

## Review Article

# Photoluminescence of Silicon Nanocrystals in Silicon Oxide

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Recent results on the photoluminescence properties of silicon nanocrystals embedded in silicon oxide are reviewed and discussed. The attention is focused on Si nanocrystals produced by high-temperature annealing of silicon rich oxide layers deposited by plasma-enhanced chemical vapor deposition. The influence of deposition parameters and layer thickness is analyzed in detail. The nanocrystal size can be roughly controlled by means of Si content and annealing temperature and time. Unfortunately, a technique for independently fine tuning the emission efficiency and the size is still lacking; thus, only middle size nanocrystals have high emission efficiency. Interestingly, the layer thickness affects the nucleation and growth kinetics so changing the luminescence efficiency.

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## 1. INTRODUCTION

Since the discovery of luminescent properties of porous silicon [1–3], many research efforts were dedicated to the light emitting properties of nanometric-sized silicon. Light emitting Si-based materials promise to allow merging of electronics and photonics in a single chip, thus overcoming the restrictions settled by the power dissipation bottleneck on the short/medium distance interconnects [4, 5]. Unfortunately, bulk Si is a poor light emitting material because of its indirect band gap. Excited electron-hole pairs have very long radiative lifetime (milliseconds), thus competing nonradiative recombinations rule and cause most of the excited electron-hole pairs to recombine nonradiatively. Silicon nanocrystals (Si-nc) are the most promising material to turn Si in an effective light emitter. Quantum confinement and spatial localization in a small region of excited electron-hole pairs push up the radiative efficiency to values as high as 10–50%.

Si-nc have also emerged as promising biophotonics materials [6–8]. Due to their spectral emission in the region of transparency of biological tissues, they could be used as luminescent markers for biological matter. The great advantage with respect to III-V or II-VI semiconductors is the low toxicity of silicon. Many efforts are dedicated right now to the luminescence stabilization of water-dispersed Si-nc by surface passivation with organic compounds [9, 10].

Room temperature luminescence emission in silicon nanocrystals (Si-nc) is routinely observed independently of

the preparation method [11–14]. The emission is characterized by a wide band in the wavelength range 600–900 nm. Qualitatively in agreement with the quantum confinement model, the emission band redshifts with the increase of the Si-nc mean size, which allows to attribute this band to electron-hole recombination in Si-nc. Luminescence efficiency is similar to that reported elsewhere [15, 16] for PECVD samples produced in Catania. Often, the second band, centered at 500 nm, can be observed in the luminescence spectra. It is different by the Si-nc-related band because it does not shift by changing crystallites size. This second band can be related to recombination in matrix defects which can be quenched by post-growth treatment, such as hydrogen passivation.

A way to obtain well-passivated Si-nc is the deposition of Si rich oxide (SiO<sub>x</sub>) layers on a substrate (silicon or quartz) by plasma-enhanced chemical vapor deposition (PECVD). Si-nc are formed as a consequence of Si segregation and clustering during high-temperature annealing [13, 14]. In the following, the luminescence properties of PECVD growth Si-nc will be presented.

## 2. EXPERIMENTAL

A series silicon-rich oxide films were grown on Si (100) wafers by PECVD using SiH<sub>4</sub> and N<sub>2</sub>O as precursor gases. The working pressure was maintained at 500 mTorr and the supplied power was 100 W with a radio frequency of

TABLE 1: Samples characteristics and thickness.

Sample	S1	S2	S3	S4	S5	S6	S7
$\Gamma$ ( $\text{N}_2\text{O}/\text{SiH}_4$ )	15	15	15	15	25	25	25
Thickness (nm)	50	50	200	200	50	200	200
$\text{Si}_3\text{N}_4$ capping layer	Yes	No	Yes	No	Yes	Yes	No

13.56 MHz. Si incorporation into the silicon-rich silicon oxide (SRO) layer is controlled by the  $\text{N}_2\text{O}$  to  $\text{SiH}_4$  flow rate ratio, we will refer to this parameter as  $\Gamma$ . The higher is  $\Gamma$  the lower the Si content into the film. Typically, since we are using  $\text{N}_2\text{O}$ , about 1% to 2% atoms of nitrogen were incorporated during the deposition. Si-nc segregation was obtained by one-hour long annealing at  $1000^\circ\text{C}$  or  $1100^\circ\text{C}$  in a nitrogen atmosphere. In order to explore the application for light-emitting device, films were deposited with two different thicknesses. Some of them were covered by a capping layer to avoid oxygen and nitrogen in-diffusion during the annealing. The description of these films is summarized in Table 1.

Photoluminescence (PL) measurements were performed with two different spectrometers and two different pumping wavelengths for a total of three different configurations.

- (i) "Vis-CCD." Samples were excited with the 488 nm line of an argon laser, pumping light was filtered with a 488 nm bandpass filter. Pump power was 50 mW corresponding roughly to a pump intensity of  $20\text{ W}/\text{cm}^2$ . Photoluminescence (PL) emission, in the wavelength range from 500 nm to 1000 nm, was collected by a single grating monochromator coupled with a cooled CCD. A long wavelength pass filter (cutoff at 550 nm) was put on the collection line in order to avoid noise coming from the scattering of pump light from the samples surface.
- (ii) "Vis-PMT." The same exciting condition as mentioned above. PL emission, in the wavelength range from 500 nm to 900 nm, was collected by a double-grating monochromator coupled with a cooled GaAs photomultiplier.
- (iii) "UV-PMT." Samples were excited with the 360 nm line of an argon laser. Pump power was 5 mW corresponding roughly to an intensity of  $2\text{ W}/\text{cm}^2$ . PL emission, in the wavelength range from 400 nm to 900 nm, was collected by a double-grating monochromator coupled with a cooled GaAs photomultiplier.

### 3. RESULTS AND DISCUSSION

#### 3.1. PECVD samples. Detailed variation of $\Gamma$

Detailed variation of Si content was obtained with a fine tuning of  $\Gamma$  ( $\text{N}_2\text{O}/\text{SiH}_4$ ) in the range from 2.5 to 30.  $\Gamma = 2.5$  corresponds roughly to 52% of atomic Si ( $\text{SiO}_{0.9}$ ).  $\Gamma = 30$  corresponds to a stoichiometric silicon oxide ( $\text{SiO}_2$ ). Photoluminescence measurements were performed in the Vis-CCD configuration (488 nm pump light, monochromator +

CCD). PL spectra are reported in Figures 1(a) and 1(b) for annealing temperatures of  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$ , respectively. PL emission from samples with  $\Gamma$  below 8 is extremely low and is not reported in Figures 1(a) and 1(b). Despite the large variation in silicon content, the luminescence emission is confined in the wavelength range from 500 nm to 1000 nm. The maximum of PL emission is obtained at  $\Gamma$  15– $\Gamma$  16 for both the annealing temperatures. Peak intensity and peak wavelength are reported in Figures 1(c) and 1(d) as a function of  $\Gamma$  for  $1000^\circ\text{C}$  and  $1100^\circ\text{C}$ , respectively. In both cases, peak intensity shows a bell-like shape as a function of the ratio between  $\text{N}_2\text{O}$  and  $\text{SiH}_4$ . Peak wavelength blue shifts increasing  $\Gamma$ . This indicates a reduction of Si-nc mean size with the reduction of Si content into the SRO layer.

In principle, Si-nc size can be controlled by the annealing temperature and Si content of the SRO. Keeping fixed the content of silicon, Si-nc size can be increased by increasing the annealing temperature or, similarly, at a fixed temperature Si-nc size can be increased by increasing the content of Si into the SRO. The search for high luminescent Si-nc imposes to find a trade-off between Si concentration and annealing temperature.

Figures 1(c) and 1(d) clearly demonstrate that the luminescence emission is not effective in SRO samples with extremely high or extremely low Si concentrations. The reasons are different for the two cases. With high-Si concentration, large size Si-nc are obtained. Quantum confinement effect is highly reduced for Si-nc radius larger than exciton Bohr radius and, as a consequence, oscillator strength for the luminescence transition tends toward the value of bulk Si. Thereby, the luminescence efficiency decreases as the nanocrystal radius increases due to a pure quantum confinement effect. Conversely, the reduction of Si concentration determines the development of smaller size Si-nc, then high emission efficiency can be expected due to quantum confinement effect. This is not the case because two detrimental effects are in competition with the quantum confinement effect and dominate at low Si concentration. The first is the reduction of the Si-nc density with the reduction of Si concentration. The second is connected with the thermodynamics of Si crystallization. Quantum dots crystallization is favored by the size increase because of an increased gain in the volume-free energy during the amorphous to crystalline transition. At a fixed temperature, crystallization process is favored at large Si content thanks to the increase of clusters mean size whereas, at very low Si content, aggregates persist in their amorphous phase also at high temperatures ( $1000^\circ\text{C}$  and above). Amorphous quantum dots have PL efficiency orders of magnitude lower than crystalline because of the presence of nonradiative centers in the disordered structure. The combined action of density reduction and amorphous fraction growth determines the lowering of PL efficiency at high  $\Gamma$  despite the positive action of quantum confinement.

#### 3.2. Thickness variation

The characterization of the optical properties of Si-nc is performed typically on SRO films hundred of nanometers thick. SRO is intrinsically an insulating material also when Si-nc are

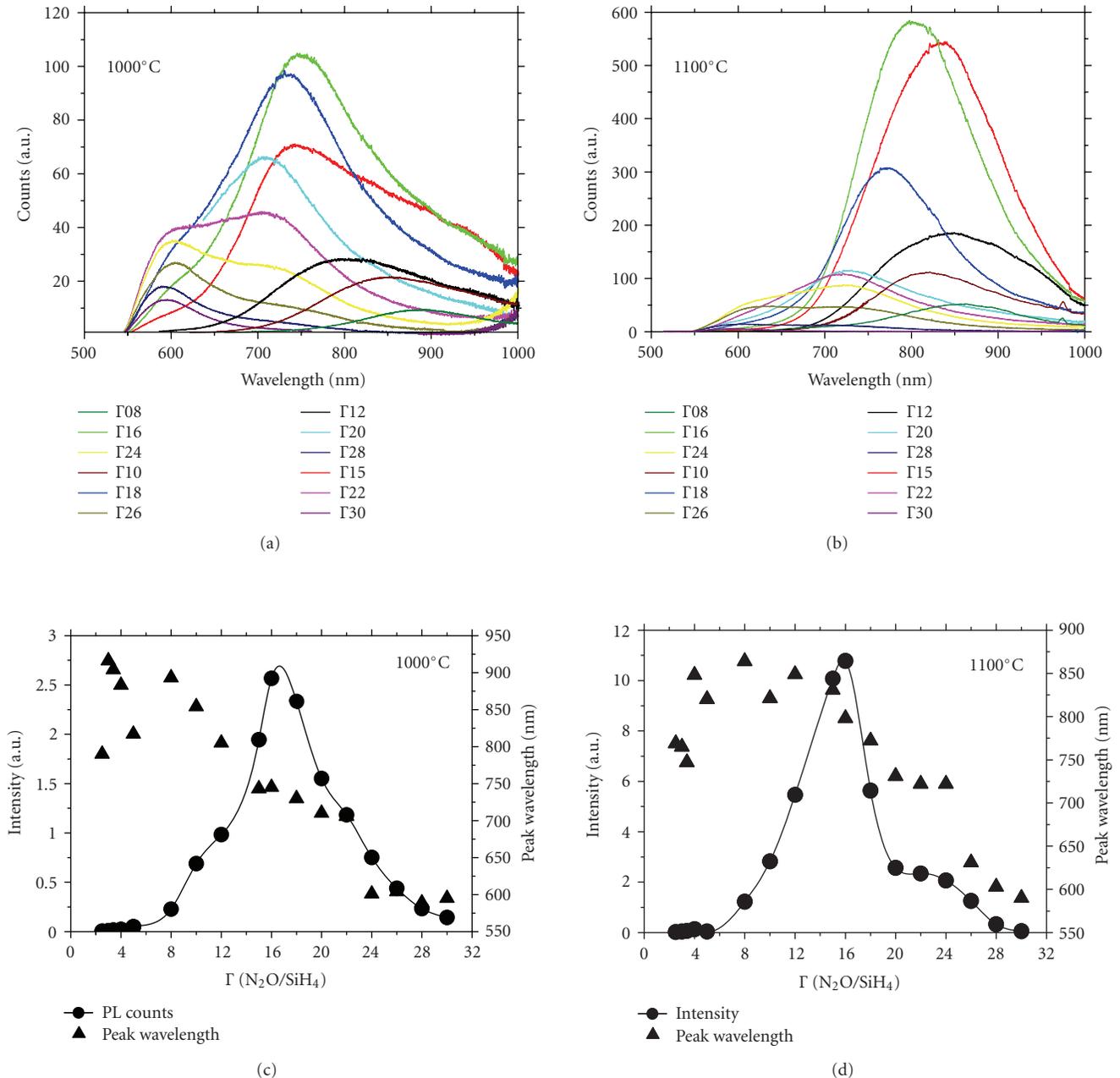


FIGURE 1: (a)-(b) Luminescence spectra of PECVD samples annealed at 1000°C and 1100°C, respectively. The samples are identified by the values of the  $\Gamma$  ( $N_2O/SiH_4$  flow ratio) parameter. (c)-(d) Total luminescence emission and peak wavelength as a function of  $\Gamma$  for samples annealed at 1000°C and 1100°C, respectively. The line is only a guide for eyes.

developed in. In order to explore the possibility of efficient charge injection at low bias for on-chip device integration, a small thickness is required. To explore the formation dynamics and optical properties of Si-nc in very thin films, 50 nm and 200 nm thick SRO layers, with two values of  $\Gamma$ , have been deposited by PECVD. After the deposition, samples were annealed at 1100°C in  $N_2$  atmosphere; detailed characteristics are reported in Table 1. Some samples were covered with a capping layer of  $Si_3N_4$  in order to avoid oxygen in-diffusion

during the annealing process. PL measurements were performed with the UV-PMT (pump wavelength 360 nm) configuration. The luminescence peak intensity was normalized to the samples thickness and reported in Figure 2. Normalized peak intensity (NPI) can be considered as a measure of the PL efficiency of the sample. As can be seen from the figure, thin samples show NPI values one order of magnitude lower than thick samples. The difference is of two orders of magnitude for uncapped samples. A blue shift of the

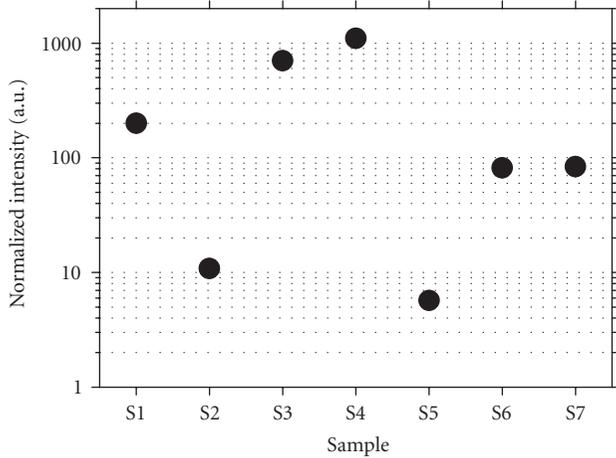


FIGURE 2: Photoluminescence peak intensity normalized to the film thickness. Sample details are reported in Table 1.

luminescence peak can be observed combined with the efficiency reduction (Figure 3) thus indicating the presence of smaller Si-nc.

The whole ensemble of Si-nc seems affected by the thickness of the layer (blue shift of peak wavelength). This means that the kinetics of Si-nc nucleation and growth is influenced by the layer thickness. The reduction of efficiency well correlates with the reduction of mean size and can be attributed to the reduction of nc-Si density and to the increase of Si-nc amorphous fraction as already mentioned.

As a matter of fact [17], SRO can suffer of oxygen in diffusion during the annealing process due to the presence of residual oxygen into the furnace. As a consequence, nc-Si are oxidized and consequently their mean size and their density can be reduced. The capping layer has the purpose of blocking the oxidation process. Thick samples (200 nm thick) are marginally affected by the oxygen in-diffusion process; both intensity (Figure 2) and peak wavelength (Figure 3) are only slightly different in capped and uncapped samples (samples S3, S4, S6, and S7).

Oxygen in-diffusion is, instead, really a detrimental effect for thin samples (S1, S2, and S5); PL emission is noticeably blue shifted (Figure 3) and the efficiency is highly reduced (Figure 2). The presence of the capping layer on the S1 sample is capable of slowing down the oxidation process of nc-Si but it is not enough to completely stop it. PL efficiency of sample S1 is reduced with respect to that of sample S3 and also the peak wavelength is clearly blue shifted. The effect is much more evident on the uncapped S2 sample where the PL efficiency is reduced of two orders of magnitude with respect to the corresponding uncapped thick sample (S4).

### 3.3. Different pumping wavelength

Silicon rich oxide samples typically develop Si nanocrystals with a wide distribution of size [13, 14]. nc-Si absorption

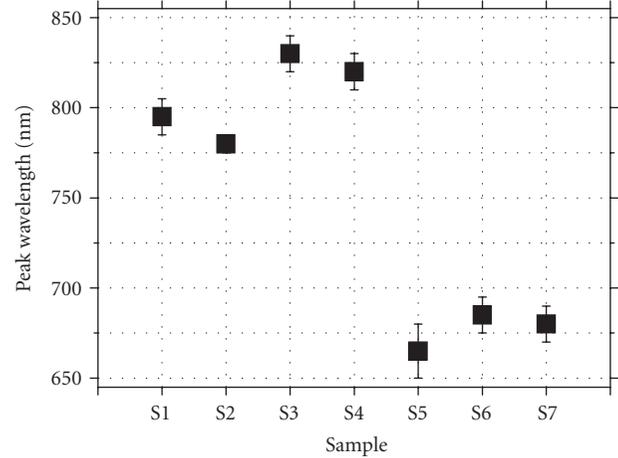


FIGURE 3: Photoluminescence peak wavelength for different samples. Sample details are reported in Table 1.

edge blue shifts with the reduction of the particle size because of the bandgap enlargement. This means that the PL emission can be affected by the choice of the pumping wavelength, that is, by the penetration depth of the laser light or by the selective excitation of a subset of the Si-nc. In order to clarify this effect, photoluminescence measurements were performed with the UV-PMT (pumping wavelength 360 nm) and Vis-PMT (pumping wavelength 488 nm) configurations. Luminescence spectra of sample S3 are reported in Figure 4(a) for both pumping wavelengths. The spectral shape does not change with the change of the pumping wavelength. In Figure 4(b), luminescence spectra of sample S6 are reported for both pumping wavelengths. A slight blue shift can be observed in the case of 360 nm pump. Samples S3 and S6 are different for the Si content, S6 is expected to have smaller size Si-nc than S3. Figure 4(b) clearly indicates that small size Si-nc are better excited by short wavelength light because of bandgap enlargement due to quantum confinement. From the experimental point of view, despite the effect of quantum confinement, PL spectra do not change dramatically and the results obtained with both the wavelength (360 nm and 488 nm) are comparable.

## 4. CONCLUSIONS

Efficient light emitting silicon nanocrystals of different sizes can be effectively produced by means of PECVD deposition followed by high-temperature annealing of SRO layers. Data point out that luminescence efficiency is a trade-off between positive and negative factors. Light emission is clearly influenced by quantum dots size, being poor for very large or small Si aggregates. A rough control on Si-nc size can be obtained by playing with Si concentration and annealing temperature and time. Unfortunately, a deposition technique capable of independently affecting PL efficiency and Si-nc size is still lacking. Oxygen in-diffusion, during the annealing

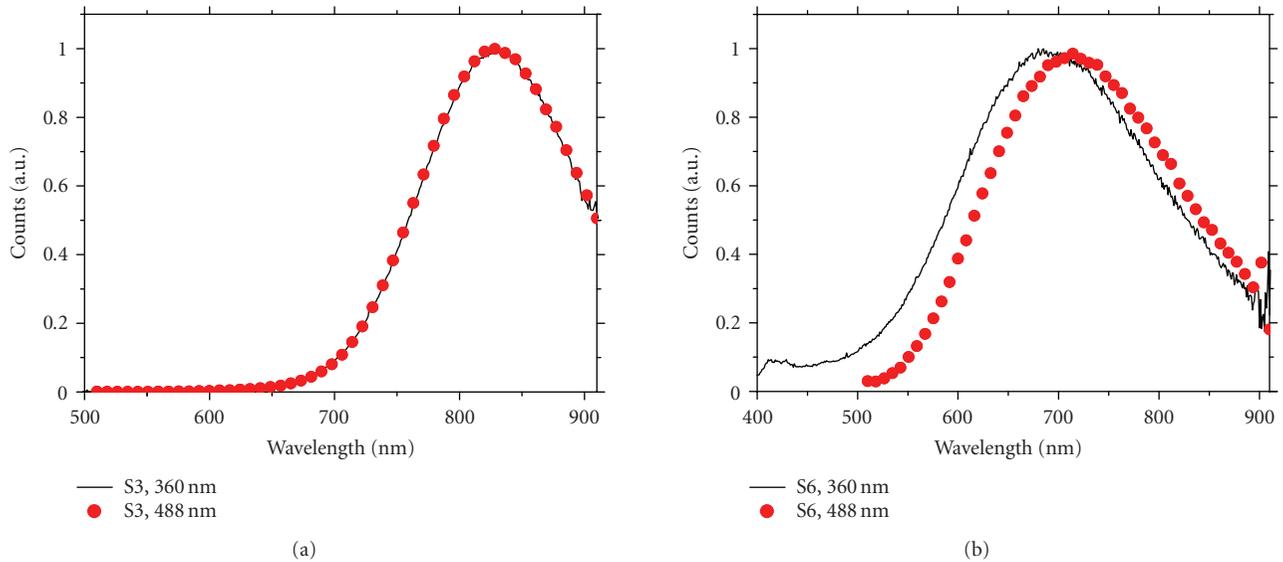


FIGURE 4: (a) Sample S3 luminescence emission for 360 nm (red line) and 488 nm (black line) pumping wavelength. (b) Sample S6 luminescence emission for 360 nm (red line) and 488 nm (black line) pumping wavelength. Sample details are reported in Table 1.

process, affects the PL properties of thin ( $\sim 50$  nm) SRO layers. The presence of an  $\text{Si}_3\text{N}_4$  capping layer is useful to slow down the oxidation process of nc-Si but is not capable to completely stop it especially in thin films. This has to be taken in mind when thinking to device integration.

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