New Journal of Physics
The open-access journal for physics

On the origin of the fast photoluminescence band in small silicon nanoparticles

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New Journal of Physics **10** (2008) 073022 (6pp)
Received 13 February 2008
Published 11 July 2008
Online at http://www.njp.org/
doi:10.1088/1367-2630/10/7/073022

Abstract. Colloidal suspensions of small silicon nanoparticles (diameter around 2 nm) with fast and efficient ultraviolet–blue photoluminescence (PL) band are fabricated by enhanced electrochemical etching of Si wafers. The detailed study of photoluminescence excitation spectra in a wide range of excitation photon energies (270–420 nm) reveals specific behavior of the Stokes shift of the fast PL band that agrees well with theoretical calculation of optical transitions in small silicon nanocrystals and is distinct from emission of silicon dioxide defects.

Efficient photoluminescence (PL) of porous silicon (PSi)—first observed by Canham [1]—provoked intensive research on silicon-based nanocrystalline materials. There are mainly two types of PL emission in Si nanostructures at room temperature. The yellow–orange–red PL band with a slow decay of the order of μs to ms (the so-called ‘slow band’, abbreviated as the S-band) is usually dominant and therefore attracts the most attention [2, 3], while the fast blue–green PL band (the so-called F-band with a characteristic decay time on the order of ns) is observed and reported infrequently [4, 5] (predominantly in rapidly oxidized porous silicon

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1367-2630/08/073022+06$30.00

structures, for a review see e.g. [6, 7]). The F-band has been interpreted in the past as two distinct mechanisms: (i) intrinsic optical recombinations in ultrasmall Si nanoparticles [8, 9] (with the strong quantum-confinement effect and a large bandgap opening) or (ii) recombinations in defective silicon oxide particles [5]. It has been considered difficult—if not impossible—to distinguish the correct model for the F-band in a given Si nanostructure. However, since the F-band exhibits attractive features (high efficiency and fast decay) for potential application in silicon nanophotonics, it is desirable to throw light on its origin.

In this paper, we present a study of the F-band emission in small nanoparticles extracted from porous silicon. The most important feature is shown to be the specific behavior of the PL excitation spectra, namely, the breakdown in the Stokes shift size-dependence for particles with diameter about 1.4 nm and smaller. This observation matches closely the recently published numerical calculations by Wang *et al* [10].

PSi was prepared by electrochemical etching of Si wafers ($\langle 100\rangle$ p-type, $\rho \sim 0.1\,\Omega\,\mathrm{cm}$) in a mixture of HF (50%), ethanol (UV grade) and hydrogen peroxide (30% aqueous solution), using a volume ratio of (13 : 37 : 2). Continuous stirring and a relatively low etching current density ($2.3\,\mathrm{mA\,cm^{-2}}$) was applied during the etching (2 h). In addition, the freshly prepared PSi was post-etched in hydrogen peroxide for 20 min in order to obtain higher porosity, i.e. smaller mean diameter of Si nanoparticles. Subsequently, PSi powder was obtained by mechanical removal of the PSi film from the Si substrate. Colloidal suspension was prepared by pouring ethanol onto the PSi powder and stirring in an ultrasonic bath. In order to remove bigger grains of PSi from the suspension, we applied filtering of supernatant part of the sedimented colloidal suspension by membranes with pores of 100 nm in diameter (Millex millipore). This procedure gives a low-concentrated, optically clear suspension [11].

For comparison, we also studied colloidal suspensions of Si nanocrystals prepared via quite a different approach—a prolonged chemical etching (in a mixture of HF and cyclohexane, without applying electrical current) of Si particles created by the pyrolysis of silane [12, 13]. Nearly identical PL properties are observed for the two differently fabricated suspensions, but in this paper, we only present the results on PSi suspensions.

PL emission and excitation spectra of PSi suspensions were studied at room temperature in 1 cm quartz cuvettes using a fluorescence spectrometer (Fluoromax-3, Horiba Jobin-Yvon), where a continuous Xe lamp is used for excitation. The excitation and detection bandwidths were set at 4 nm. For each experimental setting, a reference sample containing clear solvent was measured and used for subtracting the Raman-scattering signal superimposed on the PL spectra. All spectra were also corrected for the spectral sensitivity of the apparatus and changes of the excitation power with wavelength. The PL spectra are presented in the photon energy scale but measured with the constant slit width in wavelength. Therefore, the spectral density must be corrected by multiplying the spectra by λ^2 when transforming wavelength scale to photon energy. (The upper wavelength scale in the figures presented is added just for fast orientation of readers.)

The small mean size of Si nanoparticles under study manifests itself through a dominant short-wavelength yellow PL band peaked at around 580 nm, but also a pronounced blue F-band at 400 nm can be seen (figure 1). While the yellow S-band is dominant in non-filtered suspension (figure 1), after filtering this band almost completely disappeared and exclusively the blue F-band could be observed (see figure 2).

To obtain information on the size of the nanoparticles that resulted from filtration, we dropped a small amount of the filtered suspension onto a substrate of highly oriented pyrolytic

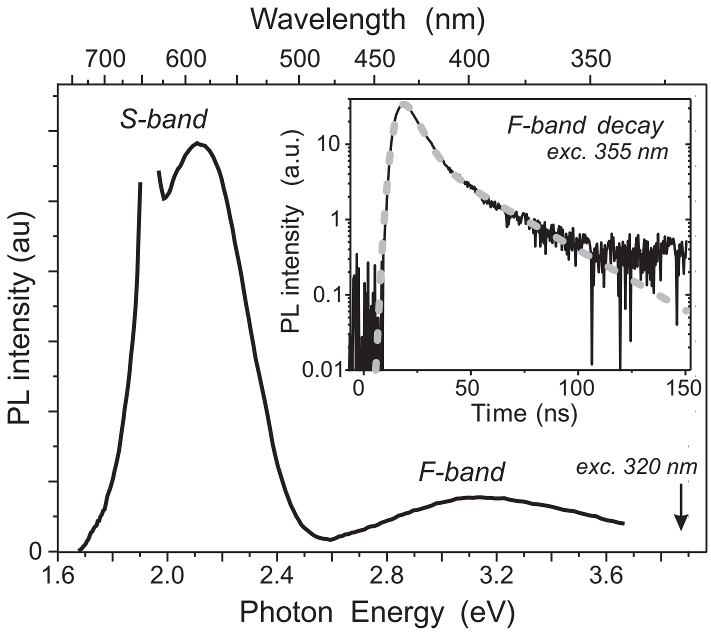

Figure 1. PL spectrum of a (non-filtered) PSi/ethanol suspension excited at 320 nm. The inset demonstrates the fast dynamics of the blue F-band (dotted curve is a fit with the double-exponential decay $\tau_1 = 2.7$ ns, $\tau_2 = 27$ ns (6%) convoluted with the 7 ns and 355 nm pump pulses).

graphite (HOPG) and let the ethanol evaporate. Subsequently, we visualized the HOPG surface using an Agilent 5500 atomic force microscope (AFM). The topography image (figure 3) shows clearly resolved particles at a height of 1–2 nm (their lateral dimensions are seemingly much larger due to AFM tip-convolution). However, this observation does not solve the question whether they are Si nanoparticles (probably covered with a SiO_2 shell) or (fully oxidized) SiO_2 nanospheres.

To resolve this problem, we take advantage of the fact that, besides the difference in PL decay time, the F- and S-bands have different spectral behaviors. While the S-band has an almost stable position under different excitation wavelengths, the F-band peak is shifted with the excitation wavelength. The shift between the excitation photon energy and the PL peak energy, called the Stokes shift, is the important quantity we extracted from the PL spectra. If we assume that our sample contains a relatively broad distribution of nanocrystal sizes (figure 3), then the PL spectrum is strongly affected by an inhomogeneous broadening. With increasing excitation photon energy, smaller and smaller nanocrystals (with wider bandgap) can be excited that contribute to the PL spectrum. In order to roughly eliminate the inhomogeneous broadening and to see the PL contribution of certain particle sizes, we calculate the differences of PL spectra excited with λ_{exc} and $(\lambda_{exc} - 10)$ nm. Some of the differential PL spectra are plotted in figure 2(b).

In figure 4, we have plotted the differential PL peak energies versus excitation photon energies. The Stokes shift increases slowly with increasing excitation photon energy from about 0.2 eV at 2.5 eV up to about 0.4 eV at 3.5 eV. The most interesting feature is found for excitation around 3.7 eV, where the differential PL peak starts moving backward to low

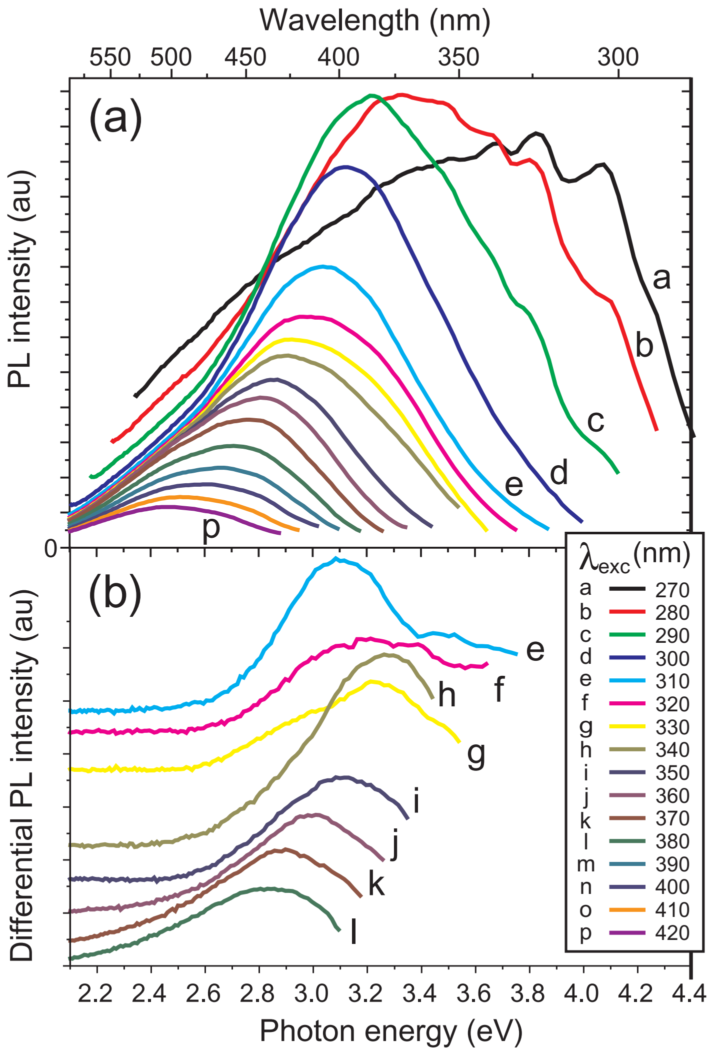

Figure 2. (a) PL spectra of a filtered PSi/ethanol suspension detected under excitation wavelengths ranging from 270 to 420 nm with a step of 10 nm. (b) Differential PL spectra calculated as a difference between neighboring spectra from the upper panel.

energy (consequently greatly enhancing the Stokes shift). Comparison with the Stokes shift theoretically calculated for nanometre-sized Si nanoparticles in [10] (circles in figure 4) shows a striking agreement between the experiment and the theory up to the excitation photon energy of about 4 eV. The calculation by Wang *et al* [10] was based on self-consistent-charge density-functional tight-binding (SCC-DFTB) structural optimization of the ground states of Si nanoparticles and a time-dependent linear response extension of the DFTB scheme applied for studying the excited states. The resulting unusual size-dependence of optical emission gaps of the small hydrogenated Si nanoparticles is ascribed to the strong excited-state structure relaxation in the particle core region, due to considerable geometrical distortions in the excited state (the change in Si–Si distances) [10]. For larger sizes, the increased structural rigidity leads to similar size-dependence of both the absorption and the emission bandgaps.

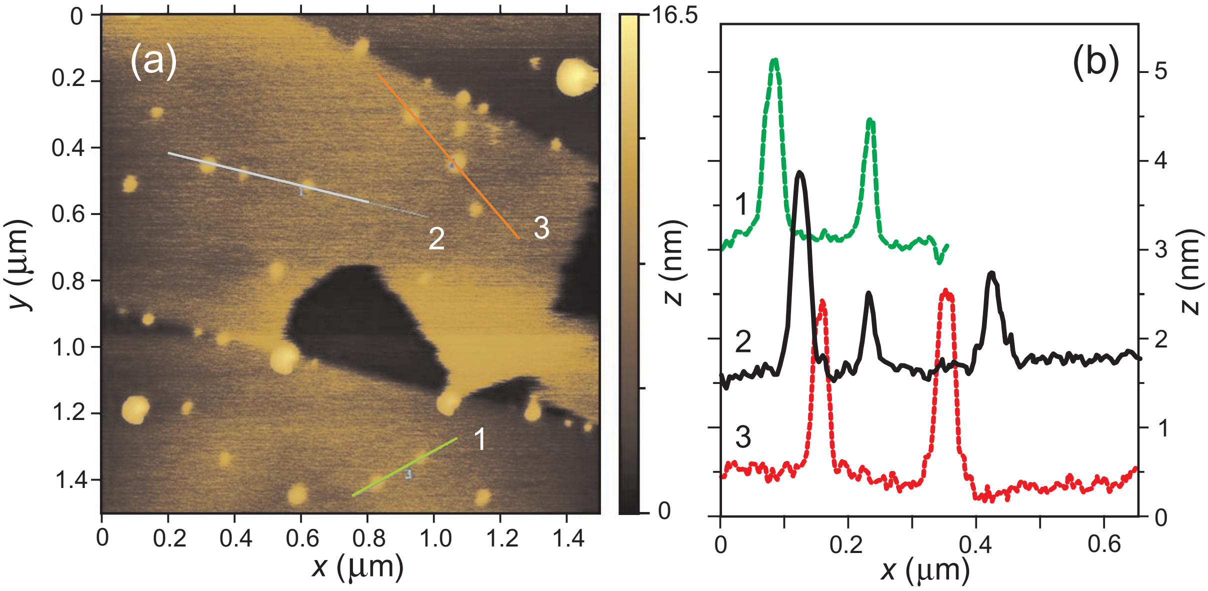

Figure 3. (a) AFM image of PSi nanoparticles dispersed on HOPG. (b) Cross sections along the lines shown in (a) reveal particles with size distribution between 1 and 2 nm. The curves are displaced vertically for clarity.

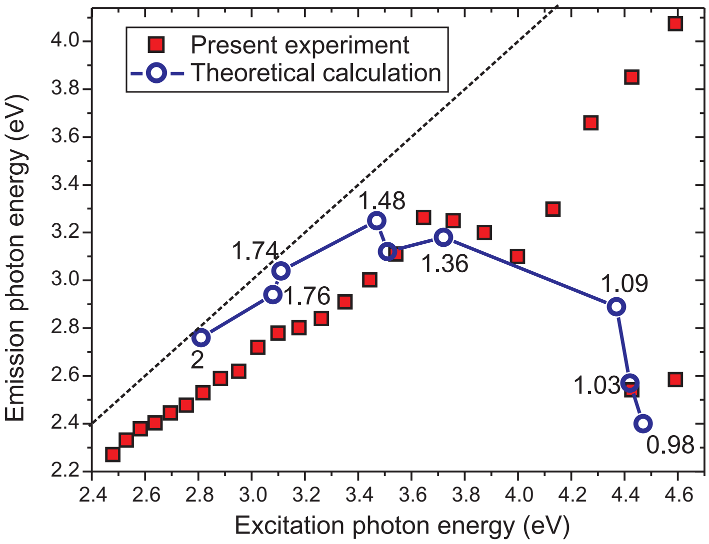

Figure 4. Differential PL peak energy as a function of the excitation photon energy (rectangles) compared with theoretical calculations (dots and line) of Si clusters taken from [10]—the size in nm is indicated at each calculated point. The dashed line indicates equal excitation and photon energy and the Stokes shift is the vertical distance of an experimental point below the line.

This agreement strongly indicates that the origin of the F-band, at least in the colloidal suspensions under investigation, lies in small Si nanocrystals rather than in defective SiO_2. For excitation photon energies above 4 eV, the comparison is hampered because the differential PL spectrum starts becoming more complicated than just exhibiting a single peak (see figure 2(a)).

The reason why there are several PL peaks for Si nanoparticles with diameter around 1 nm and smaller is not clear at present. There may be several stable conformations of such small clusters (depending on the surface passivation) with different energies of optical transitions.

In conclusion, our study of PL excitation spectra of the UV–blue emission band of Si-related nanostructures strongly indicates that the origin of this band lies in small silicon nanocrystals (around 2 nm in diameter), in which structure distortion takes place. The F-band emission of Si nanocrystals possesses many advantages useful for potential applications. Namely, high efficiency and short lifetime that produce much higher PL-emission rate compared to that of the S-band. Moreover, the emission is located partly in the UV–B spectral region, in which semiconductor light sources are still not commonly available.

Acknowledgments

This work was supported by the Czech Ministry of education, youth and sports through the research centre LC510 and the research plans MSM0021620835 and 60840770022, the project 202/07/0818 of the Grant Agency of the Czech Republic and the projects IAA101120804 and KAN401220801 of the Grant Agency of the Academy of Sciences. Research carried out in the Institute of Physics was supported by the Institutional Research Plan AV0Z10100521.

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