Available online at www.sciencedirect.com
ScienceDirect
Physics Letters A 360 (2006) 336–338
PHYSICS LETTERS A
www.elsevier.com/locate/pla

Stability of luminescent 3C-SiC nanocrystallites in aqueous solution

J.Y. Fan [a,b], X.L. Wu [a,*], P.Q. Zhao [a,c], Paul K. Chu [b]

[a] National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China
[b] Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
[c] Department of Applied Physics, College of Science, Nanjing University of Technology, Nanjing 210009, China

Received 5 June 2006; received in revised form 1 July 2006; accepted 3 August 2006

Communicated by J. Flouquet

Abstract

We study the long-term stability of luminescent suspended 3C-SiC nanocrystallites. Polycrystalline 3C-SiC wafers were electrochemically etched in HF-ethanol electrolyte and then ultrasonically treated in water to achieve spherical crystallites with diameters of 1–7 nm. The suspended 3C-SiC nanocrystallites exhibit tunable intense emissions which follow well the quantum size effect. After storage in air for over 7 months, partial larger 3C-SiC crystallites aggregate and form precipitates, while smaller ones remain uniformly dispersed in water and retain well luminescent properties. This characteristics makes small 3C-SiC crystallites excellent micro-emitters which are especially useful in biological and medical applications.

PACS: 78.67.Bf; 78.55.-m; 82.45.Yz

Keywords: 3C-SiC nanocrystallites; Photoluminescence; Suspension

Quantum dots have become one of the hottest research topics in recent years because they have huge range of potential applications in nanophotonics and biomedicine [1–3]. According to quantum size effect [4,5], the emission wavelength of semiconductor quantum dots changes with particle size. They have tunable and strong emissions and thus are suitable as micro-emitters used in biotechnology for in vivo cancer targeting and imaging [6,7], long-term imaging of live cells [8], and so on. Compared with other semiconductors, the quantum dots of silicon carbide are superior in several aspects. Firstly, SiC has wide bandgap (2.2 eV for 3C-SiC) as well as ultra thermal and chemical stabilities, so the nanocrystallites can be taken as blue or UV light emitters especially for uses in harsh environments. Next, SiC has low weight, high rigidity, and good biocompatibility [9], thereby being appropriate as biomedical tags.

Much research has recently been done on luminescence property of SiC nanocrystallites using different fabrication methods such as anodization and plasma immersion [10–13]. The obtained emissions from SiC crystallites behaved quite differently in different experiments and were generally attributed to surface or defect centers which were generated in crystal growth or crystallite fabrication processes. Recently, we fabricated suspended 3C-SiC nanocrystals which exhibit intense emissions with wavelength tunable from yellow to UV [14]. Detailed analysis shows that the photoluminescence (PL) originates from band edge recombination of electrons and holes inside single 3C-SiC crystallites and follows well the quantum size effect [15]. This fabrication method is very simple and reproducible, based on which Si-based solid blue luminescent films can be synthesized [16]. In this Letter, we perform a detailed study of long-term stability of 3C-SiC crystallites suspended in water. Our result shows that only partial larger 3C-SiC crystallites tend to aggregate after naturally aged in air. In contrast, smaller ones remain well dispersed and retain their luminescence properties.

We electrochemically etched polycrystalline 3C-SiC wafers in an HF-ethanol (40 wt.% HF: 98 wt.% $C_2H_5OH = 2:1$) electrolyte under UV illumination by a halogen lamp at current den-

---

[*] Corresponding author.
E-mail address: hkxlwu@nju.edu.cn (X.L. Wu).

0375-9601/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physleta.2006.08.006

Fig. 1. Optical image of the newly-prepared water suspension of 3C-SiC nanocrystallites with illumination of room light by using fluorescent lamps.

sity 90 mA/cm^2 (measured after illumination) for 60 min. UV illumination can facilitate generation of holes at SiC surfaces thereby accelerate the etching process [17]. After the anodization the wafer was ultrasonically treated in water for 20 min, where the porous layer on the 3C-SiC surface was crumbled into small crystallites and dispersed in the solution [14]. After performing microstructural and spectroscopic characterization, the 3C-SiC suspension was stored in airtight vessels under air for 7 months. After that it was shortly agitated in ultrasonic bath and PL spectra were measured again. Transmission electron microscopy (TEM) observations were conducted on a TECNAI_F20 TEM at an accelerating voltage of 200 kV. The PL spectra were taken by using a FluoroMax-2 fluorescence spectrometer which has a resolution limit of 1 nm. For comparison, the intensities of Xe lamp lines are normalized. All measurements had been performed at room temperature.

Our TEM observation shows that the fabricated 3C-SiC crystallites are nearly spherical in shapes, with diameters ranging from 1 to 7 nm following an approximate normal distribution [14,15]. High resolution transmission electron microscopy (HRTEM) images indicated that the particles are highly crystalline and have the crystal structure of bulk 3C-SiC. The obtained water solution of 3C-SiC crystallites was uniform, exhibiting a color of weak olivine under illumination of room light from fluorescent lamps (Fig. 1). Room light can be scattered by the suspended 3C-SiC particles. And photons with energies higher than bandgap of 3C-SiC crystallites would result in photoluminescence. These two effects, combined together, cause the color of the suspension. After the storage for over 7 months, some precipitates appear at the bottom of the 3C-SiC solution, suggesting that some particles have aggregated. The remaining solution is still uniform.

Fig. 2 depicts the PL spectra of the as-prepared and stored samples, taken under different excitation energies. For the newly prepared sample, its PL shows continuous redshift with increasing excitation wavelength. The PL curves are broad and asymmetric. Single 3C-SiC nanocrystallites should have narrow emission lines with wavelength dependent on their sizes [18]. However, under one specific excitation many particles with different sizes are excited and contributed to the full emission curve [15]. Because smaller particles have greater optical gaps [4,5], lowering the excitation energy would reduce the number of excitable 3C-SiC crystallites, thereby resulting in the continuous redshift of the PL. No emissions could be observed for excitation energies lower than ∼ 2.48 eV (500 nm) in the as-prepared samples. This result shows that this ∼ 2.48-eV value is near the absorption edge of the largest 3C-SiC particles (∼ 7 nm) in the solution, thus no particles can be excited for lower energies. The maximum emission wavelength is 544 nm, which corresponds to the optical gap of the largest 3C-SiC particles. It is very close to the bulk bandgap and thus lies in the weak confinement regime [1]. Since the radius of the largest suspended SiC nanocrystallites (3.5 nm) is a little greater but very near the Bohr radius of the exciton in bulk SiC (2.7 nm), according to quantum size effect, their band gap should be slightly widened [14,19]. The PL peak wavelength increases monotonously with increasing excitation wavelength in the aged sample (Fig. 2(b)), being the same as that in the as-prepared sample. However, it disappeared under higher excitation energy of ∼ 440 nm, showing that some larger 3C-SiC particles have aggregated.

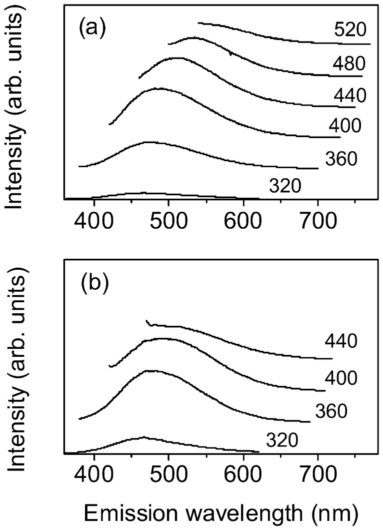

Fig. 2. PL spectra of the as-prepared (a) and stored for over 7 months (b) samples under different excitations.

Fig. 3 shows the PL peak wavelength as a function of excitation wavelength in the as-prepared and aged samples. For the as-prepared sample, the emission wavelength shows first slow and then fast redshift with increasing excitation wavelength. This variation can be explained based on quantum size effect combined with the normal size distribution of 3C-SiC crystallites [15]. The PL is also continuously shifted to red as the excitation wavelength increases in the aged sample (Fig. 3). However, the emission wavelengths exhibit small redshifts for excitations between 360–420 nm in the aged sample with respect to those in newly prepared sample. This could be caused by several reasons. Firstly, the size distribution changes and becomes irregular for the aged sample. Secondly, in this size range, the size distribution for the aged sample shows a much

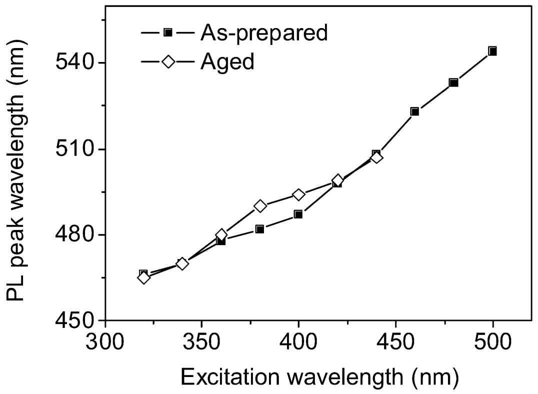

Fig. 3. The PL peak wavelength as a function of excitation wavelength for the as-prepared and aged samples.

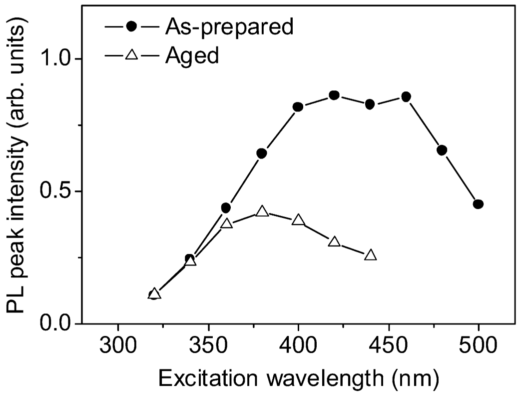

Fig. 4. The PL peak intensity as a function of excitation wavelength for the as-prepared and aged samples.

smaller changing magnitude compared with the as-prepared sample, which can result in a greater redshift in aged sample with increasing excitation wavelength.

Fig. 4 displays the PL peak intensity versus the excitation wavelength in both the newly prepared and aged samples. For the as-prepared sample, the PL peak intensity increases first and then decreases as the excitation wavelength increases, and approaches a maximum at 420 nm. This change is in agreement with the original normal size distribution of 3C-SiC particles. The small peak at $\sim$ 460 nm was induced by the 467 nm line leakage of the Xe lamp. The PL peak intensity changes similarly in the aged sample. However, its maximum emission intensity is located at 380 nm, a much higher energy with respect to that of the as-prepared sample. It shows that most probable particles are much smaller in the aged sample than those in the newly prepared sample. Note that during excitations between 320–360 nm, the emission intensity shows only slight decrease after the suspension is stored, beyond which it decreases very fast. This result indicates that the aggregations of smaller 3C-SiC particles could be negligible and meanwhile they remain their luminescence properties after the storage. It also shows that surrounding oxygen has less influence on emissions of the suspended 3C-SiC crystallites. Larger 3C-SiC crystallites are more easy to collide with each other and form aggregates through Van der Waals force between them. By contrast, smaller ones could steadily stay in water as colloid-like particles.

In conclusion, we have studied the stability of luminescent 3C-SiC nanocrystallites suspended in water over a long period of time. Our result indicates that larger 3C-SiC crystallites tend to aggregate with time, while smaller ones remain well dispersed in water and meanwhile retain their luminescence properties. Because 3C-SiC has good biocompatibility and their crystallites are easy to dissolve in water, so small 3C-SiC crystallites could find wide uses as micro-emitters in biology and medicine.

Acknowledgements

This work was supported by the Grants (Nos. 10225416, 60476038, and 60421003) from the Natural Science Foundations of China, the LPEMST, and the special funds for Major state Basic Research Project (No. G2001CB3095) of China. Partial support was also provided by City University of Hong Kong Direct Allocation Grant #9360110.

References

[1] A.D. Yoffe, Adv. Phys. 51 (2002) 799.
[2] D.J. Lockwood, L. Pavesi, Topics Appl. Phys. 94 (2004) 1.
[3] N.L. Rosi, C.A. Mirkin, Chem. Rev. 105 (2005) 1547.
[4] Al.L. Efros, A.L. Efros, Sov. Phys. Semicond. 16 (1992) 772.
[5] L. Brus, J. Chem. Phys. 79 (1983) 5566.
[6] X. Wu, H. Liu, J. Liu, K.N. Haley, J.A. Treadway, J.P. Larson, N. Ge, F. Peale, M.P. Bruchez, Nat. Biotechnol. 21 (2003) 41.
[7] X. Gao, Y. Cui, R.M. Levenson, L.W.K. Chung, S. Nie, Nat. Biotechnol. 22 (2004) 969.
[8] J.K. Jaiswal, H. Mattousi, J.M. Mauro, S.M. Simon, Nat. Biotechnol. 21 (2003) 47.
[9] G. Cirero, A. Catellani, G. Galli, Phys. Rev. Lett. 93 (2004) 016102.
[10] T. Matsumoto, J. Takahashi, T. Tamaki, T. Futagi, H. Mimura, Y. Kanemitsu, Appl. Phys. Lett. 64 (1994) 226.
[11] L.S. Liao, X.M. Bao, Z.F. Yang, N.B. Min, Appl. Phys. Lett. 66 (1995) 2382.
[12] Z. Makkai, B. Pécz, I. Bársony, Gy. Vida, A. Pongrácz, K.V. Josepovits, P. Deák, J. Appl. Phys. 86 (2005) 253109.
[13] For a review, see J.Y. Fan, X.L. Wu, P.K. Chu, Prog. Mater. Sci., accessible online.
[14] X.L. Wu, J.Y. Fan, T. Qiu, X. Yang, G.G. Siu, P.K. Chu, Phys. Rev. Lett. 94 (2005) 026102.
[15] J.Y. Fan, X.L. Wu, H.X. Li, H.W. Liu, G.G. Siu, Paul K. Chu, Appl. Phys. Lett. 88 (2006) 041909.
[16] J.Y. Fan, X.L. Wu, H.X. Li, H.W. Liu, G.S. Huang, G.G. Siu, P.K. Chu, Appl. Phys. A 82 (2006) 485.
[17] J.S. Shor, R.M. Osgood, A.D. Kurtz, Appl. Phys. Lett. 60 (1992) 1001.
[18] S.A. Empedocles, D.J. Norris, M.G. Bawendi, Phys. Rev. Lett. 77 (1996) 3873.
[19] J.P. Wolfe, Phys. Today 35 (1982) 46.