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Optical Materials 27 (2005) 1046–1049

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Colloidal suspensions of silicon nanocrystals: from single nanocrystals to photonic structures

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Abstract

Colloidal suspesions of Si nanocrystals (NCs) are prepared from light-emitting porous Si grains obtained by mechanical pulverization of electrochemically etched layers. Sedimented and/or filtered Si NCs sols reveal a green photoluminescence (PL) band around 530 nm, which is interpreted as radiative recombination of electron–hole pairs inside Si NCs with diameter about 2 nm. These colloidal solutions have multiple advantages for both fundamental investigations and for nanotechnology. In one extreme, single molecule spectroscopy techniques can be applied to investigate PL of single grains of Si NCs dispersed on substrates from highly diluted solutions. On the other hand, concentrated suspensions enable us to fabricate bulk samples with embedded Si NCs or to prepare self-organised nanostructures on surfaces.

1. Introduction

Among many techniques to prepare silicon nanocrystals (Si NCs), electrochemical etching of porous Si remains the cheapest and fastest method. It may be the most promising for production of large amounts of Si NCs required for potential applications in nanotechnology.

In this paper we investigate properties and technological prospects of colloidal suspensions formed by dispersing a Si NCs sol (from pulverized porous Si layers) in different organic solvents. Special attention is paid to a surprising observation of intense green photoluminescence (PL) in sedimented and/or filtered suspensions.

2. Sample preparation and experimental techniques

Porous Si (PSi) powder has been prepared by standard electrochemical etching of Si wafers ($\langle 100 \rangle$p-type, $\rho \sim 0.1\,\Omega$cm) in a HF-ethanol (1:2.5) solution. The etching current density was kept relatively low (1.6 mA/cm^2) in order to obtain higher porosity and, consequently, resulting in a low mean size of Si-NC (the PL band peak is around 680 nm). PSi powder (i.e. grains of interconnected oxidized Si NCs) is then obtained by mechanical pulverization of the PSi film from the silicon substrate. Such a powder (showing intense orange PL under UV excitation) is a starting material for production of various Si nanostructures through colloidal phase—see schematical illustration in Fig. 1.

Colloidal suspensions were prepared by pouring different organic solvents (ethanol, isobutanol, heptanol, hexane, heptane) onto the PSi powder and mixing with

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doi:10.1016/j.optmat.2004.08.060

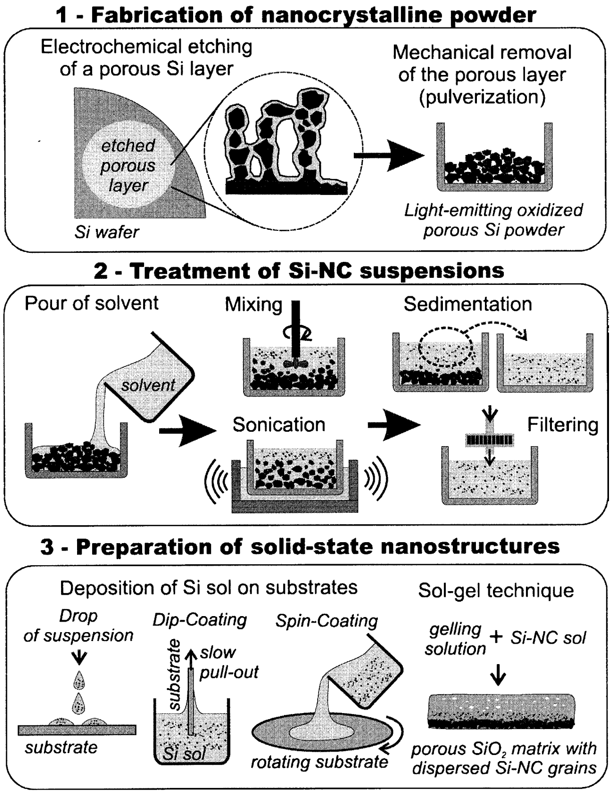

Fig. 1. Schematic illustration of the fabrication procedure of Si nanostructures from PSi powder through colloidal suspensions. See text for details.

a small propeller (Ultra-turrax) and in ultrasonic bath. Microscopical observation shows that the original powder contains many large PSi grains of several µm or even tens of µm. The mixing is breaking the largest grains but it is inefficient to decrease their size below a few µm. Further size selection is possible by repeated sedimentation or centrifugation. Some suspensions were filtered by teflon membranes (Sartorius) with pores of 200 nm.

Colloidal suspensions can be used to prepare Si NCs structures of various forms. For studying individual Si NC particles we deposit highly diluted suspensions onto cleaned substrates (Si wafers, glass or fused silica plates) by means of spin- or dip-coating techniques. On the other hand, concentrated suspension can form interesting self-organised structures when deposited under appropriate combination of solvent and substrate.

Solid-state samples with high concentration of Si NCs are formed by dispersing PSi powder into the commercially available SiO_2-based undoped or doped spin-on-glasses [1]. The solution solidifies at room temperature and atmosphere within a few hours. At the first stage of the solidification, the samples are kept in ultrasonic bath for 1 h to avoid agglomeration. During the next step, the Si NCs are sedimenting on the bottom of the cell creating ~50 µm thick layer containing densely packed Si NCs. The solidified samples of typical dimensions $10 \times 10 \times 1\,mm^3$ with a wide range (3–45 vol.%) of Si NCs concentrations were prepared.

PL spectra were measured under excitation by a cw Ar-ion laser (emission lines from 457 nm to 514 nm) and detected with Pentamax iCCD camera connected to an imaging spectrometer (Jobin-Yvon Triax 320). PL excitation spectra were measured with a fluorescence spectrometer (FluoroLog 2, excitation with monochromatized continuous Xe lamp). PL kinetics were excited by nanosecond pulses of a XeCl excimer laser (30 ns, 5 Hz, $\lambda = 308$ nm), emission was spectrally selected with narrow band interference filters, and detected by a Hamamatsu R928 photomultiplier connected to an oscilloscope. Raman scattering of the suspensions was detected by the LabRam spectrometer using a macrolens and by excitation with the 532 nm output of a cw YAG laser. Micro-PL images were studied using an imaging spectrometer (Triax 190) connected to an optical microscope Nikon Optiphot 120. Light from the sample was collected by an objective lens (100×/0.73 NA), imaged onto the entrance slit of a spectrometer and detected by a LN-cooled CCD camera Hamamatsu C 4880. An unfocused UV line (325 nm) of a cw He–Cd laser was used as excitation source.

3. Experimental results and discussion

The prepared suspensions of Si NCs are yellowish, light diffusive liquids in which sedimentation of µm sized grains occur on a time scale of hours (depending on specific density and viscosity of solvent). They show strong orange PL (peaking around 640 nm, with small shifts depending on applied solvent) under UV or blue excitation (see Fig. 2a). After filtering (filter pore size 0.2 µm) the suspensions lost its yellow colour and became clear colourless, this means most likely that the majority of

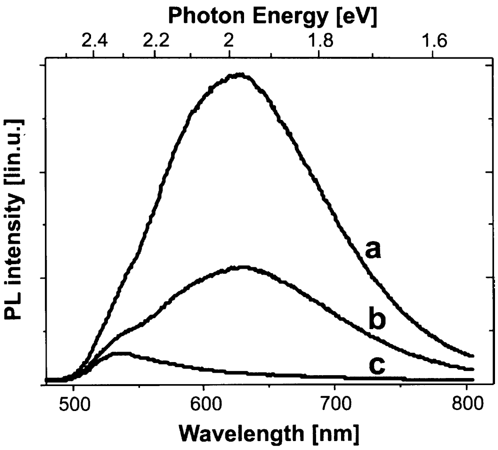

Fig. 2. PL spectra of a Si NCs suspension in ethanol (excitation by 457 nm line of Ar-laser): (a) freshly shaked colloid, (b) 1 h sedimented colloid and (c) filtered colloid.

PSi grains was lost in the filter and possibly only very small Si NCs grains remained in the colloid. The presence of Si NCs is indeed proved by absorption spectroscopy (the continuous absorption spectrum typical for Si NCs is observed slightly blue-shifted compared to non-filtered suspensions) and Raman spectroscopy which indicates Si NCs of mean diameter around 2 nm in both filtered and non-filtered suspensions.

The most peculiar observation in filtered or well-sedimented colloidal suspensions is a green photoluminescence. In Fig. 2 we show how the otherwise hidden green PL band becomes apparent when large grains of PSi go away by sedimentation or more efficiently by filtering. The effect is observed for all solvents used in this study. It is repeatable and not related to the solvent itself (no such PL signal is observed in pure solvents under the same experimental conditions).

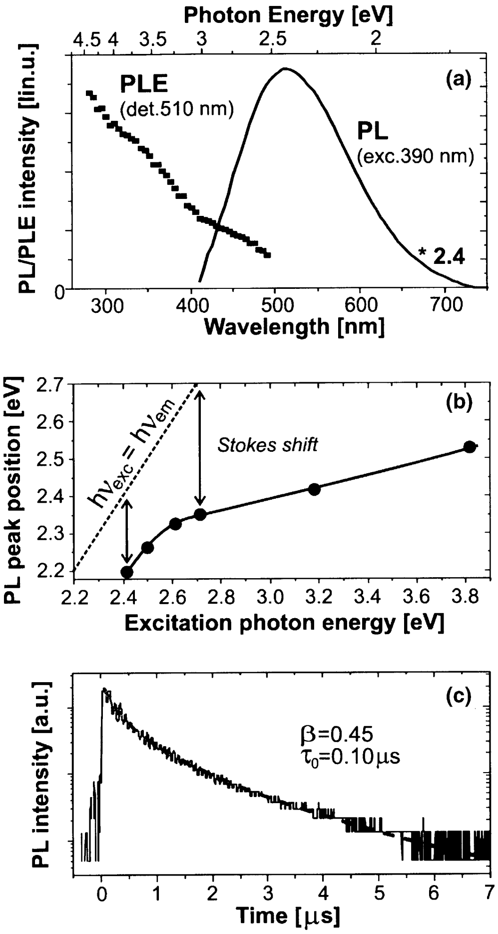

Fig. 3. PL characteristics of a filtered suspension of Si NCs in heptane: (a) PL emission (solid line) excited by a filtered Xe lamp at 390 nm and PL excitation (black dots) detected at 510 nm. (b) PL peak position as a function of excitation photon energy, the Stokes shifts are indicated, (c) Kinetics of PL (at 550 nm) decay after nanosecond pulse excitation (by XeCl excimer laser: 308 nm, 60 kW/cm^2, 5 Hz). The experimental curve (black line) is fitted by a stretch exponential function with parameters $\beta = 0.45$ and $\tau_0 = 0.10\,\mu$s.

The main characteristics of the green PL are summarised in Fig. 3 for Si NCs suspension in heptane. The PL excitation spectrum (Fig. 3a) has no evident resonances and resembles results obtained in other Si nanocrystalline structures (e.g. [2,3]). The green PL peak position (Fig. 3b) shifts with excitation wavelength and the Stokes shift becomes smaller for longer excitation wavelength—such behaviour is typical for an inhomogeneously broadened peak. The kinetics of the PL decay (Fig. 3c) is rather fast—time constant around 0.1 μs—compared to the orange PL band of Si NCs (tens of μs [3]) but it has the same typical non-exponential shape often modelled by a stretch-exponential function.

What is the mechanism of the green PL? When adopting the model of Wolkin et al. [4] the above described experimental characteristics suggest that the green PL is connected with the presence of small Si NCs (diameter of about 2 nm) in which Si═O surface centres (responsible for orange PL) are no more affecting radiative recombination of electron-hole pairs in the core of NCs. We have to mention that there are several well-described observations of green (or even blue) PL of Si nanocrystals in the literature, e.g. in porous Si [2,4], Si colloids made by gas evaporation [5], Si NCs synthesized in inverse micelles [6] or in sterically stabilized Si NCs made by thermal degradation of diphenylsilane [7].

The reason why surface traps are not effective in our small Si grains has to be investigated in the future. Here we can speculate that the surface of very small Si NCs (not stacked in large aggregates) get relaxed in a colloidal suspension. Consequently the Si═O bonds, which are stable only under stress in the silicon–silica interface, are replaced by ordinary Si–O–Si or Si–OH bonds. Also carbon chains of solvent molecules can take part in passivation of the surface bonds of Si NCs, very much like sterical stabilization described by Holmes et al. [7], The advantage of such green-light emitting Si NCs is that the emission rate is much higher than for those emitting orange PL and therefore they are more favourable for construction of optoelectronic devices.

The green PL emission of the Si NCs can be studied by means of single quantum dot spectroscopy by dispersing a diluted suspension of Si NCs on ultra-clean substrates (see Fig. 4a). The green emission remains stable even after evaporation of the solvent. Our single Si NCs experiments were described in [8]. The main observation that proves the single nanocrystal origin of the observed PL emission is an intermittence effect (ON–OFF blinking) and a high value of the fluorescence auto-correlation function. The single Si NC spectra have asymetrically-enlarged shape to lower energies with a possible low-energy sub-band 120 meV below the main peak. Similar single Si NC spectra were observed by English et al. [9] and the sub-band was explained as a Si–O–Si vibrational feature.

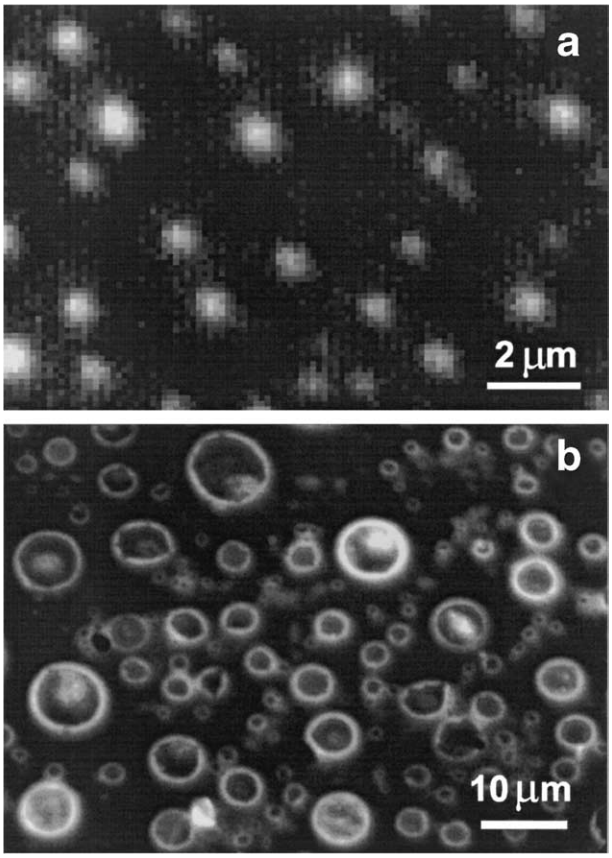

Fig. 4. Micro-PL images (objective lens 100 × /0.73, excitation 325 nm) of Si NCs deposited from isobutanol colloidal suspension on a cleaned fused silica substrate: (a) Dispersed individual Si NC particles from highly diluted suspension (the size of emitting dots corresponds to the diffraction limited spots), (b) Self-organised ring resonators from deposition of concentrated suspension. (Optical resolution of the imaging system is about 0.5 μm.)

Si NCs in colloidal suspensions can be used as building blocks of various interesting photonic structures. Here we show for example micron-sized ring resonators (Fig. 4b) formed by self-assembly during evaporation of isobutanol suspension deposited onto a clean fused silica substrate. Under optimal conditions almost perfect resonators are formed in which spectral narrowing due to resonance effects is observed. For example the most intense ring in Fig. 4b has a PL spectrum almost three times narrower and more than twice as intense as the PL outside the resonator ring (details will be published separately). Other examples of interesting structures are highly concentrated layers of Si NCs formed in a porous SiO_2 matrix by mixing PSi powder with commercially available spin-on-glass. This sol–gel method creates samples with exceptionally high concentrations of Si NCs (up to 45 vol.%) in which optical gain was observed [10]. A disadvantage of the sol-gel structures is inhomogeneity, which causes diffusion of propagating light.

4. Conclusions

Production of colloidal suspensions of Si NCs from pulverized porous Si layers presents an inexpensive and fast way to produce important amounts of light-emitting Si-based nanomaterial. It can be used as building blocks of various nanostructures with promising optoelectronic applications. Moreover, an interesting blue-shift of the PL from the orange to the green spectral region is easily achieved in these materials.

There are however many technological aspects to improve. In particular, an efficient method to break the micrometer-sized grains of PSi into sub-micron parts has to be found. One possible way to be investigated is exploitation of spontaneous or induced charging of Si grains in colloids [11].

Further development of chemistry and physics of colloidal silicon materials is important not only from the point of view of Si-based optoelectronics but also for possible application of bio-compatible and bio-degradable Si nanostructures in bio-nanomaterials.

Acknowledgements

This work was supported by GACR (202/03/0789), GA AVCR (IAA1010316 and IAA1010413) and the Ministry of Education CR (projects LNOOA141 and ME 486). Partial funding was received from the Swedish Research Council (VR) and the Royal Swedish Academy of Sciences. One of the authors (JV) thanks J. Buršík and V. Machovič for technical assistance.

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