

Time-Resolved Gain Dynamics in Silicon Nanocrystals

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ABSTRACT

Time-resolved variable stripe length (VSL) experiments on a set of silicon nanocrystal waveguides obtained by plasma enhanced chemical vapor deposition (PECVD) have revealed a fast recombination dynamics (20 ns) related to population inversion under 6 ns optical pumping at 355 nm. Modal gain values about 10 cm^{-1} have been measured at 760 nm by VSL technique for the fast recombination component while optical losses about 15 cm^{-1} are measured for the integrated signal in the slow (lifetime of about 10 μs) recombination tail. Threshold behavior in the emission intensity together with a pumping length and pumping power dependence of both the intensity and the time duration of the fast recombination component has been observed. These results are explained within an effective four level model to describe the strong competition among different Auger processes and stimulated emission.

INTRODUCTION

One of the main future challenges for silicon microphotronics consists in the demonstration of a laser action in Si-based materials. Following the initial observations of optical gain in silicon nanocrystals (Si-nc) prepared by ion-implantation [1], other works have recently demonstrated the presence of stimulated emission in Si-nc [2,3,4]. As in other quantum dot based systems [5,6] Si-nc present a severe competition with efficient non-radiative processes, mainly non-radiative Auger processes, yielding a very fast dynamics in the optical gain. Although a clear understanding of the microscopic gain mechanism is still under debate, it has been suggested that interface radiative states associated with oxygen atoms can play a crucial role in determining the emission properties of Si-nc systems [7,8]. Here we report on light amplification dynamic studies in Si-nc and discuss a possible phenomenological gain model.

We studied Si-nc samples produced by high temperature annealing of substoichiometric silicon oxide (SiO_x) thin films grown by plasma enhanced chemical vapor deposition (PECVD). The structural and luminescence properties of such systems have been fully discussed in Ref. [9]. We focus on two different samples characterized by different total Si content: 42 at. % (named 3A, Si-nc mean radius 1.7 nm) and 39 at. % (named 5A, Si-nc mean radius 1.5 nm) both annealed at 1250 °C for one hour in nitrogen atmosphere. The oxide layer containing Si-nc was 250 nm thick and was embedded between two 100 nm thick stoichiometric SiO_2 layers to form a waveguide. Planar waveguides were formed on a transparent quartz substrate and had an optical confinement factor of 0.74 and 0.62 for samples 3A and 5A, respectively.

EXPERIMENTAL RESULTS

Time-resolved experiments were performed in the one-dimensional amplifier configuration (pumping through the surface and collection of the guided light from one edge of the sample as a function of the pumping length) [10]. High fluence (J_p) short optical pulses (6 ns, 10 Hz, 355 nm) produced by the third harmonic of Nd-YAG pulsed laser were used to excite the samples. Care has been used to keep the fluence lower than the sample damage threshold. A single grating spectrometer and a visible streak camera have been used to detect the time resolved signal. Edge emission was collected by a 20x optical microscope objective with a numerical aperture of 0.3, larger than the output numerical aperture of the waveguide sample.

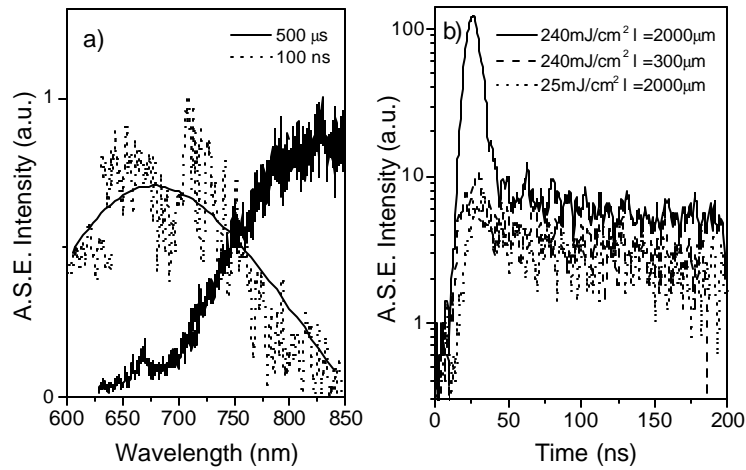


Figure 1. (a) Amplified spontaneous emission (A.S.E.) lineshapes measured with the 500 μs time window (black line) and with the 100 ns time window (dotted line) at the pump fluence of 200 mJ/cm^2 . The stripe length ℓ was 2000 μm . (b) Time resolved A.S.E. decay measured as a function of pump fluence and pump length under variable stripe length configuration. Detection wavelength was 750 nm.

Figure 1a shows the time resolved ASE spectra at two observation time scales. For long integration times (500 μs) the usual broad emission lineshape centered around 900 nm is measured. This emission has similar spectral feature as the usual luminescence from Si-nc. On the contrary, when the first 100 ns are considered, a fast recombination component appears in the decay dynamics (figure 1b) and the spectral shape of the ASE signal appears strongly blue shifted, as shown in figure 1a (dotted line). The fast component disappears when either the excitation length ℓ is decreased at a fixed J_p or when J_p is decreased for a fixed ℓ . These observations rule out the non-radiative Auger processes as the origin of the observed fast component, since the J_p intensity does not depend on ℓ , whereas the fast recombination peaks are critically dependent on the pumping length, keeping fixed the excitation conditions.

The spectral dependence of the fast and slow component (figure 1a) demonstrates a strong blue-shift of the Si-nc light emission in the early nanoseconds after the pulse excitation. The comparison with the continuous wavelength VSL measurements [10] shows that the fast component has a spectral shape similar to the ASE band measured for long ℓ (where strong amplifica-

tion is expected), while the slow component spectrally overlaps the luminescence measured for short ℓ (where negligible amplification occurs). To our opinion these are evidences of presence of the stimulated emission lifetime in Si-nc. The peak intensity of the fast component in sample 3A shows a super linear increase vs ℓ for high J_p , which can be fitted with the usual one-dimensional amplifier equation yielding a net optical gain of $12 \pm 3 \text{ cm}^{-1}$ at 760 nm (figure 2a). Modal gain values ranging between 8 cm^{-1} and 20 cm^{-1} are measured depending on the detection wavelength. When the same fit is performed on the slow emission component, optical losses in the range $10\text{-}30 \text{ cm}^{-1}$ can be extracted.

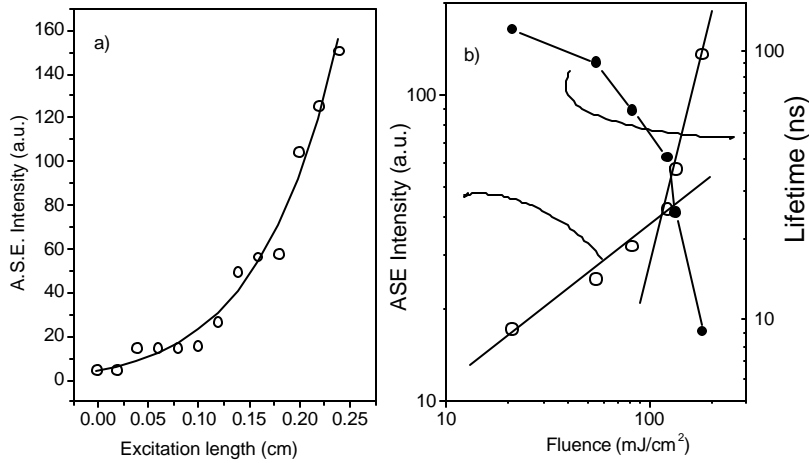


Figure 2. Sample 3A (42 at. % annealed at 1250 °C): a) amplified spontaneous emission intensity versus excitation length at 760nm. Pump fluence of 200 mJ/cm² ; b) ASE intensity (open circles) of the fast emission peak versus pump fluence, (black circles) fast luminescence lifetime versus pump fluence. The lifetime has been extracted from the experimental decays as the 1/e intensity time. Excitation length was 2 mm.

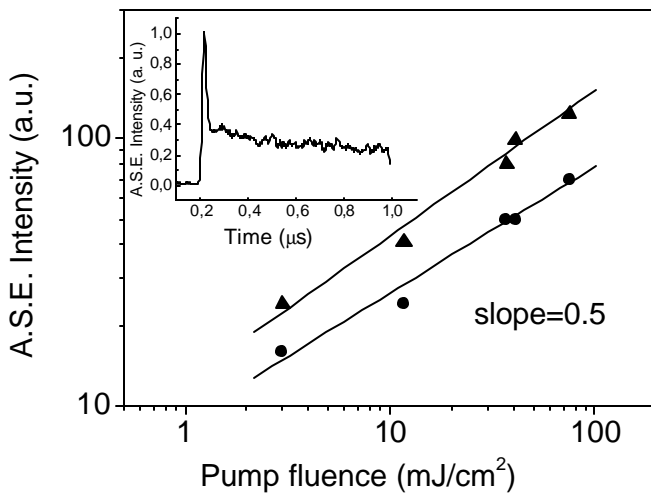


Figure 3. Amplified spontaneous emission intensity versus pump fluence ($\ell=2 \text{ mm}$) for sample 5A (39 at. % annealed at 1250 °C) for two different detection wavelengths: $\lambda=730\text{nm}$ (circles),

$\lambda=830\text{nm}$ (triangles). The inset shows the time resolved luminescence decay at 730 nm where the fast component appears in the sub-linear emission regime.

The fast component peak intensity of sample 3A shows a threshold behavior vs J_p : at low J_p the emission is sub linear to a power 0.5, suggesting a strong Auger limited regime [11]; while for higher J_p , population inversion is achieved and a super linear increase to a power ≈ 3 is measured, suggesting the onset of the stimulated regime (figure 2b). Moreover, the lifetime of the fast component significantly shortens when the stimulated regime is entered. The emission threshold therefore separates two different regimes (Auger limited and stimulated emission) where more likely two distinct physical recombination mechanisms are present: either two different recombination centers in the same Si-nc (defect centers and quantum confined excitons) or two different emission centers in the system (distinct Si-nc populations, SiO_2 defects pumped efficiently through the smallest Si-nc). The presence of different recombination mechanisms in our samples is also evidenced by the clear difference in the spectral lineshape of the fast and slow emission components. However, for sample 5A (figure 3) the fast recombination dynamic without threshold behavior vs J_p can be explained by the Auger mechanisms [11,12].

RATE EQUATION MODEL

Although a full theoretical model of the stimulated emission processes in Si-nc is still lacking, a rather simplified phenomenological approach is possible. We propose a four-level rate equation model to explain the fast recombination component with the power threshold behavior observed in our time resolved VSL measurements [10]. We can suggest a possible nature for these four levels. From x-ray absorption studies and ab-initio calculations [13], strong evidences emerge that a transition region between Si-nc and SiO_2 exists, and it consists of a shell of stressed silica on Si-nc. One can speculate that this stressed SiO_2 shell enhances the formation of interface oxygen-related states (silanone?) on the surface of Si-nc or decreases the non-radiative Auger rate because of the resulting smoothing of the potential barriers. Within this scheme levels 1 and 4 (inset in figure 4) of the rate equations are associated with pure Si-nc states while levels 2 and 3 to the ground and excited silanone states. Based on this scheme, a four level rate equations model can be set for photons and carriers, which includes both amplified spontaneous emission and Auger recombination [10]. In particular, we assume that levels 2-4 are empty before the excitation occurs. Once the pumping starts, levels begin to be populated and two different Auger non-radiative recombination processes can in principle take place. The first mechanism (Auger 1) involves two electrons in the same level 3, and therefore the rate of such a process depends quadratically through a coefficient C_{A1} on the level population N_3 . Another Auger mechanism (Auger 2) is proportional, through a coefficient C_{A2} , to the product of the population of the emitting level 3 (N_3) and the holes concentration in the valence band edge (N_h). N_h equals the total concentration of electrons in the various excited levels that is $N_h = N_2 + N_3 + N_4$. Within the four level scheme we are proposing, the relaxation times of electrons from levels 4 and level 2 are so fast that N_4 and N_2 are always almost empty: $N_h \gg N_3$.

The effect of pumping on the recombination dynamics is illustrated in figure 4 (top plot) where the normalized number of emitted photons is simulated by solving the set of rate equations as a function of the pumping rate, and by neglecting for simplicity the Auger coefficients. The set of parameters used is a reasonable one, while no systematic attempt has been made to fit existing data to derive the parameters. A fast recombination component builds up as the pumping

rate becomes high enough to create population inversion. A more realistic comparison among the measured luminescence decays and the numerical simulations is reported in figure 4 (bottom plot), where also the contribution of the Auger recombination has been included in the simulations. At this stage of the development of our model no comparison with TR-VSL data is possible. Good qualitative agreements are observed for a reasonable set of simulation parameters. Note that such agreement cannot be reached when stimulated emission is turned off, unless the Auger contribution is set extremely large. Within the four level recombination model it turned out that an emission (gain) cross section of the order of 10^{-17} cm^2 is large enough to compensate for Auger processes with typical lifetime as fast as 2-10 ns.

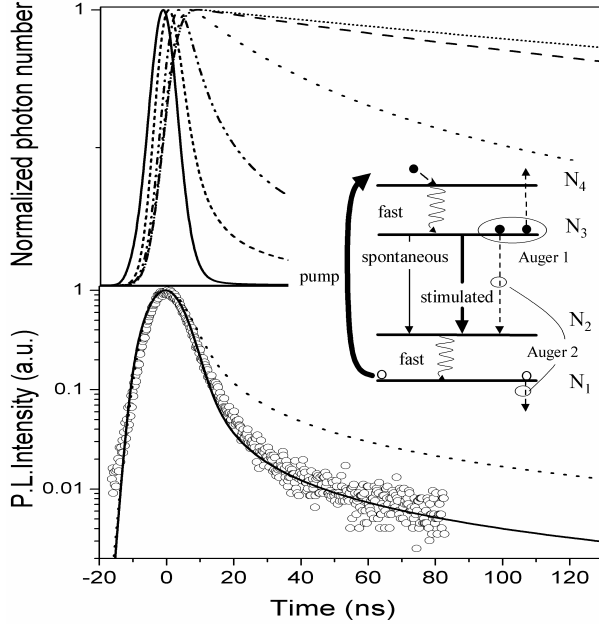


Figure 4. (Top) Simulations of the normalised PL intensity as a function of the incident photon flux ϕ_p . The peak of the incident photon flux ϕ_p was varied between 10^{16} and 10^{24} photons $\text{s}^{-1}\text{cm}^{-2}$. The main parameters used in the simulation were the pump absorption cross section $\sigma_p=10^{-14}\text{cm}^2$, the emission cross section $\sigma=10^{-17}\text{cm}^2$, the active centers concentration $N=8\times 10^{18}\text{cm}^{-3}$, the spontaneous emission factor $\beta=4.5\times 10^{-4}$, the optical losses $\alpha=25\text{cm}^{-1}$. No Auger recombination has been considered here. (Bottom) PL decay (open circles) of Si-nc produced by PECVD deposition of a 46% at. of Si annealed at 1250° for 1h. The solid line is a simulation obtained with the same parameters as in the top panel plus an effective Auger coefficient $C_A=10\times 10^{-10}\text{cm}^3\text{s}^{-1}$ (peak Auger lifetime of 3ns) and a pump photon flux of 5×10^{22} photons $\text{s}^{-1}\text{cm}^{-2}$. The dashed line is a simulation where no stimulated emission was present, only Auger recombination. In this case an Auger coefficient of $C_A=2\times 10^{-8}\text{cm}^3\text{s}^{-1}$ (peak Auger lifetime of 90 ps) is needed.

It is possible to observe optical gain whenever the stimulated emission rate is greater than the Auger recombination rate. It is possible to define a stimulated emission lifetime and an equivalent Auger recombination time as follows:

$$t_{se} = \frac{1}{Bn_{ph}} = \frac{4}{3} p R_{nc}^3 \frac{1}{\alpha S c n_{ph}} \quad t_A = \frac{1}{2C_A N_3} \quad (1)$$

where we have introduced the Si-nc volume fraction ξ and where the relation, $B = \frac{S c}{V}$, valid under the assumption of monochromatic incident light, is used. It is worth noticing the inverse dependence of τ_{se} on ξ and on σ , as discussed in Ref [6]. It is clear that to observe optical gain $1/\tau_{se} \geq 1/\tau_A$. This poses a condition on the volume fraction.

Fast recombination dynamics in the range of some ns are typical of Auger non-radiative processes in porous silicon [11,12], and the fast dynamics of its own is not enough to claim for optical amplification. A strong competition between Auger fast processes and stimulated emission is present in Si-nc. For some samples Auger can prevail. In fact, sample 5A shows a fast recombination dynamics in the ns range (figure 3), but unlike the amplifying sample 3A, no exponential VSL lineshape, nor intensity threshold, have been measured. On the contrary to sample 3A, negative gain of the order of -5cm^{-1} has been found at the maximum pumping fluence. The loss behavior of sample 5A can be explained by the low refractive index of its light guiding layer ($n=1.66$ instead of $n=1.82$ of sample 3A), which suggests a low modal confinement, yielding too high optical losses that overcome the modal gain.

CONCLUSIONS

Optical gain dynamics has been studied in Si-nc PECVD samples. High power time-resolved VSL measurements show the onset of stimulated emission with fast inversion lifetime. A four-level model, which includes amplified spontaneous emission and Auger processes, has been proposed. Good qualitative agreement with measured time-resolved decays has been obtained.

REFERENCES

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1. L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzò, F. Priolo, *Nature* **408**, 440 (2000).
 2. L. Khriachtchev, M. Rasanen, S. Novikov, J. Sinkkonen, *Appl. Phys. Lett.* **79**, 1249 (2001).
 3. M. Nayfeh, S. Rao, N. Barry, A. Smith, S. Chaieb, *Appl. Phys. Lett.* **80**, 121 (2002).
 4. K. Luterova, *et al.*, *J. Appl. Phys.* **91**, 2896 (2002).
 5. A. V. Malko, *et al.*, *Appl. Phys. Lett.* **81**, 1303, (2002).
 6. V. I. Klimov, *et al.*, *Science* **290**, 314, (2000).
 7. M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, C. Delerue, *Phys. Rev. Lett.* **82**, 197 (1999).
 8. A. B. Filonov, S. Ossicini, F. Bassani, F. Arnaud d'Avitaya, *Phys. Rev. B* **65**, 195717 (2002).
 9. F. Iacona, G. Franzò, and C. Spinella, *J. Appl. Phys.* **87**, 1295 (2000).
 10. L. Dal Negro *et al.*, *Physica E* **16**, 297 (2003).
 11. C. Delerue, M. Lanoo, G. Allan, E. Martin, I. Mihalcescu, J.C. Vial, R. Romenstain, F. Muller, A. Bsiesy, *Phys. Rev. Lett.* **75**, 2228 (1995).
 12. R. M'ghaieth, H. Maaref, I. Mihalcescu, J.C. Vial, *Phys. Rev. B.* **60**, 4450 (1999).
 13. N. Daldosso, M. Luppi, S. Ossicini, E. Degoli, R. Magri, G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, L. Pavesi, F. Priolo, and F. Iacona, *submitted to Phys. Rev. B*