

PHOTO AND CATHODOLUMINESCENCE OF Si/SiO₂ NANOPARTICLES PRODUCED BY LASER ABLATION

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Photo and cathodoluminescence of Si/SiO₂ nanoclusters produced by laser ablation is reported. The study was made on untreated nanopowders (size 2-10 nm, 64% of primary nanoparticles < 5 nm), aged 18 months in normal atmospheric conditions. Photoluminescence spectra at room temperature and 77 K revealed a broadband spectrum (two bands 1.8 and 2.5 eV) in an approximate range from 400 nm to more than 800 nm. The maximum intensity emission of the main band, measured at room temperature (RT), is centered at ~ 690 nm. At 77 K the photoluminescence emission peak increased by a factor of 3, and intensities for shorter wavelengths increased too (the luminescence color changed from red to orange). The cathodoluminescence spectra measured at 5 kV-30 kV, presents also two band components, 1.75 and 2.5 eV. When the accelerating voltage is increased, the main peak intensity (1.75 eV) increases dramatically, without changing the shape of the emission profile, whereas the second band intensity remains unchanged.

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1. Introduction

The task of achieving efficient luminescence in silicon nanocrystals has stimulated extensive studies on their structure and luminescence properties. In the recent years significant effort was devoted to the control of structure, size, size distribution, Si/SiO₂ interface or surface condition of silicon nanoparticles (Si NPs).

A wide range of experimental results are reported in the literature, however many aspects are still not clear and sometimes controversial. In spite of general knowledge available on the mechanisms of photoluminescence (PL), many questions remain unexplained, partially due to the strong dependence of the properties of the PL on the fabrication procedure and the stabilizing treatment. The experimentally determined optical properties of Si quantum dots can vary significantly depending on the synthesis technique and preparation conditions. Among the synthesis techniques, pulsed laser ablation (PLA) is a versatile method for silicon NPs preparation, and highly suitable for synthesizing high purity functional nanocrystallites [1-12].

Photoluminescence and cathodoluminescence (CL) spectroscopy techniques have already demonstrated to be useful for studying optical and electronic properties of Si nanocrystals. Most of the experimental work on Si/SiO₂ nanocrystal emission has been performed using photoluminescence techniques [1, 3, 6-10, 13-33], while cathodoluminescence has been less frequently applied [34-41]. To gain further insight into the emission mechanism measurements at low temperatures have been also performed [28, 31-33].

Concerning Si nanocrystal luminescence, many investigations have been performed on porous silicon or silicon nanoparticles deposited on a substrate [1,2,8,10,11,31-34]. The luminescence of free-standing Si NPs also has been reported [3,17,19]. In many cases an additional post-treatment (annealing, chemical) [1,8,10,22,23,17-19,42] was necessary to enhance the PL

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intensity, or to maintain PL for larger period, or because the original NPs were nonluminescent. Concerning CL investigations the studies have been mostly performed on porous silicon.

In this work, we present a spectroscopic study of photoluminescence and cathodoluminescence on the Si/SiO₂ NPs produced by laser ablation. The study was made on free standing NPs clusters, 18 months aged without any additional post-treatment (chemical, thermal, etc.). Also, it is important to note that the studied samples were as-produced Si nanopowders stored 18 months in normal atmospheric conditions, without any precautions.

2. Experimental

The synthesis of silicon nanoparticles by pulsed laser ablation technique was performed by irradiating a silicon target in an ambient gas, such as argon or helium. The gas was introduced into the chamber at a constant gas flow rate and at a constant pressure, using a differential evacuation system. The gas-suspended nanoparticles were collected on a filter without any cooling or heating.

Additional details of the apparatus and growth process have been described elsewhere [12].

For the PL investigations the NPs were excited by the UV line (325 nm) of a cw He-Cd laser (Kimmon Electric Co., model IK3301R-G, output power 30 mW). In order to remove any harmonics or spontaneous emission of the laser beam, we used a band-pass filter at 325 nm, and a cut-off filter at 340 nm. The silicon nanopowder was irradiated with a fluence of 40 mW/cm².

The spectral measurements were performed using a grating monochromator (CT-25C JASCO) and a photomultiplier Hamamatsu R1477. The system can measure in the wavelengths range 340-800 nm and has a spectral resolution of 1 nm.

The PL measurements were performed at room temperature and 77 K. In the low temperature case, the NPs were immersed in liquid nitrogen. The sample was prepared by sticking the nanopowder on a double-sided carbon tape (Nisshin EM Co. Ltd.). The tape with around 5-7 μm thick NPs layer was securely fastened to a holder and introduced into a glass Dewar flask.

The CL measurements were carried out on a Horiba MP-32M-DMT system: scanning electron microscope JEOL JSM 5510 and fully automated imaging spectrometer Jobin-Ivon Triax 320, resolution 0.5 nm. The electron beam parameters were: 5-30 kV, beam current of 0.05-1 nA and beam spot diameter around 0.2-0.4 μm.

Both PL and CL spectra were corrected for the system response.

Once more we have to underline that the PL and CL measurements were performed on Si nanopowders after 18 months aging in normal conditions (ambient natural atmosphere, room temperature, without any special precautions).

3. Results and discussion

Before presentation of the results, we'll briefly outline the optimal conditions for synthesis and the morpho-structural characteristics of the NPs, (described in detail in [12]).

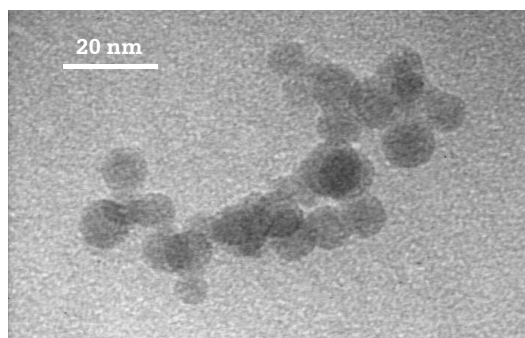


Fig. 1. Typical TEM image of a silicon nanoparticle cluster, as-collected on a filter, (experimental conditions: He / 550 mbar / 355 nm / 8 J/cm²; transmission electron microscope, Philips CM 120).

As it is well known an efficient PL in the visible range can be achieved for nanopowders having NP diameter less than 10 nm. Therefore, in the work [12] we determined the optimal

experimental conditions for an efficient synthesis of minimum sized silicon nanoparticles. They were: laser wavelength 355 nm, fluence 8 J/cm², ambient gas helium 99.99% purity, at 550 mbar. In these conditions, 98.8% of total NPs were less than 10 nm and 64% were in the range 2-5 nm; the arithmetic mean value of the diameter was 4.9 nm, and the peak of the lognormal size distribution function was at 4 nm. Most of the nanoparticles were almost spherical and consisted of a silicon core coated with an amorphous silicon oxide layer. The silicon core of the majority of particles was crystalline. The silicon nanopowder was brown in color. Figure 1 shows a typical TEM image of Si NPs clusters.

The NPs exhibited a strong red luminescence, clearly visible to the naked eye in day-light. The PL spectrum is shown in figure 2. The PL emission measured at room temperature consists of a broadband spectrum in the approximate range of 400 nm to more than 800 nm (800 nm being the upper limit of our spectroscopic system). The maximum intensity emission is centered at ~ 690 nm (~ 1.8 eV). Orii *et al.* [10] have reported the spectrum profile for the monodispersed Si NPs prepared by laser ablation, post-annealed and size selected. The PL spectrum for NPs of 4.3 nm (total diameter) is almost identical to ours, which demonstrates that the major contribution to spectrum is given by NPs with diameters in the range 2-5 nm. In our case by TEM evaluation [12], an average size of 4.9 nm was established. Also, Cullis *et al.* [34] reported a quasi-similar profile for highly oxidized porous silicon attributing the PL to Si quantum dots in the range of 3-5 nm.

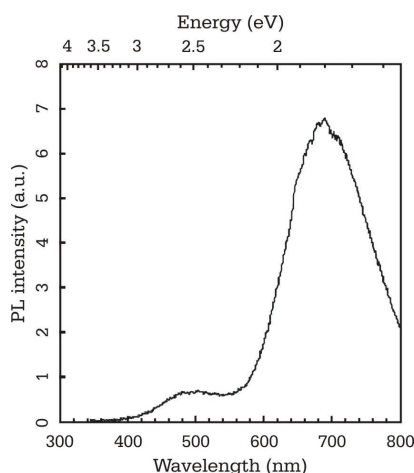


Fig. 2. The photoluminescence spectrum of Si/SiO₂ NPs, as-collected on filter, measured at room temperature; excitation wavelength 325 nm, excitation fluence 40 mW/cm².

The broadness of the emission band is generally ascribed to the existence of a large distribution of particle size. NPs produced by Patronne *et al.* [25] with the same technique, but in slightly different conditions (3.9 J/cm², 4 Torr, He), exhibited a quasi-similar spectrum profile similar to ours. Assuming that the main contribution to the PL was given by NPs with completed outlayers, they reconstructed the spectrum using a set of 3 Gaussians with maxima at 1.7 (main contribution) and 1.9 and 2.15 eV. A much more significant similarity with our case is offered by Botti and Coppola [13]. In their case, the PL emission has a well defined double band structure (as we have); it consists of two contributions: one in red, at 1.75 eV, and the other at 2.1-2.2 eV (yellow). They revealed that yellow emission was strongly decreased after an oxidation process. In our case after the 18 months aging in air, the NPs oxidation could be considered complete; the spectrum has the same shape, the main peak being at 1.8 eV with the full width at half maximum (FWHM) of 377 meV.

The second peak is shifted slightly towards shorter wavelengths, at ~ 2.5 eV. This band was unambiguously attributed to a radiative recombination through defects in SiO₂ structure while 1.8 eV band was ascribed to quantum confinement mechanism.

On the other hand, it is most interesting to compare with PL spectra of single Si NP. Valenta *et al.* [26] have reported the spectra of different individual nanoparticles produced by electron beam lithography and reactive ion etching. The NP spectrum was in the range 1.58-1.88 eV with FWHM of 120-210 meV, while the spectrum of nine NPs had a larger width of 236 meV. Since our nanopowder has a larger size distribution of NPs, the PL presents a broadened spectrum (about 1.6

times larger). Comparable results were obtained by Martin *et al.* [30] for Si NPs prepared by gas-phase method and etching. Typical single-particle emission was between 530 and 700 nm with a FWHM of about 150 meV, and for clusters of nanoparticles was between 500 and 800 nm, with a FWHM of 400 meV, close to our result.

Photoluminescence of the samples immersed in liquid nitrogen could also be observed by the naked eye. Moreover, in this case the luminescence was much more intense, and the light color changed from red to orange. Figure 3 shows the PL spectrum measured at 77 K. In comparison with previous spectrum (fig. 2), where the NP clusters were directly excited and the luminescence was transmitted to spectrometer without any distortions, in the new experimental arrangement we used a glass Dewar flask. In these measurements there could be some small influence of the glass of the double-wall Dewar flask. Therefore for an accurate comparison of the luminescence intensities at RT and 77 K, fig. 3 shows the spectrum emission at room temperature recorded in the same conditions as at 77 K.

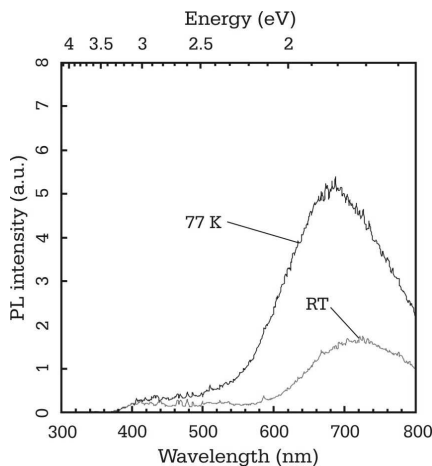


Fig. 3. The photoluminescence spectrum of the Si/SiO₂ NPs, measured at room temperature and 77 K.

The room temperature measurement looks quite similar to the spectrum in Fig. 2. At 77 K, the increase in the luminescence emission is remarkable, a factor of 3, and intensity for shorter wavelengths is much higher (the FWHM is increased by 55 meV). The emission of the Si NPs powder specimen exhibited a slight shift of about 82 meV towards the shorter wavelengths.

In [31], Letant and Vial performed PL measurements on oxidized porous silicon in the temperature range 77–300 K, in nitrogen atmosphere. The results are like ours. They also noticed an enhanced intensity of a factor of 1.7, when the temperature decreased from RT to 77 K. This temperature dependence might be attributed to a decrease of the recombinations on nonradiative centers at low temperatures. Also, Heitmann *et al.* [32] showed that the PL intensity increases with decreasing temperature between 300 and 70 K and peak position was slightly shifted towards shorter wavelengths. Orii *et al.* [33] observed the same dependence of the peak energy for mono-dispersed Si NPs. Recently, Sychugov *et al.* [28] reported PL measurements on a single Si nanocrystal fabricated by beam lithography and plasma etching. The quantum dots exhibited quite a broad featureless emission line at RT in the range from 1.5 to 2.0 eV. Their work showed that at 80 K some fraction of the nanocrystals revealed emission with or without a second peak.

Concerning the spectrum peak, our NPs show qualitatively the same trend, but at the same time there is a difference in FWHM, which increases at 77 K. The aforementioned works, showed that in contrast to our case, at low temperature the PL band narrowed. The striking difference between the behavior of NPs in our study and [28, 31–33], could be explained by different preparation techniques of quantum dots, but particularly and mainly, in our opinion, by different cooling methods. The fact that we immersed the NPs in liquid nitrogen could be very important in the PL process.

The cathodoluminescence spectra were measured at different accelerating voltages from 5 kV to 30 kV. The CL spectra for 15 and 30 kV only, are shown in fig. 4. The spectra are comparable to the PL spectra, although the excitation energy for CL is much higher and the energy density incident on the sample is also higher. The CL spectrum consists of two components: 1.75 eV and 2.5 eV. When the accelerating voltage is increased from 5 kV to 30 kV, the 1.75 eV peak intensity

increases dramatically; this is explainable because at higher voltages the electrons penetrate farther into the sample and generate larger interaction volumes. The second band which is generated by SiO₂ layer, on the contrary is not influenced by the accelerating voltage. In comparison with PL spectra, the CL peak is shifted 10 nm (~ 50 meV) towards longer wavelengths. Similar results were reported by other authors. Thus, Yang *et al.* [36] observed two band emissions at 1.6–1.9 eV and 2.7 eV for the electron beam energy between 1 and 2 keV. Cullis *et al.* [34] investigated highly oxidized porous silicon and two dominant CL bands were observed at 1.9 and 2.5 eV (accelerating voltage 6 kV). The measurements carried out by Suzuki *et al.* [35], on thermal-oxidized porous silicon samples, (15 kV accelerating voltage), showed a CL spectrum dominated by a band at 2.7 eV, and a weak band at 1.9 eV. We have to emphasize that in most cases the analyzed samples were oxidized porous silicon, while in our case a Si/SiO₂ nanopowder was used.

It is also interesting to note that the dominant peak intensity of CL, measured at the same place, for the same area, with the same electron beam parameters, decreases after each sample scanning, while the 2.5 eV band intensity remains unchanged. We observed 40% decrease of the CL intensity, after 20 seconds scanning of an 1×1 mm² area.

The luminescence degradation has been previously reported in [35, 36, 38, 41]. Suzuki *et al.* [35] showed that the electron beam irradiation caused degradation and/or increase in luminescence, in a different way for each of the two bands. This behavior is explainable due to the two different mechanisms responsible for luminescence generation. For dominant band is responsible the quantum confinement mechanism which is located in the crystalline core of the NP, whereas the 2.5 eV band emanates from SiO₂ amorphous layer. The crystalline core is significantly damaged by strong electron irradiation, but the amorphous SiO₂ layer is not affected. Yang *et al.* [36] confirmed that there is a certain exposure threshold value at which the specimens are damaged. Batstone *et al.* [39] noticed a 50% decay in the peak intensity after 25 seconds irradiation (15 kV, 1.6 nA, 50 nm spot size). The phenomenon in many cases is irreversible and it was attributed to structural defects generated by electron irradiation

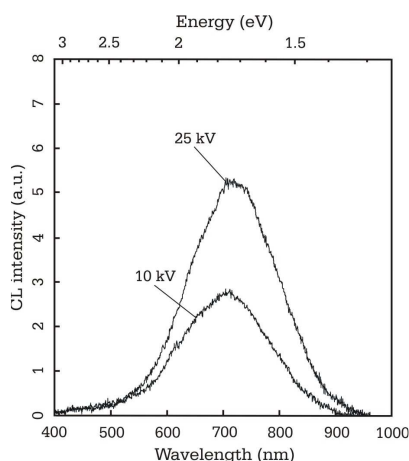


Fig. 4. Cathodoluminescence spectra of the Si NPs measured at two accelerating voltages.

4. Conclusions

We have presented the photo and cathodoluminescence measurements of Si/SiO₂ nanoclusters produced by laser ablation. The study was made on untreated nanopowders (size 2–10 nm, 64% < 5 nm), aged 18 months in normal atmospheric conditions. The photoluminescence spectra at RT revealed a broadband spectrum in a range of 400 nm to more than 800 nm, with two peaks: the main peak at ~ 1.8 eV (FWHM 377 meV), and a second smaller one at ~ 2.5 eV. At 77 K, the luminescence emission exhibited a slight shift to the shorter wavelengths of about 82 meV, and the peak intensity increased by a factor of 3 (the light color changed to orange).

Cathodoluminescence spectra are comparable with the PL ones. The emission peaked at approximately 710–720 nm (~ 1.73 eV, FWHM of 460–480 meV), for the accelerating voltages 5 kV–30 kV. The CL emission profile is the same, regardless of the accelerating voltage, but the peak intensity is increasing dramatically with accelerating voltage, due to a higher penetration depth. Also, 40 % degradation of the CL was observed, following 20 seconds of electron irradiation.

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