



# Ultrafast time-resolved spectroscopy of Si nanocrystals embedded in SiO<sub>2</sub> matrix

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## ABSTRACT

In this work, we present a comprehensive study of ultrafast transient photoinduced absorption of silicon nanocrystals (NCs) embedded in SiO<sub>2</sub> matrix. The samples under investigation are single monolayers of Si-NCs embedded in SiO<sub>2</sub>. Our investigation gives an important insight of carrier relaxation channels of NCs in the picosecond to femtosecond time scale. Our analysis is based on theoretical predictions, where the coupling between the oxygen-related states and the quantized sublevels plays a crucial role to the relaxation of the confined excitons. We have time-resolved ultrafast relaxation paths of this material and we have compared our observations with recently published results. Finally, we have extracted information about the insertion of modified surface states within the gap that results in an observable pinning of the gap for NC sizes in the strong confinement regime. This study has important implications in the understanding of fundamental optical properties for the studied nanosystem.

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## 1. Introduction

Optical properties of semiconductor quantum structures with reduced dimensions have been the subject of many experimental and theoretical studies. Nowadays, silicon nanocrystals (Si-NCs) embedded in a silicon dioxide (SiO<sub>2</sub>) matrix appear to be very promising material for nanoelectronics and photonics [1–3]. Their properties are strongly related to their size and surface passivation. It has been previously shown that for NCs with diameter  $d < 5$  nm the band gap opens due to quantum confinement effect which pushes the photoluminescence (PL) in the visible region [4]. In hydrogen-passivated Si-NCs, PL is tunable down to the UV spectral region. However, in the case of oxidized NCs, PL tunability follows size tunability only down to NCs sizes of  $d \sim 2.5$  nm. In smaller NCs, an important pinning of the gap, attributed to localized states at the interface of Si-NCs with the surrounding SiO<sub>2</sub> amorphous matrix, blocks further PL blue shift [5–7].

In this paper, the mechanism that leads to the pinning of the gap in the strong confinement region of NCs has been studied in detail using ultrashort laser technology. The available technology of femtosecond lasers source has led to an enormous progress, in understanding the basic carrier relaxation mechanisms in nanostructures [8]. The time-resolved dynamic behaviour of photoinduced absorption following ultrashort optical excitation reveals fundamental information about the initial relaxation mech-

anisms/channels of carriers, contributing in the understanding of the optical properties of these structures.

## 2. Experimental

In this work, ultrashort carrier dynamics are used to investigate transient photoinduced absorption (TPA) in single monolayers of Si-NCs embedded in amorphous SiO<sub>2</sub>. The NCs-containing amorphous SiO<sub>2</sub> layer is in the form of a thin film on a transparent quartz substrate. The fabrication technique is based on low-pressure chemical vapour deposition (LPCVD) of amorphous silicon, followed by solid-phase crystallization and high temperature thermal oxidation. Sample fabrication has been described in more detail elsewhere [9]. With the fabrication technique used, NCs size in the  $z$ -direction is controlled with accuracy, while in the  $x$ - $y$  direction this size is slightly larger. Two different samples with different NCs size (2.5 and 4 nm in the  $z$ -direction respectively) were investigated. The size and density of NCs was verified by transmission electron microscopy (TEM) measurements [9]. The density of NCs in the two-dimensional NCs monolayers is of the order of  $10^{12}$  NCs/cm<sup>2</sup>. Because of the discrete energy spectrum resulting from three-dimensional (3D) confinement, the carrier energy relaxation dynamics in NCs should be significantly different from those in systems with continuous energy spectrum. Optical absorption and PL measurements at room temperature have been performed in our samples at the beginning of this work in order to investigate the existence of oxygen-related states, as well as the quantized sublevels originated by the quantum confinement of NCs.

The utilized experimental technique is a non-collinear degenerated pump probe configuration in conjunction with a regenerative Ti:Sapphire amplifier system with 100 fs pulses at 800 nm. This system amplifies the pulses to approximately 1 mJ at a repetition rate of 1 kHz. The temporal resolution of our experimental setup over the entire probing wavelength range has been measured to be better than 150 fs [10]. The temporal variation in the optical absorption was monitored as a change in the reflectivity and transmission, which was a direct measure of the photo-excited carrier dynamics within the probing region. In this work optical pumping at a fluence of 2 mJ/cm<sup>2</sup>, which corresponds to an absorption fluence of 100  $\mu$ J/cm<sup>2</sup>, was used to excite the NCs samples and determine their temporal behavior.

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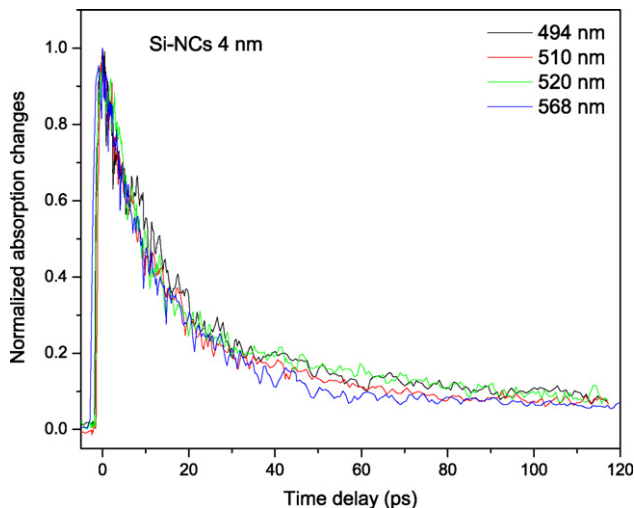


Fig. 1. Ultrafast degenerated TPA measurements from 4 nm Si-NCs at various probing wavelengths.

### 3. Results

In Fig. 1, we present the experimental data of normalized TPA for the larger Si-NCs (4 nm) embedded in SiO<sub>2</sub> matrix following degenerated pump-probe configuration at various wavelengths. In all measurements we observed an initial fast rise of the induced absorption followed by a single exponential decay which corresponds to 11 ps. This decay time is the same for all wavelengths used in this work up to 568 nm. This gives us an important insight of the relaxation mechanism of the carriers within the band structure of this material, as it will be explained below. Here, we should point out that in all measurements state filling effects [11] are negligible compared with the efficient coupling between the oxygen-related states. By increasing the wavelength, the rise time of our measurements changed between 1.8 and 1.4 ps.

In Fig. 2, we present the experimental data of normalized TPA for Si-NCs with an average size of 2.5 nm following degenerate pump-probe measurements at different wavelengths. As in the case of larger Si-NCs, the TPA presents a positive rise followed by a faster exponential recovery of 3 ps. The relaxation time in smaller NCs is

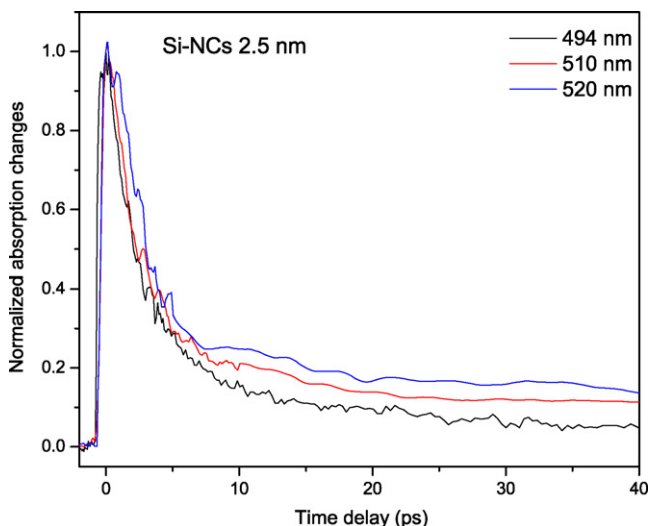


Fig. 2. Ultrafast degenerated TPA measurements from 2.5 nm Si-NCs at various probing wavelengths.

strongly related with the present of higher density of surface states in the strong confinement regime of NCs. With increasing the wavelength the relaxation time also increases. The rise time in this case is faster (between 0.8 and 0.57 ps, as increasing the wavelength) compared with that of larger Si-NCs and this is attributed to the increased surface to volume ratio in the smaller NCs leading to an enhanced coupling.

### 4. Discussion and summary

To further investigate the optical properties of our samples, we found the longer wavelength at which each sample absorbs. The results are presented in Fig. 3 with open circles. In order to verify the agreement of our results with the quantum confinement model [12–14], we plotted the theoretical curve of this model with the red line in Fig. 3. The results indicate that for Si-NCs of 4 nm the experimental energy gap from our measurements agrees well with the predicted value of quantum confinement model, whereas for Si-NCs of 2.5 nm we observe a diversion from the model. Similar results were obtained for 4 nm Si-NCs using spectroscopic ellipsometry [15] (open square in Fig. 3). The extracted gap in that work was 1.74 eV which is very close to the current value. The diversion in smaller energies is due to the coupling of quantized levels with the surface vibronic states [16]. It should be noted that this is the first time in the literature that the method of TPA is used to estimate the absorption band edge of Si-NCs. As shown from our results, the experimental method indicates a pinning of the gap in small NCs. This pinning of the gap has been theoretically predicted from Monte-Carlo simulations [17] and has been experimentally confirmed also by PL measurements [18–20] in porous passivated by oxygen (star symbols, in Fig. 3) and five NCs/SiO<sub>2</sub> bilayers (solid square, in Fig. 3). It is believed that the NCs surrounding environment causes defect states in the surface of Si-NCs or shape distortions [21,22] of NCs. In the smaller NCs, the ratio of surface to volume states is more pronounced than in the larger ones. Shape distortions are also more pronounced in smaller NCs.

As mentioned above, in both 4 and 2.5 nm NCs the maximum absorption is followed by a single exponential decay towards equilibrium for all probing energies under investigation. The time

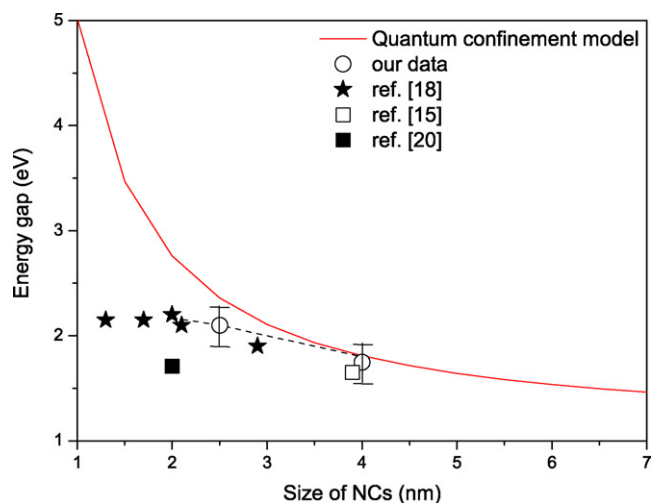


Fig. 3. Energy gaps of 2.5 and 4 nm Si-NCs embedded in SiO<sub>2</sub> matrix. The red line represent the quantum confinement model [12] whereas the dashed line shows the deviation of our data from this model due to the coupling of quantized levels with the surface vibronic states. The star symbols represent the experimental data measured by PL [18] in porous silicon passivated by oxygen, the open square represents the ellipsometric extracted value [15] and the solid square represents the measured by PL [20] in five NCs/SiO<sub>2</sub> bilayers.

constants of these mechanisms are respectively 11 and 3 ps for 4 and 2.5 nm NCs sizes. It is clearly evident that there is only one relaxation mechanism/channel for the photoexcited carriers in each case, which is independent of the probing energy. It is suggested that this relaxation channel corresponds to the relaxation of quantized electronic sublevels related to NCs in the case of 4 nm NCs while it involves interface states between NCs and SiO<sub>2</sub> in the case of the 2.5 nm NCs. Previous TPA measurements in 3.1 eV pump energy [23] showed double exponential relaxation depicting the co-existence of both two relaxation channels for the photogenerated carriers. In the present measurements we separated these two mechanisms by changing the probing wavelength. We thus showed that in samples with larger Si-NCs the lower energy state in the conduction band is a quantized sublevel depicted by the quantum confinement model, while in samples with smaller Si-NCs, the relaxation time obtained from previous measurements in the same set of samples [23], suggests that the lower energy states in the conduction band for this material are strongly related with states at the interface of NCs with SiO<sub>2</sub>. This is in agreement with theoretical band gap calculations [21] and other experimental results [22]. Furthermore, we should point out that the fact that the time constants are independent of the probing wavelengths in larger NCs helps us to understand that with all wavelengths we probe the corresponding particular quantized energy state, while this is not the case in smaller nanocrystals. Our study supports the general result in the literature [18,19] of a red shift of the PL in the case of small Si-NCs ( $d < 2.5$  nm), compared to values predicted by the quantum confinement model. This red shift comes from the coupling between quantized levels and interface states between NCs and SiO<sub>2</sub>. PL does not related to free exciton recombination, but it also involves localized levels in the band gap due to surface states.

## 5. Conclusions

In conclusion, we have studied TPA in single monolayers of oxidized Si-NCs embedded in amorphous SiO<sub>2</sub> matrix with two different NC sizes. From our experimental results we have observed one relaxation mechanism for the photogenerated carriers at the first few picoseconds before radiative recombination for both sizes of NCs. For the larger Si-NCs sample under investigation in this work (4 nm), we probe a slow relaxation process (11 ps) which may be attributed to the formed quantized levels due to the quantum confinement in these small nanoclusters. On the other hand, in smaller Si-NCs sample, a faster relaxation mechanism is observed which corresponds to the internal relaxation in surface states. Further-

more, we have found that in 4 nm Si-NCs sample the energy band gap agrees well with the predicted value of quantum confinement model, whereas in the case of the 2.5 nm Si-NCs sample we have observed a diversion from the model. This is attributed to the pinning of the gap due to states at the interface between NCs and SiO<sub>2</sub>, located within the gap of the NCs creating an effective band gap smaller than that of hydrogen-passivated NCs.

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