Physica E 41 (2009) 982–985

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Yellow-emitting colloidal suspensions of silicon nanocrystals: Fabrication technology, luminescence performance and application prospects

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ARTICLE INFO

Available online 15 August 2008

PACS:
78.55.−m
78.67.−n
78.55.Ap

Keywords:
Silicon nanocrystals
Colloidal solution
Photoluminescence

ABSTRACT

Pulverized porous silicon, fabricated by the electrochemical etching of silicon wafers, is used to prepare colloidal suspensions of silicon nanocrystals (ncSi) in various organic solvents including xylene. The porous silicon powder aggregates into large clumps, making the suspensions scatter light strongly. The suspensions are subsequently gently stirred in optical cuvettes for a period of weeks, in air and at room temperature. The temporal development of spatially resolved photoluminescence emission spectra in the cuvette with xylene + ncSi is monitored at regular intervals. The spectra show a slow evolution from the original orange color through blue to a yellow one. After approximately 5 weeks, a yellow emitting (~560 nm) transparent colloidal solution can be extracted from the cuvette, with a high and stable photoluminescence yield (~20%).

1. Introduction

Recently, there has been great interest in silicon nanocrystals (ncSi) or quantum dots. The properties of nanoscale materials differ substantially from those of their bulk counterparts. Bulk silicon, having an indirect band gap, is a very bad phosphor, emitting only extremely weak photoluminescence (PL) in the near-infrared region. On the other hand, ncSi with a typical size of 2–6 nm become excellent light emitters and display bright PL in the visible region [1,2]. It is believed that an interplay between the effect of quantum confinement and a surface-related radiative recombination is responsible for this remarkable modification [3,4]. Luminescent ncSis hold promise for potential applications in silicon photonics, optoelectronics and biological/medical imaging.

The surface passivation of ncSis has turned out to be of critical importance for their PL performance. In parallel with the investigations of the assemblies of closely spaced ncSis embedded in transparent solid matrices (such as SiO_2), as is preferred by physicists (e.g. Refs. [5–7]), recently many papers applying a rather chemical approach, namely colloidal techniques, for the synthesis of ncSi, have appeared. These techniques have the advantage of allowing an easier manipulation with surface chemistry. Indeed, various organic molecules such as allylamine or 1-heptene [8], toluene [9] and 1-octyne [10] are being used to encapsulate the ncSi surface. However, the final product—a colloidal solution of properly passivated ncSis—always emits in the UV/blue region.

In this paper we report on the mechanochemical synthesis of a colloidal solution of yellow luminescent silicon nanoparticles in xylene. The solution is transparent (i.e. it exhibits only extremely weak light scattering) and keeps its high PL yield (~20%) for at least 6 months in air.

2. Sample preparation

The ncSi powder was prepared by the pulverization of electrochemically etched p-type Si wafer (B-doped, (0.075−0.100) Ω cm, (1 0 0)-oriented, 2.5 mA/cm^2). Two types of ncSi powder were used. In the first-type sample, denoted as 1sed, the etching solution contained solely 50% HF and pure ethanol in the ratio of 1:3. The pulverization was then followed by the dispersion of ncSis in ethanol, 1-h ultrasonic treatment and subsequent sedimentation to remove the largest clusters. In the second-type sample, denoted as WSi, 30% H_2O_2 was added to the etching solution while setting the HF:ethanol:H_2O_2 ratio to 13:37:2. The post-etching (pre-pulverization) treatment consisted of 30% H_2O_2 bath for 10–15 min and aging at 50% humidity in air for several days. Due to more intense etching and different surface passivation in the latter case, PL of WSi is shifted to shorter wavelengths when compared to 1sed [11]. However, in both types of the powder, the surface of ncSis is oxygen- (or OH-) passivated and both exhibit similar behavior in colloidal suspensions.

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doi:10.1016/j.physe.2008.08.022

The colloidal suspensions were prepared by mixing the ncSi powder (2.5 mg) with the chosen solvent (500 µl) in a low-volume (inner dimensions $10 \times 4\,\mathrm{mm}^2$) quartz cuvette designed for magnetic stirring and subsequent 15-min ultrasonic treatment to break the largest clusters. Stirring of the mixture then continued ceaselessly on a magnetic stirrer at the speed of approximately 600 rpm. At intervals, solvent was added to the suspension to maintain a constant level.

When preparing the suspensions, 96% UV ethanol, pure xylene (mixture of isomers) and 99% cyclohexane were used. To measure the PL quantum yield, the reference *Lambda Physik* rhodamine 6G was mixed with 96% UV ethanol and left to dissolve for at least several days, as lower PL signal was observed from freshly dissolved samples.

3. PL experimental

The time-evolution PL spectra were excited with a continuous-wave HeCd laser (325 or 442 nm, 5 and 40 mW, respectively) and collected with a silica optical cable (Fig. 2a). The input of the optical cable was equipped with a 50 µm slit and placed in the distance of approximately 1 mm from the measured cuvette to achieve higher spatial resolution. The spatially resolved PL spectra were then acquired with the sampling distance of 250 µm. The detection system comprised a grating-based spectrogragh and a charge-coupled device (CCD) camera. This setup (without the slit) was also used for periodic monitoring of overall PL and light scattering during mixing.

All spectra were corrected for the spectral response of the experimental setup.

4. Results and discussion

4.1. The effect of long-term stirring

We investigated the effect of long-term stirring on the mixtures of ncSis in three different solvents covering a wide range of relative polarities from 0.654 (ethanol) through 0.074 (xylene) to 0.006 (cyclohexane) [12]. The suspensions were constantly stirred and the overall (i.e. spatially non-resolved) PL signal was monitored. The photographs of resulting mixtures are shown in Fig. 1.

In the case of ethanol (Fig. 1a), discernible changes in orange-band PL could be observed for about a week. Besides a decrease in the intensity of the orange-band PL during this time by about $\frac{1}{3}$ of its original value after which it reached a saturated level, a slight shift of the PL maximum of 8 nm (from 642 to 650 nm) occurred. As we are interested in samples with low light scattering, the intensity of 90 °C-scattered laser line (442 nm) was monitored besides the 325-nm-excited PL. The PL changes were accompanied by about two-fold increase in the scattered signal intensity, which indicates that stirring helped break large clusters into smaller ones. However, despite the quite bright orange PL of the stable suspension, it was still murky and we did not manage to obtain a transparent solution.

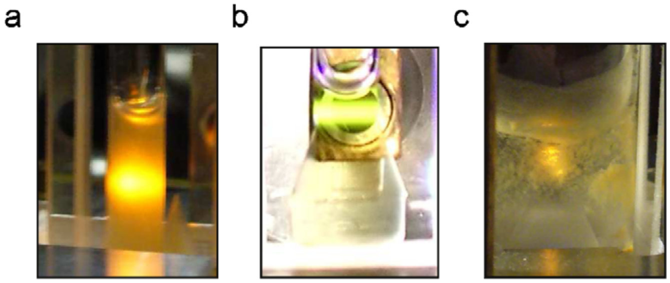

Fig. 1. The photographs of luminescent silicon nanocrystals (type 1sed powder) dispersed in different solvents (ethanol (a), xylene (b) and cyclohexane (c)), shown in the order of decreasing polarity, under 325-nm ((a) and (c)) and 442-nm (b) excitation. While (a) and (b) are excited from the side, (c) is excited from the back as ncSis agglomerate only on the walls and no PL would be visible if the sample were excited from the side. Significantly reduced light scattering in (b) when compared to (a) is clearly visible. The circular opening visible in (b) below the meniscus of the liquid is the input ferrule of the optical cable.

The colloidal suspension of ncSis in cyclohexane (Fig. 1c) showed a different behavior. Apart from quick PL quenching (even to a half of the original value just after ultrasonic treatment), flocculation appeared within two days. The ncSi clumps gathered at the cuvette walls and were the source of orange PL whereas the PL of the solvent remained unchanged. The maximum of ncSi PL again shifted, this time by 20 nm (from 640 to 660 nm) and the scattered laser-line signal abruptly decreased (due to flocculation).

In contrast to the previous two cases, more complex effects appeared while stirring ncSis in xylene. The scattered laser-line signal fell abruptly after one day of stirring to half of the initial value, but slightly increased again after two weeks. What is more, its value was one order of magnitude lower than in the case of ethanol (this difference is clearly visible when Figs. 1b and a are compared). The decrease in scattered signal was accompanied by the formation of macroscopic ncSi clumps in the solvent, which partly circulated in the mixture and partly stayed at the surface. The overall orange-band PL signal was gradually decreasing for two weeks, after which it stabilized at $\frac{1}{3}$ of the original value. However, in this case, the PL was clearly inhomogeneously distributed inside the cuvette (with the orange-band PL mostly located at cuvette walls) and the effect of stirring could not be judged from the overall PL monitoring.

In order to further investigate this interesting effect, spatially resolved measurements were employed during the whole stirring process (Fig. 2). The freshly prepared mixture exhibited an orange 600-nm-centered PL peak together with a much smaller blue (440 nm) one (Fig. 2b). During the first week of stirring, the larger nanocrystals (with red-shifted PL) tended to aggregate more at the cuvette walls than in its center as can be seen from the blue-shift of PL maximum when measuring closer to the center (Fig. 2c), which is what caused the orange-band intensity decrease in the overall PL monitoring. However, after about two weeks of stirring, the orange band started to disappear completely (Fig. 2d), whereas after another week a new yellow peak (550–570 nm) appeared (Fig. 2e). The PL intensity of the yellow peak further increased (Fig. 2f) and reached a saturated level after about 5 weeks from the beginning of the stirring.

After 5 weeks, the stirring was stopped and the big clumps were left to sediment. Then, the remaining solution was carefully transferred into a new clean cuvette. Thus, we obtained a transparent, though yellowish solution exhibiting bright yellow (442-nm excited) PL (Fig. 1b), changing into white when excited by 325 nm due to the presence of the blue peak (Fig. 3). On the other hand, the PL of the remaining big clumps was orange (Fig. 3) when excited with 325 nm. We would like to point out that the resulting PL spectra are in stark contrast with PL of the pure solvent (as is shown in the inset of Fig. 3), especially when blue excitation laser lines are used.

4.2. Quantum efficiency

In order to quantify the intensity of PL from the transparent solution (particularly that of the yellow band at 560 nm), quantum

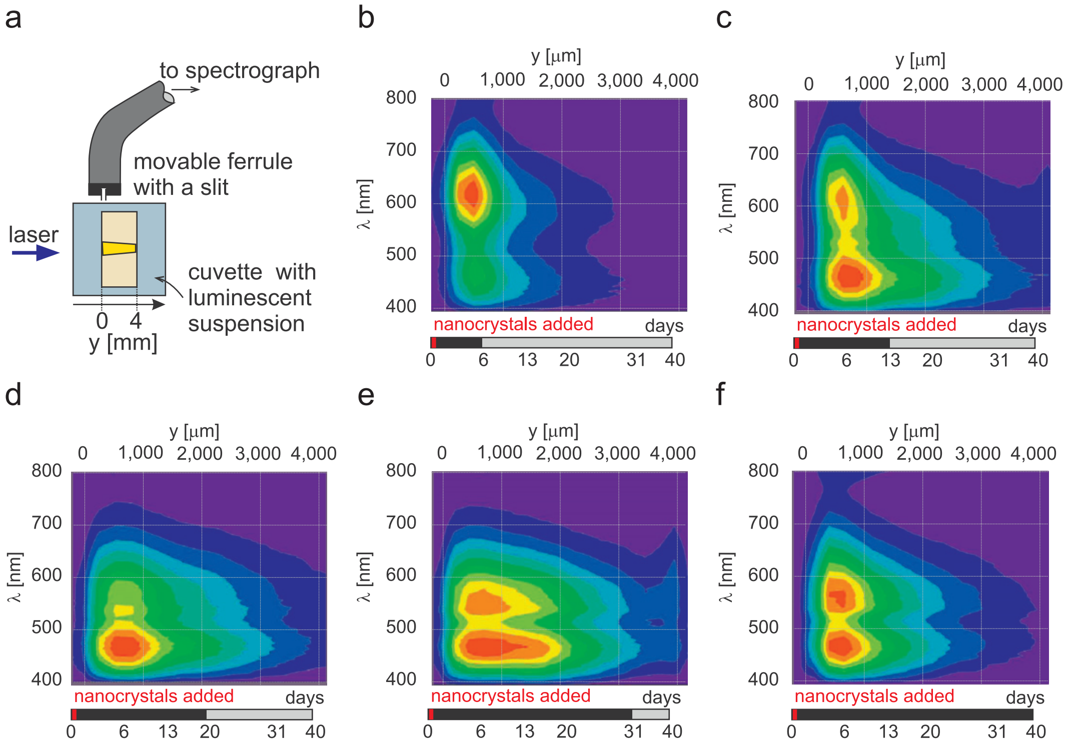

Fig. 2. Experimental setup (a) and the time evolution of PL spectra (vertical axis) of ncSis (type WSi) in xylene after 6, 13, 20, 31 and 40 days of stirring excited with 325 nm ((b)–(f), the maxima of the *z*-axis are not set to the same value). The horizontal axis (*y*) stands for the position inside a 4-mm wide cuvette.

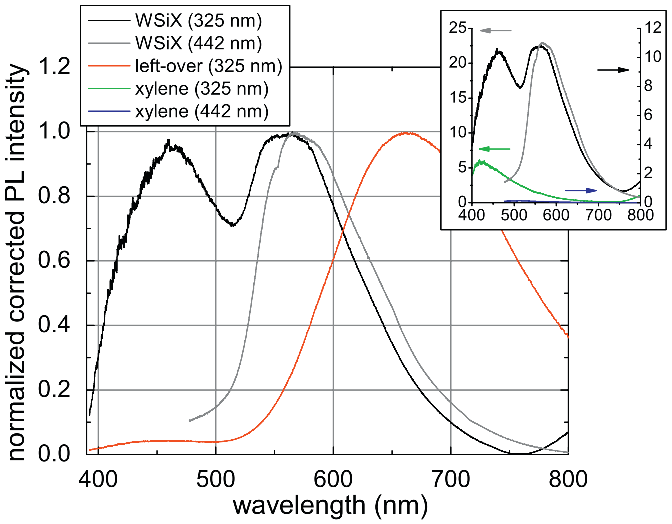

Fig. 3. The PL spectra from the transparent solution of ncSis in xylene extracted after 5 weeks of stirring (black for 325-nm excitation and gray for 442-nm excitation) are plotted together with PL from the big ncSi clumps (325 nm—red curve), whereas the inset depicts the absolute comparison with xylene (325 nm left axis—green curve, 442 nm right axis—blue curve).

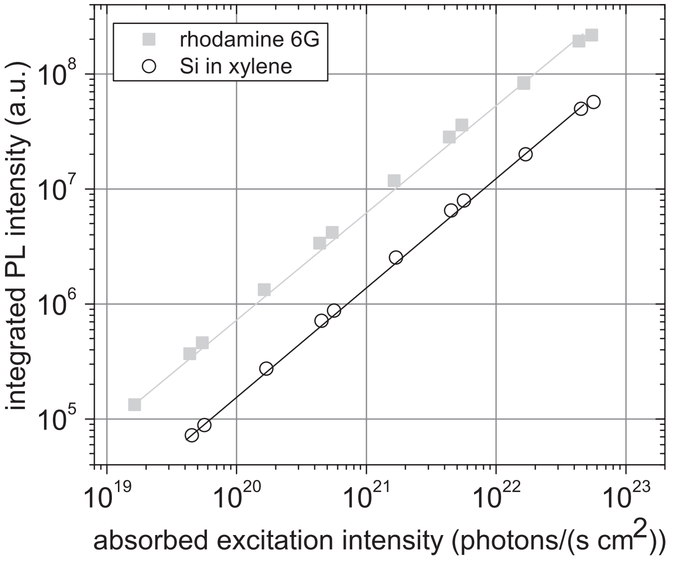

Fig. 4. Luminescence QE measurements of the transparent solution (open circles) if R6G is used as a reference (solid gray rectangles). Our samples show the quantum yield of 20% (taking into account the fact that QE of R6G under similar experimental conditions amounts to 94%).

efficiency (QE) was measured. Our method is based on the comparison of PL of an ethanol solution of rhodamine 6G (R6G) (whose quantum efficiency under 488-nm excitation is well known [13]) and the studied sample while diluting R6G to set its absorption coefficient to the same value and keeping the same experimental conditions.

The QE measurements were performed with the 480-nm excitation from an Nd:YAG+ optical parametric oscillator system (pulse duration and repetition rate 5 ns and 10 Hz, respectively). The emitted light was collected and imaged by a two-lens achromatic system (~3 × magnification) on the entrance slit of an imaging spectrometer coupled with a gated iCCD camera. The detected volume was defined by the beam diameter (~140 µm) and the slit width image on the sample (~70 µm). This enabled the assessment of the total number of absorbed photons. 10-ms-gated detection by the iCCD camera ensured the integration of the whole PL time-decay tail (which may significantly vary for the sample and the reference). Then, the signal was plotted over several orders of excitation intensities (Fig. 4) and the results revealed high PL yield of the transparent solution of ncSis in xylene: 0.22 × QE_{R6G} corresponds to the QE of 20% if the value of 94% is used as the QE of the reference sample [13]. Further details of the method, including how the correction for remaining light scattering was performed, will be published elsewhere.

5. Discussion and conclusions

We shall briefly touch two points in the section: firstly, which processes take place during the long-term stirring in the mixture (ncSi + xylene) and, secondly, what kind of applications one can expect for similar colloidal solutions.

As for the long-term stirring and periodic monitoring of PL, we are currently unable to submit a detailed understanding of what occurs. A tentative scenario to describe the course of events shown in Fig. 2b–f can be as follows. Mechanical collisions of the clumps of originally oxygen-passivated ncSi cause them to crumble into smaller pieces, possibly releasing even single nanocrystals (or tiny clusters of them). This is accompanied by the disappearance of the orange band (at ~620 nm) and by an enhancement of the blue one (Fig. 2b–d). The newly created fragments uncover, at least partially, fresh silicon surface. Xylene molecules can then be absorbed on such reactive sites [14] and this progressive capping of ncSi can substantially modify the internal electronic charge distribution, energy band gap and also the oscillator strength of nanocrystals, which is reflected in the gradual growth of a new emission band at ~560 nm (Fig. 2e and f). The yellow (instead of blue) coloration of PL can be due to the remaining imperfect oxygen passivation of ncSis. The fact that the non-dissolved ncSis with orange PL (Fig. 3—red curve) remain in the solvent in the form of big clumps and can later be easily removed from the solution, contributes significantly to the final solution's transparency.

Although this effect of spectral selection might seem to imply that PL intensity (or the concentration of luminescent ncSis in the solution) reached a saturated level and thus cannot be further increased, we verified that the addition of ncSis followed by another period of stirring results in a two-fold PL intensity increase, which, together with the high PL yield, holds promise for a bright PL source.

Regarding the outlook for applications of colloidal ncSi, the fields of biological labels [15] or colloidal LED diodes [16] can be envisaged. Other potential application can be found in e.g. in vivo sensing with non-toxic nanocrystals. A transparent colloidal solution of ncSi with high QE is also of particular attraction for the investigations of optical gain.

In conclusion, our results indicate that properties of even oxygen-terminated ncSi powder can be significantly modified by organic surface chemistry. In particular, xylene has proved to be very efficient passivation agent for luminescent ncSis.

Acknowledgments

This research has been supported by the Institutional Research Plan AV0Z 10100521, MŠMT Research Center LC510, GAAVČR Project nos. IAA101120804 and GAČR Project no. 202/07/0818.

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