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All-silicon solid films with highly efficient and tunable full-color photoluminescence

Jing Wang,[a,b] Xinglong Wu,[b,*] Tinghui Li[b,c] and Paul K. Chu[d]

[a]*School of Electronic Science and Engineering, Nanjing University of Posts & Telecommunications, Nanjing 210003, People's Republic of China*

[b]*Key Laboratory of Modern Acoustics, MOE, Institute of Acoustics, Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China*

[c]*College of Electronic Engineering, Guangxi Normal University, Guilin 541004, People's Republic of China*

[d]*Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China*

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Silicon nanocrystals with the most probable diameter of 2 nm are surface passivated by glycerol and deposited on porous silicon (PS) substrate with intrinsic red photoluminescence. Tunable full-color emission is observed from this composite film and the quantum efficiency varies from 17% to 28% under different excitation wavelengths. Spectral analysis reveals that the full-color emission arises from combined quantum confinement in the silicon and PS nanocrystals with glycerol passivation. The nanostructured all-silicon film is robust and compatible with microelectronic processing.

Keywords: Si nanocrystals; Glycerol passivation; Quantum confinement effect; Tunable photoluminescence

Low-dimensional silicon nanomaterials, including nanowires, nanosheets, nanoribbons and nanocrystals (NCs), have been extensively investigated, and silicon NCs in particular have attracted much interest. For instance, their optical characteristics, which are based on their electronic states, have been studied and found to be potentially useful for light emitting devices [1,2], bioprobes [3,4], fluorescence detectors [5] and spintronic devices [6]. According to previous studies on silicon NCs fabricated by laser irradiation [7], plasmon-enhanced chemical vapor deposition [8], the non-thermal plasmas approach [1,9], electrochemical etching [10], chemical dissolution [11], annealing [12] and scanning transmission electron microscopic lithography [6], the silicon NC surface is chemically active and often bonded to oxygen atoms [7,10], hydrogen atoms [8,11,12], hydroxyl groups [8] or other groups [7,11]. Surface-modified silicon NCs can exhibit different optoelectronic properties due to changes in the band structure, suggesting large potential in different applications [6,8,13]. Various types of hybrid silicon NCs have been produced, such as hydrogenated silicon NCs [8,11,14], oxygen-passivated Si NCs [1,12], organic group-terminated NCs [1,3,7,12,15], and silicon NCs embedded in Si-based matrices such as SiO_2 and silicon nitride [12,13].

With regard to the photonic properties, light emission has been observed from silicon NCs due to various mechanisms, such as surface states [16,17], defects [12], the quantum confinement effect [8,12] and interface localized states [13]. Light emission from silicon nanostructures in the infrared [2,8,9,13,15], red [1,2,7,10,12], yellow [7,11], green [7,18] and blue [10,16] ranges have recently been discovered and, as a result, a number of silicon-based light emitting devices [1,10,12,19] have been proposed [1,2,19]. The fabrication of silicon nanostructures is compatible with that practiced by the microelectronic and biomedical [3] industries, and can be readily integrated with other silicon-based devices. Consequently, an all-silicon structure capable of producing tunable and full-color emission has immense potential. In this work, surface-modified silicon NCs are embedded in porous silicon (PS) to produce a solid film that yields tunable full-color photoluminescence (PL) with a quantum efficiency of better than 17%. Our investigation elucidates that the tunable multi-color emission

* Corresponding author. Tel.: +86 2583686303; e-mail: hkxlwu@nju.edu.cn

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arises from the quantum confinement on silicon and PS NCs with glycerol passivation.

The approach of fabricating silicon NC colloid is similar to that used in fabricating 3C–SiC NCs [20,21]. Two major differences are the proportions of HF and HNO_3 in the etching solution, which are HF (40%):HNO_3 (65%) = 20:1 in volume, and the quantities of the chemicals. A 20 ml volume of the etching liquid was added to silicon powders weighing 8 g. The silicon powders were dissolved and ultrasonically treated to obtain silicon NCs dispersed in water. Glycerol was then added to the water suspension containing the silicon NCs to fabricate a surface glycerol-passivated NC film as described previously, because direct dry treatment of the NC suspension will lead to disappearance of the strong PL due to various surface non-radiative defects [20]. The PS was fabricated by electrochemical etching of a piece of p-type Si wafer (<100 > and 10 Ω cm) in a mixture of HF (40% in volume) and ethanol (volume ratio of 1 to 2) at a current of 40 mA for 20 min [22]. The glycerol-passivated NCs were subsequently added on the PS substrate.

The NCs were characterized using a JEOL JEM-2100 transmission electron microscope. The sample was prepared by putting a drop of the water suspension on a copper grid. The PL and PL excitation (PLE) spectra were acquired on an FLS920 fluorescence spectrophotometer (Edinburgh Instruments) equipped with a 450 W Xe lamp with a resolution of 1 nm. All the spectra were corrected for the response of the measurement system. X-ray photoelectronic spectra (XPS) was carried out on a Thermo Fisher Scientific photoelectron spectrometer. The narrow-scan spectra were obtained under ultrahigh vacuum conditions using monochromatic Al K_α X-ray radiation.

Figure 1(a) displays a transmission electron microscopy (TEM) image of the silicon NCs taken at an accelerating voltage of 200 kV. Most of them have a diameter of less than 2 nm and some are even smaller than 1 nm. Figure 1(b) depicts two high-resolution TEM images of the silicon NCs. They are highly crystalline, with lattice fringes corresponding to the {2 1 0} and {2 2 0} planes of Si. The size distribution in Figure 1(d) shows that the diameter of the silicon NCs varies between 1 and 4 nm, and there are no NCs larger than 4 nm. The Gaussian fit in Figure 1(d) shows that the most probable diameter is 2 nm. Since NCs smaller than 1 nm may be missed due to the TEM resolution, the actual most probable size may be less than 2 nm.

The PL/PLE spectra acquired from the silicon NC colloid, silicon NCs/glycerol film and silicon NCs/glycerol/PS film are shown in Figure 2. As shown in the PL spectra of the silicon NC colloid formed at pH 4 in Figure 2(a), as the excitation wavelength is increased from 320 to 420 nm, the PL peak changes from 400 to 520 nm. There is thus a red shift in the emitted light with increasing excitation wavelength, and the PL peak at 410 nm reaches the maximum intensity at an excitation wavelength of 340 nm. No obvious shift is observed when the excitation wavelength is longer than 440 nm because the intensity of the PL spectra decreases abruptly. Although the band gap of bulk silicon is 1.12 eV (1107 nm), no obvious signal is observed beyond

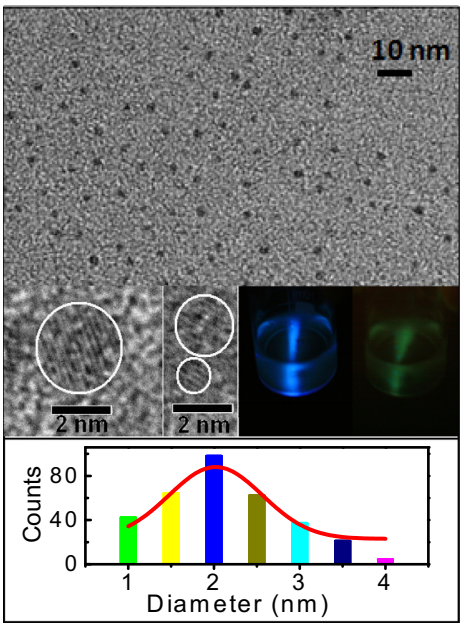

Fig. 1. (a) TEM image of the silicon NCs. (b) Two typical high-resolution TEM images of the silicon NCs. (c) Optical images of the silicon NC colloid excited at 370 and 420 nm, corresponding to emission wavelengths of 450 and 520 nm. (d) Size distribution of the silicon NCs calculated from TEM images. The most probable size of 2 nm is calculated according to Gaussian fitting.

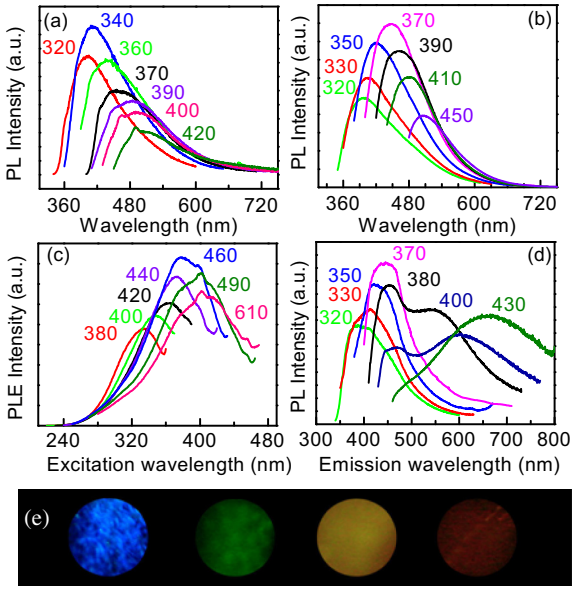

Fig. 2. (a) PL spectra of the silicon NC colloid. (b) PL spectra of the silicon NCs/glycerol solid film. (c) PLE spectra of the silicon NCs/glycerol solid film. (d) PL spectra of the silicon NCs/glycerol/PS solid film. The excitation and emission wavelengths are labeled. (e) Four optical photographs obtained from the silicon NCs/glycerol/PS solid film excited at 350, 380, 400 and 430 nm, corresponding to four different colors: blue (~450 nm), green (~520 nm), yellow (~570 nm) and red (~650 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

550 nm, unlike that observed from PS [21]. This can be explained by the absence of NCs bigger than 4 nm in diameter and most of the NCs having a diameter of