm in diameter, quantum confinement prevails over all other recombination mechanisms in the Si nanocrystal system.

Silicon nanocrystals (Si-nc) have been synthesized using the experimental procedure described in Ref. [14]. Four samples labeled A–D have been characterized by X-ray diffraction (XRD) and high resolution transmission electronic microscopy (HRTEM) to determine the average size of Si nanocrystals embedded in the Si oxide matrix [19]. The mean sizes of the Si-nc were found to be 4, 2.5, 2, and 1.5 nm, respectively. The PL spectra of samples were measured at room temperature. The temperature dependence of the PL spectra between 77 and 300 K was measured using a 488 nm argon laser with samples cooled by liquid nitrogen flow. The time-resolved PL is measured by exciting the sample with a 30 μs pulse at 405 nm and a power of 50 mW. The emission energy ranging from 1.2 to 1.9 eV is selected by an optical filter and the data are collected by a photomultiplier/amplifier system with a time resolution of 1 μs.

It is generally agreed that the complex mechanism occurring in the recombination of the electron–hole pair gives rise to non-exponential decays. It was first suggested that the mechanism of

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"exciton hopping" combined with a nanocrystal size distribution in the sample explained this non-exponential decay. Alternatively, Delerue et al. proposed that the non-exponential nature of the decay could be an inherent character of quantum confined indirect gap nanostructures [20] and recently, blinking phenomena have been invoked [21]. Nevertheless, without any assumptions on what affects the expected exponential behavior, one can evaluate the general decay timescale by using the stretched exponential empirical law [22,23]

$$I(t) = I_0 e^{-(t/\tau)^{\beta}} \quad (1)$$

where $I_0$ is the initial intensity, $\tau$ the carrier lifetime and $\beta$ the non-exponential parameter. All our experimental data have been very well fitted with this equation. The corresponding rates $k = 1/\tau$ are plotted in Fig. 1 together with the $\beta$ parameter as a function of emission energy for our four characterized samples. In the energy range considered here, $\beta$ remains constant indicating that $\tau$ provides a good indication of the PL decay timescale. A first observation is that the energy dependence of the decay time ($\tau$) is the same for all samples, consistently to previous findings [24]. More interestingly, these measurements clearly indicate a logarithmic energy dependence of $k$ with a characteristic energy $E_0 = 0.3 \pm 0.02$ eV, remarkably consistent with the theoretical calculations of Delerue et al. based on the quantum confinement model ($k(E) \propto e^{E/E_0}, E_0 = 0.31$ eV) [20].

To investigate the nature of carrier recombination in Si nanocrystals embedded in Si oxide matrix, we performed a study of the PL spectra as a function of temperature for samples A–D. As previously mentioned, recombination of exciton can occur via two main mechanisms. Recombination at interface states does not incur a shift of the PL peak as a function of sample temperature, while quantum confinement will produce a shift via electron–phonon interaction [25]. Fig. 2a shows the evolution of the PL peak position for samples A–D as a function of temperature in the range 70–300 K. For all samples, the PL peak position shows a red shift with increasing temperature. This behavior is consistent with the shrinkage of the energy gap of silicon induced by electron–phonon interaction. In this case, the dependence of carrier recombination energy as a function of temperature can be

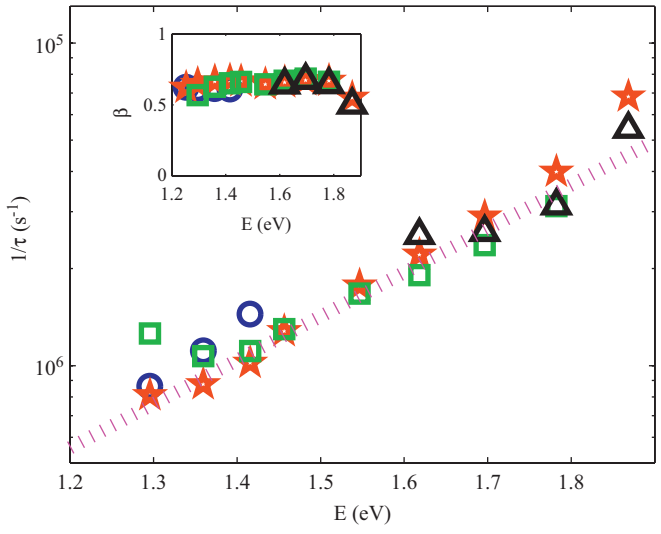


**Fig. 1.** Recombination rate of the PL mechanism for four characterized samples of different mean size diameter: A: 4 nm (triangles), B: 2.5 nm (squares), C: 2 nm (stars) and D: 1.5 nm (circles). The dotted line represent a linear fit corresponding to $1/\tau(E) \propto e^{E/E_0}$ with $E_0 = 0.3$ eV [20].

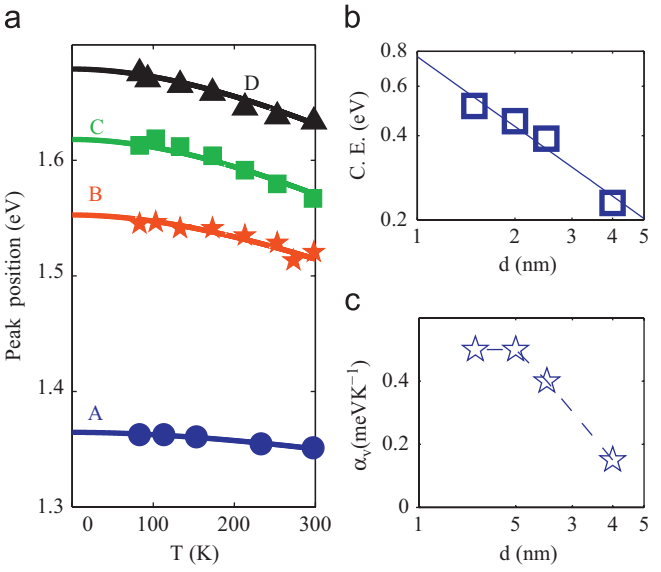


**Fig. 2.** (a) Temperature dependence of the PL peak position for samples A (circles), B (stars), C (squares) and D (triangles). The continuous lines are fit of the data according to Eq. (2). (b) Size dependence of the confinement energy ($E_c$) at room temperature for samples A–D on a logarithmic scale; the continuous line represents a linear fit with a slope equal to −0.6. (c) Evolution of the fit parameter $\alpha_v$ as a function of average nanocrystal size.

described using the Varshnis ad hoc equation [26]

$$E_{gap}(T) = E_0 - \frac{\alpha_v T^2}{\theta_D + T} \quad (2)$$

where $E_0$ is the peak position energy at $T = 0$ K, $\theta_D$ the Debye temperature of the material ($\theta_D = 645$ K) and $\alpha_v$ a parameter related to the material. The experimental data shown in Fig. 2a, have been fitted using Eq. (2). The gap, $E_0$, was found to be equal to 1.36, 1.56, 1.62 and 1.68 eV for samples A–D, respectively. The values of $\alpha_v$ are reported in Fig. 2c. The order of magnitude of about 1 meV is in good agreement with data previously reported in the literature [27]. The good fit of the experimental data with this law indicates that the mechanism governing the carrier recombination in Si nanocrystals is related to the quantum confinement effect.

One can more accurately describe the quantum confinement in terms of confinement energy ($E_c$) which is defined as the energy shift between the nanocrystal gap and the gap of bulk silicon (1.12 eV). Fig. 2b presents the confinement energy, at 300 K, as a function of nanocrystal size on a logarithmic scale. According to theoretical calculations [28], $E_c$ is expected to follow a power law as a function of nanocrystal size. The slope of the curve in Fig. 2b is −0.8, which is in fair agreement with the theoretically predicted value of −0.6 [28] and previously reported experimental data [29,30].

Interestingly, the coefficient $\alpha_v$ varies with nanocrystal size (see Fig. 2c). For small nanocrystals (samples C, D), the value of $\alpha_v$ is equal to 0.5 meV K$^{-1}$. At 2.5 nm, this value gradually decreases, reaching 0.2 meV K$^{-1}$ for a nanocrystal diameter of 4 nm. This observation corroborates the theoretical work of Franceschetti [31] which predicts a stronger temperature dependence for smaller nanocrystals.

A recent study of Si-nc PL which invokes the blinking phenomena [21] to explain the non-exponential decay gives interesting new insight on this matter by noting a change of regime between a low energy regime ($E < 1.5$ eV) where the blinking exponent $\alpha$ is constant ($\alpha = \frac{3}{2}$) and a high energy regime ($E > 1.5$ eV) where $\alpha > \frac{3}{2}$. As discussed in Ref. [32], the ideal value $\alpha = \frac{3}{2}$ corresponds to the assumption of exchange between

trapped states in the low energy regime. In the high energy regime, the blinking phenomena might be controlled by the excursion to only one trapped state. In this case, the dynamics is mainly controlled by the backward tunneling rate from the trapped state to the nanocrystal, increasing the value of $\alpha$ towards 2 [33].

In this study, the variation of $\alpha_v$ (Fig. 2c), observed to change regimes with increasing nc size, might be related to the similar change of confinement strength with nc size. When the nc size becomes larger, tunneling to trapped states might be possible and more likely as energy decreases. This is consistent with previous observations [8] and theoretical work [13] which identified a recombination mechanism via the so called interface states. We demonstrated here that this regime might take over but at lower energy and nc bigger than 4 nm (i.e. lower confinement energy).

In conclusion, we presented diverse experimental evidences (logarithmic evolution of the timescale as a function of energy, gap associated PL, and logarithmic evolution of size as a function of confinement energy) which converge towards the signature of the quantum confinement effect in the Si-nc embedded in Si oxide. Finally, here we establish a quantitative range of sizes going from 1.5 to 4 nm where quantum confinement is confirmed to be the main mechanism of PL in silicon quantum nanocrystals.

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