

In situ passivation and blue luminescence of silicon clusters using a cluster beam/H₂O codeposition production method

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(Received 18 March 2009; accepted 9 June 2009; published online 29 June 2009)

Si clusters are produced in a gas aggregation source and fly through ultrahigh vacuum onto a cold target where they are codeposited with water vapor. Melting of the ice yields immediately a suspension of nanoparticles that emits intense, nondegrading luminescence in the blue wavelength range. Spectroscopic analysis reveals a Si/SiO core-shell structure where the luminescence stems from oxygen deficient defects. The main advantage of our production method is that it yields the luminescent Si nanoparticles in one step. © 2009 American Institute of Physics.

[DOI: [10.1063/1.3167355](https://doi.org/10.1063/1.3167355)]

The process of light emission from materials with an indirect band gap in the bulk has attracted much interest both from a fundamental point of view and from the prospect of applications.^{1,2} Since the discovery of luminescence from porous silicon at room temperature^{3,4} twenty years ago, fabrication of devices such as silicon-based light emitting diodes (Ref. 5) and lasers⁶ has been achieved, and a large variety of types of photoluminescent silicon have been reported in the literature. These include nanowires and nanorods,^{7–13} Si/SiO₂, Si/SiOH sandwich, and core-shell systems,^{14–16} as well as Si clusters produced by laser photolysis^{17,18} or by Si ion implantation in silica glass.^{19,20} Furthermore, luminescent Si quantum dots in solutions have been investigated.^{21–23} Nanoparticles in solution receive great attention because of applications in biological imaging and diagnostic labeling.²⁴

In all the above-mentioned examples the production method plays a crucial role in the way the luminescence wavelength and luminescence efficiency is controlled. Some industrial production methods require specific conditions. For instance, in complementary metal-oxide-semiconductor (CMOS) processing, a maximum process temperature of only 450 °C is allowed. The compatibility with the CMOS production process will become important because integration of light emitters is one of the major goals on the road map in semiconductor industries. This is because the performance of electronic integrated circuits is expected to be greatly increased by using optical signal transmission.²⁵

While the origins of the luminescence of porous silicon are still debated, the imperative of quantum confinement is generally accepted.²⁶ Free Si clusters down to the size of a few atoms can be produced in molecular beam machines.^{17,27–31} A further and major requirement to achieve luminescence from Si is a suitable passivation of the surface.³² Pure free Si clusters exhibit dangling bonds that efficiently quench luminescence.³³ In this paper we report on a combination of the cluster beam approach and a passivation technique that overcomes this limitation. Central to this method is the *in situ* chemical interaction between the surface of pure silicon clusters and a passivation agent. The method yields luminescent clusters in aqueous suspensions

immediately and the luminescence intensity remains stable over a period of more than three months. High temperature treatments or lengthy oxidation times are not required. The passivation agents are interchangeable and doping via further codeposition is possible.³⁴ Thus, our method provides great flexibility, control and, potentially, an alternative to ion implantation.

First, neutral and charged clusters were produced in an ultrahigh vacuum (UHV) apparatus by dc sputtering from a *p*-doped Si target in an argon-helium atmosphere at pressures of typically 10–15 mbar.^{30,31} The Si clusters then flew through an aerodynamic lens system³⁵ and differential pumping stages into two UHV chambers, of which the first housed a crystal film-thickness sensor (XTM) mounted on a linear translation stage for moving it in and out of the beam and the second chamber housed a cold finger that could be cooled to 80 K using liquid nitrogen. Both UHV chambers were evacuated to a base pressure of 1×10^{-9} mbar before the nanoparticle production started. A few millimeters away from the cold finger is a capillary leading to a needle valve and a water reservoir outside the vacuum chamber. Before production started the flux of Si clusters was monitored using the XTM which then was moved out of the beam to allow the clusters to reach the cold finger. The cold finger was cooled to 80 K and the clusters were codeposited with a vapor stream of de-ionized water flowing at approximately 0.5 ml/h for half an hour. Thereafter, the cold finger was warmed up to room temperature and the melted water was collected in a bottle. A schematic of our apparatus is shown in Fig. 1.

The photoluminescence (PL) spectra of the liquid samples were recorded using a Jobin Yvon FluoroMax-P

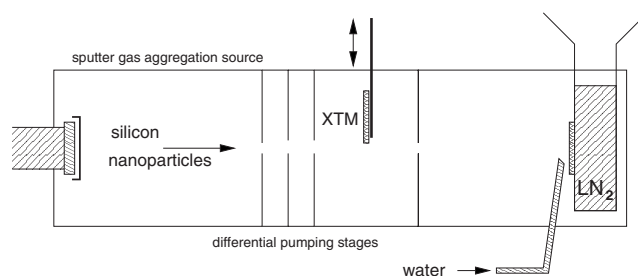


FIG. 1. Schematic of the experimental setup.

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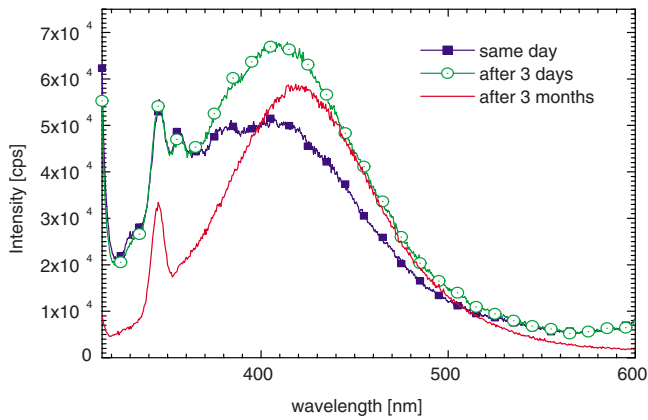


FIG. 2. (Color online) PL spectra recorded three hours, three days, and three months after sample preparation. The excitation wavelength was 307.5 nm.

spectrometer. Figure 2 shows the PL spectra of the sample under UV light exposure. The first spectrum was recorded after approximately 1–2 h after deposition and the melting of the ice, the second after three days, and the third after three months. The samples were stored in bottles under air at room temperature. The spectrum of the freshest sample consists of a prominent band with peaks at 350, 365, 380, and 407.5 nm. After three days a redshift in the band maximum from 407.5 to 410 nm was observed. This shift increased further with time. Measurement of different samples revealed that a peak position around 420 nm was reached typically after one to two weeks up to a few months. Further aging produced no further shift. Figure 2 also shows that aging affected the shape of the spectral features. The rugged features with the sharp peaks at 365 and 380 nm in the fresh sample became smeared out after three days and completely vanished after three months, resulting in a smooth band that can be fitted using a Lorentzian function. The position of the sharp peak at 350 nm shifts with the excitation wavelength and is due to the Raman Stokes resonance of water. Remarkably, over time the overall luminescence intensity does not significantly change.

The luminescence band at 420 nm is assigned to the $T_1 \rightarrow S_0$ transition of the twofold coordinated Si in SiO_2 (O–Si–O) due to the spectral similarity of the peak positions, and the line widths with values reported for defect-rich SiO_2 in the literature (2.6–3.0 eV for peak positions).^{36–39} Similar bands have also been reported from porous Si that was oxidized and annealed at 880 °C (Ref. 40) and depending on the production method, the band maxima ranges from 400 to 460 nm.⁷ The fact that the luminescence band shifted over time and changed its structure further supports our assignment of the luminescence. The defects slowly relax into lower energy structural configurations. Hence, we interpret the Lorentzian-shaped emission band as due to an inhomogeneously broadened spectrum that is caused by the distribution of bond angles and bond lengths of the optically active O–Si–O sites.

However, an important difference from the defect luminescence in silica was observed. The $T_1 \rightarrow S_0$ transition of the twofold coordinated Si in SiO_2 has a distinct excitation energy of 5 eV (250 nm).³⁶ We are able to excite 420 nm luminescence using 5 eV UV light, but we obtain a four times higher luminescence yield using lower excitation energies. The PL excitation (PLE) spectrum for luminescence at

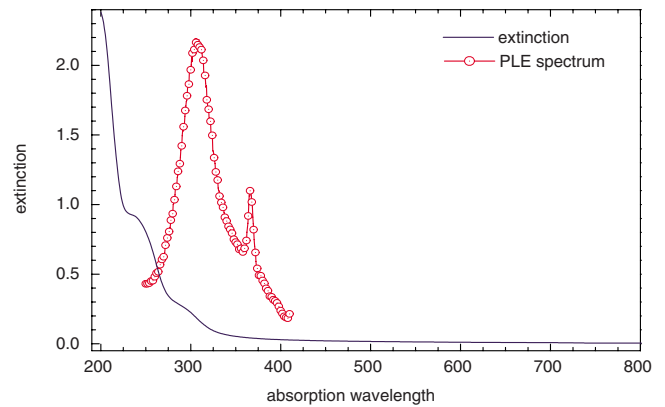


FIG. 3. (Color online) UV/visible absorption spectrum. The dotted line is the PLE spectrum for 420 nm luminescence with a maximum at 307.5 nm. The sharp feature at 365 nm belongs to the excitation of the Raman Stokes line at 420 nm.

420 nm in Fig. 3 shows this maximum at 307.5 nm. An excitation band peaking at 300 nm has not been reported in the literature before. Therefore we conclude that the $T_1 \rightarrow S_0$ emission is mainly excited via an energy transfer channel from an unknown excited state that is definitely different from SiO_2 .

To obtain further information UV/visible absorption spectra were recorded (Fig. 3). The samples are transparent down to 320 nm and show a steep onset in absorption at 330 nm.²² This onset of absorption gives evidence for the presence of pure silicon in the sample. SiO_2 has a much larger band gap energy and is completely transparent in the spectral region shown in Fig. 3. Thus, our particles have a core-shell structure with a Si core and a SiO_2 surface (Fig. 4). The band gap energy derived from our UV/visible spectra suggests a size of less than 1.5 nm diameter of the Si core.^{32,41}

The distinct PLE energy at 307.5 nm is close to the band gap. This and the high luminescence efficiency exhibit typical characteristics of excitons. We do not observe much variation in the peak wavelength between samples that contain nanoparticles with different size distributions, indicating that size effects are small.⁴² Consequently, we tentatively assign the excitation band to interface excitons because these have a low sensitivity to changes in the overall nanoparticle dimension. Band gap calculations show that the levels involved rather depend on the geometric structure,^{43,44} espe-

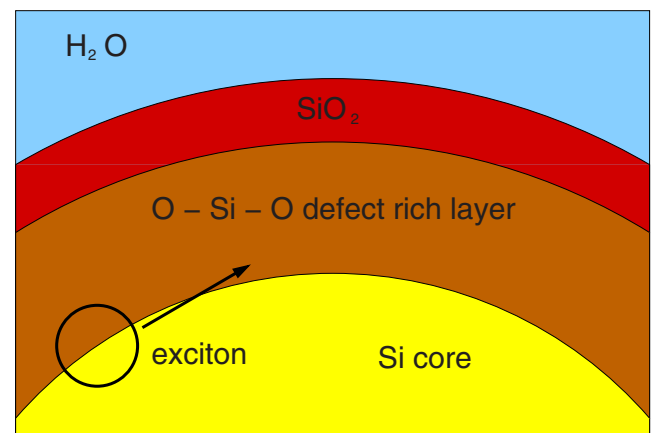


FIG. 4. (Color online) Schematic of the energy transfer mechanism.

cially on whether the oxygen atoms are located within the Si plane and bridge two Si atoms or they are above the Si plane.⁴⁵

Finally, we note that clusters directly deposited without water and oxidized in ambient air did not show luminescence. Oxidation of silicon in air and in water can be regarded as a two-step process that involves the formation of reactive sites in the primary process^{46,47} and progression via diffusion of the oxidant in the second step.⁴⁸ We believe that the following differences between oxidation in air and in water are important for luminescence activity: (i) oxidation in air is governed by diffusion of O₂ which is faster than for H₂O, (ii) in water, the reactions at the surface reach equilibrium much quicker than in air due to the higher density in the liquid which effectively stops the oxidation to further progress, and (iii) a protective layer is formed in water due to dipole forces leading to physisorption of H₂O molecules.

Our findings suggest a simple and cost-effective method for producing luminescent Si. Nondegrading PL is difficult to achieve even in solid samples⁴⁹ and a remarkable advantage of the samples produced by our method is the stability in water, suggesting applications in biological environments.

K.v.H. acknowledges funding by a Royal Society Research Grant (Grant No. RP16G0214).

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