Appl. Phys. A 82, 485–487 (2006)
DOI: 10.1007/s00339-004-3445-9

Applied Physics A
Materials Science & Processing

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Si-based solid blue emitters from 3C-SiC nanocrystals

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Received: 20 August 2005/Accepted: 11 October 2005
Published online: 19 November 2005 • © Springer-Verlag 2005

ABSTRACT A procedure for preparing 3C-SiC/SiO_2 composite nanocrystals embedded in Si matrix that emit blue light is reported. Through electrochemical etching of polycrystalline 3C-SiC wafers followed by ultrasonic treatment in water bath, we fabricated luminescent colloidal 3C-SiC nanocrystals. Porous Si samples that have been naturally oxidized in air for 12 h were immersed in agitated aqueous suspension of 3C-SiC nanocrystals for 10 min and then dried in air, followed by annealing in argon atmosphere to form core-shell structured 3C-SiC/SiO_2 nanocrystals embedded in Si matrix. Our result shows that the luminescence of 3C-SiC/SiO_2 composite nanocrystals is very stable over time or under high temperature. As robust and stable Si-based solid blue-emitters, they have important implications for engineering photonic components in optoelectronics and photonics.

PACS 78.67.Bf; 78.55.Hx; 78.66.Sq

Sincr the first observation of intense visible emission of porous silicon at room temperature in 1990 [1], many researchers have focused on exploring robust and reliable Si-based light emitters for optoelectronic and photonic applications [2, 3]. However, studies show that obtaining strong and stable blue emission from Si quantum dots is very difficult. In comparison, SiC has a much wider band gap (2.2 eV for 3C-SiC) [4], therefore, its photoluminescence (PL) is easily pushed to a short wavelength range according to the quantum confinement effect [5, 6]. Moreover, SiC has ultra chemical and thermal stabilities, particularly suitable for high-temperature and high-power applications [7, 8]. These unique characteristics make SiC nanocrystals be good candidates as blue or UV light emitters. A recent success in producing large and high quality SiC has paved the way for its wide use in high-power, high-frequency and high-temperature applications in electronics [9]. During the past decade, many experiments have been done on luminescence of SiC nanocrystals [10–14]. Due to difficulty in fabrication of SiC nanocrystals and existed complicated surface states, the reported emissions of SiC are supposed as being induced by surface or defect states.

Only recently, luminescent 3C-SiC crystallites with sizes of several nanometers which follow well the quantum confinement effect [15] were fabricated through crushing porous 3C-SiC into individual particles dispersed in water [16]. It provides a simple and reproducible method for controllably producing wavelength tunable luminescent 3C-SiC nanocrystals as building blocks for fundamental uses or technological applications. Based on this method, 3C-SiC/polystyrene luminescent composite films have been synthesized [17]. However, it is not Si-based and thus not suitable for integration into nowadays Si-based microelectronics. In this paper, we report a simple method for preparing core/shell structured 3C-SiC/SiO_2 nanocrystals encapsulated in Si matrix. The achieved systems exhibit blue emission that qualitatively matches those of parent colloidal 3C-SiC nanocrystals, and are ultra-stable over time and under high temperatures. The obtained systems can be expected to have important applications as Si-based light source in optoelectronics.

We ultrasonically dispersed electrochemically etched polycrystaline 3C-SiC wafers into water and obtained luminescent aqueous suspension of 3C-SiC nanocrystals [16]. The etching current density was 40 mA/cm^2. 3 Ω cm *n*-type Si (100) wafers were electrochemically etched in HF–ethanol solution (HF:H_2O:C_2H_5OH=1:1:2) at a current density of 30 mA/cm^2 for 10 min to obtain porous Si (PSi) samples. After naturally oxidized in air for 12 h, the PSi samples were immersed in agitated aqueous suspension of 3C-SiC nanocrystals for 10 min and then dried in air. Each achieved sample was cut into two pieces for comparison. One of them was further annealed in argon atmosphere for 5 min. After PL characterization and stored in air for 10 days, this sample was annealed in nitrogen atmosphere at 400 °C for 5 min. Finally, we annealed it in oxygen atmosphere at 1000 °C for 10 min.

We recorded transmission electron microscopy (TEM) images of 3C-SiC particles through dripping a drop of the 3C-SiC suspension on a graphite grid (Cu mesh). In the microscopy we used a TECNAI_F20 TEM at an acceleration voltage of 200 kV. Figure 1a shows the high resolution transmission electron microscopy (HRTEM) image of one typical particle. This particle was highly crystalline and lattice fringes corresponding to (111) planes of 3C-SiC

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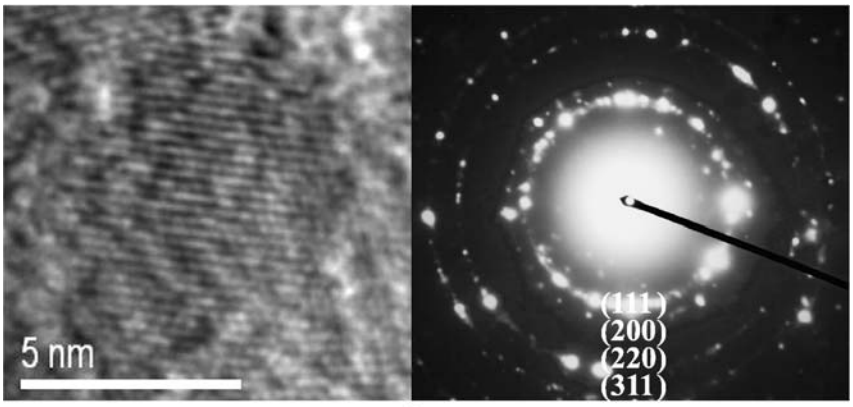

FIGURE 1 (**a**) HRTEM image of a typical 3C-SiC particle from the sample of 3C-SiC suspension. (**b**) Selected area electron diffraction pattern of such particles

can be clearly identified [18]. The selected area electron diffraction (ED) pattern shows ring structure that can be assigned to the diffractions from (111), (200), (220), and (311) planes of 3C-SiC nanocrystals (Fig. 1b). Our TEM observations show that 3C-SiC particles in the suspension were concentrated in sizes, and approximately followed a central distribution in the size range of 1–8 nm for the case with the etching current density of 40 mA/cm^2 [16]. The PL of the colloidal 3C-SiC nanocrystals exhibits clear quantum confinement with continuously tunable emission wavelengths varying from 440 to 560 nm.

Figure 2 shows PL spectra of different 3C-SiC/PSi samples, taken using excitations with the 325 nm line of a He/Cd laser. For un-annealed samples of 3C-SiC nanocrystals embedded in PSi, the PL spectrum exhibits two distinct peaks at 439 and 592 nm, respectively (Fig. 2a). A Gaussian decomposition more clearly displays such two peaks. The 592 nm PL peak is related to surface states formed on the Si=O covalent bond at the surfaces of PSi [19, 20]. The emission band at 439 nm, absent in the PL spectrum of pure PSi, can be ascribed to embedded 3C-SiC nanocrystals, which is less intense and shifted to higher energy side compared with those of the parent colloidal 3C-SiC nanocrystals. Similar shifts in emission spectra have been observed as colloidal Si crystallites were synthesized into Si/polystyrene films [21]. This shift is caused because some large 3C-SiC particles are not introduced into PSi. For samples annealed in argon atmosphere, the PL qualitatively matches those of un-annealed samples (Fig. 2b), no obvious decrease in PL intensity was observed. It should be noted that the PL line deviates from the original symmetry shape. This may be due to aggregations of some 3C-SiC particles during the annealing process. The emission band at 592 nm disappears after annealing. Similar behavior had been observed in previous reports on the investigation of PSi [22].

Figure 3 shows the Fourier transform infrared spectroscopy (FTIR) spectra taken on a Nexus 870 FT-IR spectrometer. The spectrum of the freshly prepared PSi samples shows strong absorption bands near 630–672, 907, and 2100 cm^{-1} (Fig. 3a), associated with the stretching and deformation of Si−H$_n$ (n = 1 − 3), and no peaks related to oxygen exist, indicating that the samples were well passivated by hydrogen. After exposure to air for 12 h, followed by immersion in 3C-SiC suspension and then dried, the 3C-SiC/PSi system shows three new infrared absorption peaks (Fig. 3b). The Si−C peak at 805 cm^{-1} was observed, indicating that the 3C-SiC nanocrystals had been successfully encapsulated in Si matrix. The strong peaks at 472 and 1091 cm^{-1} are related to Si−O−Si bond, while the Si−H$_n$ peaks largely reduce its intensity, showing that the surface of PSi is now passivated upon exposure to air. As a result, we infer that after annealing, 3C-SiC/SiO$_2$ core/shell particles

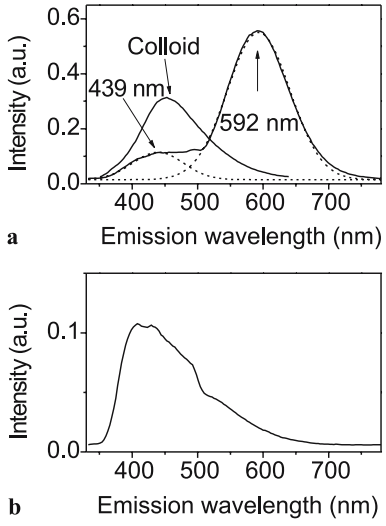

FIGURE 2 (**a**) PL spectrum of un-annealed samples of the 3C-SiC nanocrystals embedded in oxidized PSi. *Dashed lines* are two Gaussian decomposed PL peaks. PL spectrum of the parent aqueous suspension of 3C-SiC nanocrystals is marked as Colloid, whose intensity is depressed by several times. (**b**) PL spectrum of the composite sample annealed in argon atmosphere at 400 °C for 5 min

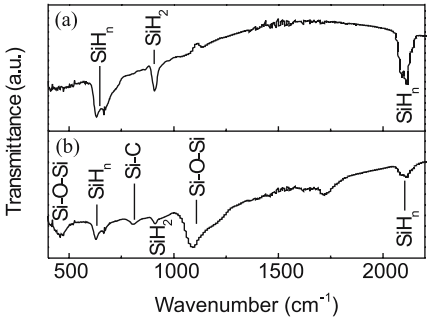

FIGURE 3 FTIR spectra of (**a**) as-etched PSi and (**b**) un-annealed samples of 3C-SiC nanocrystals embedded in oxidized PSi

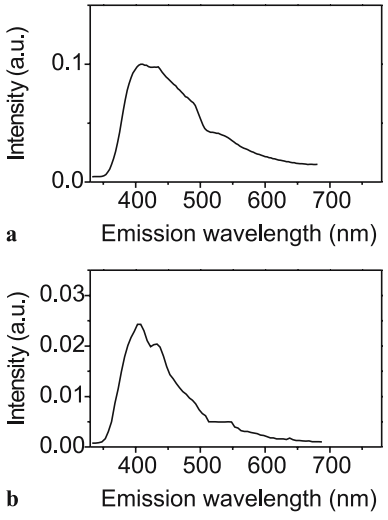

FIGURE 4 PL spectrum of the composite sample annealed in nitrogen atmosphere at 400 °C for 5 min (**a**) and further annealed in oxygen atmosphere at 1000 °C for 10 min (**b**)

encapsulated in Si matrix have been formed.

Since 3C-SiC has a much higher band gap (2.23 eV) compared with Si (1.12 eV), so carriers (electrons and holes) cannot be confined in 3C-SiC particles when they are directly embedded in Si films. To obtain well confined carriers so as to acquire a high emission intensity, we have the PSi samples naturally oxidized first before encapsulating the 3C-SiC nanocrystals in them. The large band gap (9.3 eV) of SiO_2 [23] results in a high potential barrier for carriers within 3C-SiC particles [24].

We have studied the stability of the luminescent 3C-SiC/SiO_2 nanocrystals embedded in Si films, which is an important factor to be considered when they are used as light emitters in optoelectronics. Firstly, the sample annealed in argon atmosphere was stored in air for 10 days. Afterwards, it was annealed in nitrogen atmosphere at 400 °C for 5 min. Its PL showed no detectable variation in intensity or emission wavelength compared with the original sample (Fig. 4a). Similar result was achieved when the sample was annealed in oxygen instead of nitrogen atmosphere. This observation indicates that the luminescent system is stable over time and can still work in high temperature circumstances. However, after annealing in oxygen atmosphere at 1000 °C for 10 min, the PL intensity decreased about 5 times (Fig. 4b), with a greater decrease at longer emission wavelength band with respect to shorter wavelength side. This may be induced by oxidation of partial 3C-SiC nanocrystals.

As nanometer-sized light sources, the luminescent 3C-SiC/SiO_2 crystallites embedded in Si matrix have several superiorities. First of all, they are compatible with Si-based semiconductor devices. Secondly, they are produced using pure 3C-SiC nanocrystals, rather than synthesizing 3C-SiC particles through sputtering or ions implantation processes, in which complicated surface/defect states that change the optical properties can easily be formed [25, 26]. Moreover, as indicated above, the structure of 3C-SiC/SiO_2 nanocrystals embedded in Si film is ultra stable, and can be used at high-temperature devices.

In summary, we have fabricated 3C-SiC/SiO_2 nanocrystals encapsulated in Si matrix that emit blue light. The fabrication method is simple, reproducible and controllable. This kind of composite nanostructured material possesses robust and ultra stable solid-state light emitters, and has important implications for optoelectronic and photonic applications.

One of the authors (J.Y. Fan) thanks Profs. Y.Y. Zhu and S.N. Zhu for their assistance in the TEM observations. This work was supported by the Grants (Nos. 10225416, 60421003 and 60476038) from the Natural Science Foundations of China the LAPEM. Partial support was also from the Major State Basic Research Project No. G001CB3095 of China and Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grants (CERG) #CityU 1137/03E and CityU 1120/04E, and City University of Hong Kong Strategic Research Grant (SRG) #7001642.

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