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## LETTER TO THE EDITOR

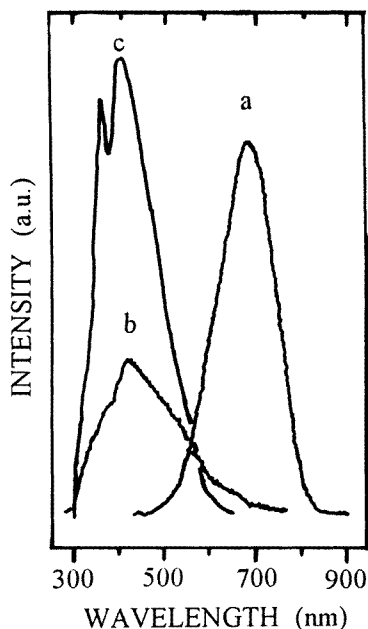
**The role of SiO<sub>2</sub> in the blue luminescence in hydrothermally prepared porous silicon**Qianwang Chen<sup>†</sup>, X J Li<sup>†</sup>, Y B Jia<sup>†</sup>, J S Zhu<sup>†</sup> and Zhang Yuheng<sup>†‡§</sup><sup>†</sup> Structure Research Laboratory, University of Science and Technology of China, Academia Sinica, Hefei 230026, People's Republic of China<sup>‡</sup> CCAST, World Laboratory, Beijing 100080, People's Republic of China<sup>§</sup> Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China

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**Abstract.** Blue photoluminescence (PL) in hydrothermally prepared porous silicon (PS) was found to be insensitive to the composition of silicon oxide, and the peak position of the blue band changes with changing excitation wavelength. All these factors suggested that silicon oxide cannot be responsible for the blue PL. High-density quantum dots were observed in the PS layer by high-resolution electron microscopy (HREM) analysis, and were suggested to be responsible for the emission.

In the literature [1, 2], it has been reported that red emission from porous silicon (PS) originates from linear quantum wires with width  $< 3$  nm. Recent reports [3–7] have provided evidence that rapid-thermal-oxidized (RTO) porous silicon can luminescence in the blue band. At present, however, the question of the origin of the luminescence has not been fully resolved. Three main possible models for the blue emission from porous silicon have been proposed: band-to-band recombination in silicon nanocrystallites, emission due to surface states, and emission from silicon oxide. The emission from silicon oxide model, widely accepted [6, 8], suggests that different types of defect in silicon dioxide can be responsible for blue PL; this idea gains support from the correlation between the intensity of the blue PL band and the intensity of the Si–O infrared absorption. The authors also found a correlation between blue luminescence intensity and the increase in feature size caused by oxidation. They further showed that the blue luminescence is identical, with respect to spectrum and fast decay, to that of high-microelectronic-quality SiO<sub>2</sub> grown on crystalline silicon using dry oxygen plus an organic chlorine compound [6, 8]. Then they suggested that the blue luminescence of oxidized PS comes from creation of oxygen-, carbon- or halogen-related defects in silicon dioxide. However, it is basically established that red PL in PS is related to two-dimensional quantum confinement [1, 2], and reduction of the size by post-anodic treatment could result in a blue shift. Hence, it is reasonably speculated that silicon crystalline quantum dots may further result in enlargement of the energy gap due to three-dimensional confinement and higher-energy emission in PS. Kanemitsu [9, 10] has also provided some evidence that the blue emission originates from the band-edge emission from the crystalline core state. This is also in agreement with the recent calculations which suggest that three-dimensionally confined silicon particles have symmetry-allowed optical transitions across the gap with a width of about 2.5 eV for sizes below 2 nm [11–13]. However, until now no direct experimental data for the quantum confinement effect such as

the size effect of the blue PL has been observed. On the other hand, it is well known that three dominant CL bands in amorphous SiO<sub>2</sub> lie at 1.9 ('red' band), 2.7 ('blue' band), and 4.4 eV ('UV' band) [14, 15], and all bands can be excited with appropriate photoexcitation. This makes the work of assigning blue emission in oxidized material to the Si nanostructures very difficult. Because the mechanism of blue photoluminescence from nanostructures of indirect-gap materials is controversial and not well understood, it is important to clarify experimentally the intrinsic optical properties of silicon nanocrystallites embedded in silicon oxide matrix in oxidized PS. Here, we report results which reveal the blue PL in oxidized PS does not originate from SiO<sub>2</sub>, and suggest that high-density quantum dots embedded in SiO<sub>2</sub> are responsible for the phenomenon observed.

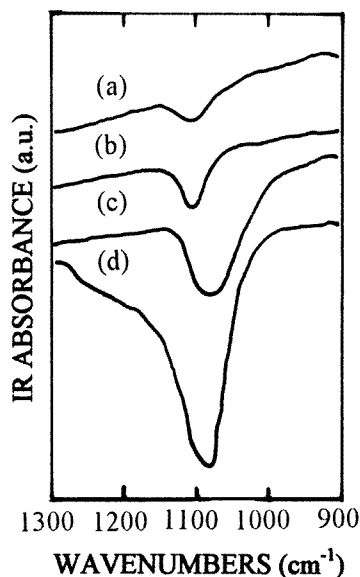


**Figure 1.** Room-temperature photoluminescence spectrum taken on PS obtained by hydrothermal erosion in a solution of 0.2 mol L<sup>-1</sup> LiF in 0.4 mol L<sup>-1</sup> HNO<sub>3</sub> before (a) and after (c) the RTO process in air at 950 °C for 30 s, and by hydrothermal erosion in 0.3 mol L<sup>-1</sup> LiF in 10.0 mol L<sup>-1</sup> HNO<sub>3</sub> (b).

In most case, the blue PL samples were obtained by rapid thermal oxidation (RTO) of anodic etched PS. We will use the hydrothermal etching technique to prepare samples; it does not use ethanol during the etching process, nor does it utilize the RTO process. Thus, our results may be capable of excluding certain mechanisms which have been brought forward for the interpretation of blue PL, such as the carbon-related defects in silicon dioxide.

For the present experiments, Si wafers were hydrothermally eroded in 0.2 mol l<sup>-1</sup> HF containing concentrated HNO<sub>3</sub> solution at 140 °C for 2 h. The luminescence wavelength is dependent upon HNO<sub>3</sub> concentration. A low concentration of HNO<sub>3</sub> (e.g. 4.0 mol l<sup>-1</sup>) gives a sample (I) with bright and clean appearance luminescence around 690 nm (figure 1(a)), while a higher concentration of HNO<sub>3</sub> (e.g. 10.0 mol l<sup>-1</sup>) can lead to the formation of a sample (II) demonstrating blue emission peaking at 430 nm (figure 1(b)) without RTO treatment.

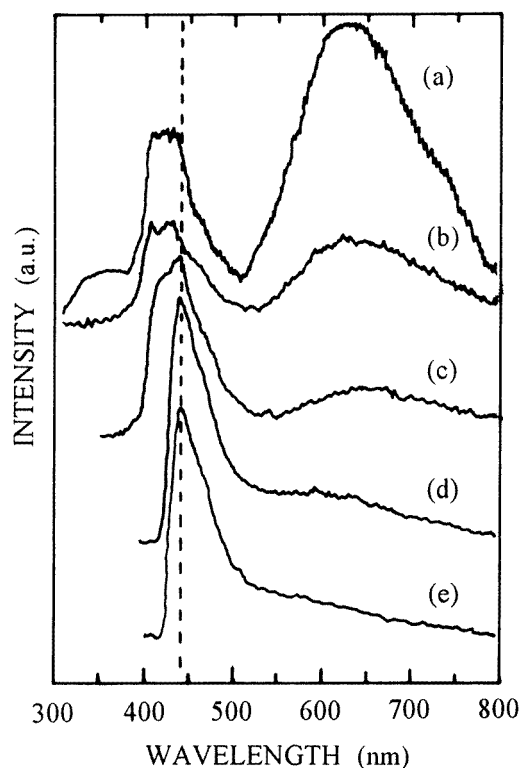
Figure 1(a) is the PL spectrum of sample I excited by a 256.6 nm ultraviolet line at room temperature. After RTO treatment of the sample at 950 °C for 30 s, the appearance of a blue band around 430 nm with a component at 370 nm is evident in figure 1, which is in agreement with the results reported [5, 6]. On the other hand, the blue band in PS can be directly obtained by hydrothermal erosion in concentrated nitric acidic HF solution as shown in figure 1(b). These facts seem to reveal that the stronger oxidation atmosphere due to the presence of a higher concentration of HNO<sub>3</sub> results in the blue PL. Combined with the fact that blue PL is usually obtained by the RTO process one easily concludes that the blue PL arises from silicon oxide [8, 16]. However, the Fourier transform infrared (FTIR) measurement results show that the blue PL is not related to SiO<sub>2</sub>. As shown in figure 2(a, b), a weak peak at about 1106 cm<sup>-1</sup> related to the asymmetric stretching vibrational model of the Si–O–Si oxygen bridge is observed for both sample I and sample II, which shows Si–O–Si bridges in a configuration very close to stoichiometry. Furthermore, after the RTO treatment of the two samples in air at 950 ° for 30 s, the Si–O–Si absorption peak position shifts to a lower frequency of 1082 cm<sup>-1</sup> (figure 2(c, d)) accompanied by an increase of intensity. The blue PL was also observed in the two samples after the RTO process. These facts show that blue PL is not sensitive to the chemical composition of silicon oxide.



**Figure 2.** The FTIR absorption spectra of freshly prepared red (a) and blue (b) PL samples. (c) and (d) are the spectra of (a) and (b) respectively after RTO treatment at 950 °C for 30 s.

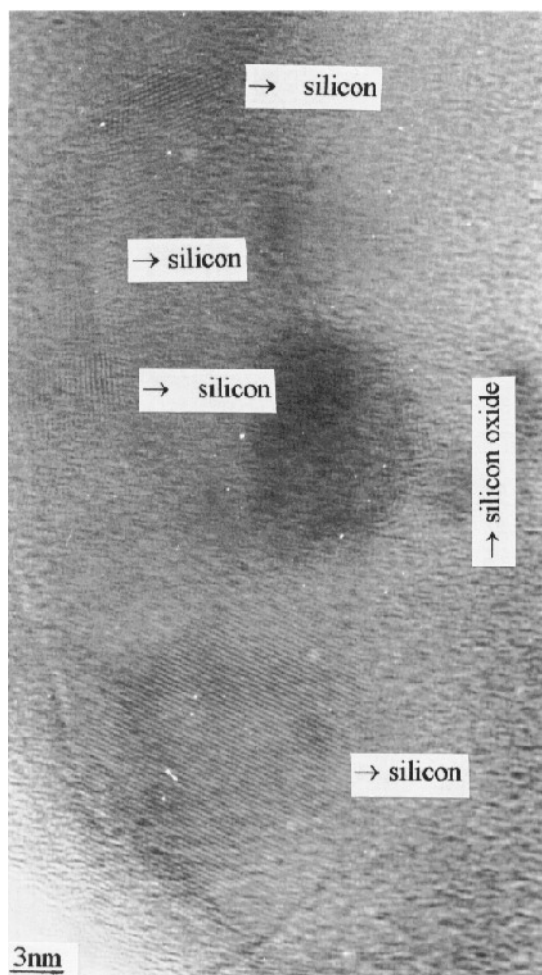
As mentioned above, the PL wavelength of PS, in our case, can be adjusted by changing the composition of the erosion solution. Figure 3(a) shows the spectrum of a PS sample prepared by hydrothermal erosion in a solution of 0.3 mol l<sup>-1</sup> HF and 10.0 mol l<sup>-1</sup> HNO<sub>3</sub> at 140 °C for 1.2 h. It shows red, blue, and ultraviolet bands peaking at 680, 430, and 370 nm respectively coexisting in one spectrum. Accompanying the increase of excitation wavelength the intensities of ultraviolet and red PL bands decrease (as will be discussed in another paper), while the blue PL band shifts to a lower energy as revealed in figure 3. When the excitation wavelength changes from 256.6 to 336.6 nm, the peak position of

the blue band shifts from 420 to 445 nm (figure 3(e)), and the higher-energy edge of the band also shifts to lower energy, while the lower-energy side remains nearly unchanged, which results in an asymmetric distribution of the peak. If we assign the blue PL in PS to the Si nanostructures present, it is not surprising that peak position and shape change with excitation wavelength since there definitely exists a wide range of Si particle sizes which results in a distribution of the energy gap, and the increasing of excitation wavelength would lead to the excitation photon energy used not being high enough to create nonequilibrium carriers across the band gap of small crystallites. To our knowledge, this is the first report of the size effect in blue emission. A conventional erosion and RTO process would lead to a size distribution of crystallites wider than that in our case due to inhomogeneous erosion [17], which makes the size effect hard to observe [9].



**Figure 3.** PL spectra from a PS sample obtained by hydrothermal erosion in a solution of  $0.3 \text{ mol l}^{-1}$  LiF and  $10.0 \text{ mol l}^{-1}$   $\text{HNO}_3$  excited with wavelengths of 256.6 nm (a), 276.6 nm (b), 296.6 nm (c), 316.6 nm (d), and 336.6 nm (e).

A suggestion that the PL peak may result from emission by a nonbridging oxygen hole centre in the oxide seems quite unlikely as we know only nonstoichiometric suboxide  $\text{SiO}_x$  with a band gap of about 3–4 eV for  $x \approx 1.4$ –1.6 and near-UV excitation may produce nonequilibrium carriers. However, our FTIR spectra suggest the presence of a very nearly stoichiometric oxide in blue emitting PS, and the blue PL is not sensitive to the composition of silicon oxide as discussed above. In addition, different types of defect in silicon dioxide (e.g. nonbridging oxygen hole centres, carbon- or halogen-related defects) have also been suggested to be responsible for the PL. However, no carbon contamination



**Figure 4.** Local HREM of a column in a blue PL PS layer.

was involved in our sample. Furthermore, if the emission is connected with the defects in silicon oxide, the PL spectra should not be sensitive to the excitation wavelength as shown in figure 3. All these facts reveal that the oxidation of PS results in the blue PL, and the  $\text{SiO}_2$  itself formed in the oxidation process cannot be responsible for the higher-energy emission. Figure 4 shows a local high-resolution electron micrograph (HREM) of a column in sample II; it reveals apart from the larger silicon crystallites individual silicon nanocrystallites of several nanometres embedded separately in an amorphous matrix, which was confirmed to be amorphous silicon oxide by thin-film x-ray scattering studies carried out by fixing the  $\theta$  angle at  $3^\circ$  with  $2\theta$  scanning (not shown). It is well established that PS layers are composed of free standing silicon columns with undulating width [1]; this was also observed in hydrothermally obtained PS [7]. Subsequent oxidation treatment leads to the formation of silicon oxide on the surface of silicon columns; meanwhile it also causes a reduction of crystal size. Appropriate oxidation treatment would result in the formation of isolated dispersed silicon nanocrystallites due to the undulation in width of the initial Si in each column. This structure would lead to high-density quantum dots in the PS layer (the

detailed formation mechanism will be discussed later).

In conclusion, blue PL in hydrothermally prepared PS was found to be insensitive to the composition of silicon oxide, and a size effect of blue PL in PS was observed; these facts suggest that silicon oxide cannot be responsible for the blue PL in our case. High-density quantum dots were observed in the PS layer, and were suggested to be related to the emission.

## References

- [1] Cullis A G and Canham L T 1991 *Nature* **353** 335
- [2] Halimaoui A, Houlton M R, Leong W Y, Pickering C and Keen J M 1991 *J. Appl. Phys.* **70** 422
- [3] Andrianov A A, Kovalev D I, Shuman V B and Yaroshetzki I D 1992 *JETP Lett.* **56** 943
- [4] Calcott P D, Nash K J, Canham L T, Kane M J and Brumhead D 1993 *J. Phys.: Condens. Matter* **5** L91
- [5] Lee M K and Reng K R 1993 *Appl. Phys. Lett.* **62** 3159
- [6] Tsybeskoy L, Vandyshv Ju V and Funchet P M 1994 *Phys. Rev. B* **49** 7821
- [7] Chen Qianwang, Zhu J Sheng, Zhou G, Song Z T, Li X-G and Zhang Y H 1996 *J. Phys. Condens.: Matter* **8** L753
- [8] Kontkiewicz A J 1994 *Appl. Phys. Lett.* **65** 1436
- [9] Konemitsu Y 1994 *Phys. Rev. B* **49** 16 845
- [10] Konemitsu Y 1994 *Phys. Rev. B* **49** 14 732
- [11] Hybertsen M S 1992 *Light Emission from Silicon (Mater. Res. Soc. Symp. Proc. 256)* ed S S Iyer, R T Collins and L T Canham (Pittsburgh, PA: Materials Research Society) p 179
- [12] Kanemitsu Y, Uto H, Masumoto Y, Matsumoto T, Futagi T and Mimura H 1993 *Phys. Rev. B* **48** 2827
- [13] Takagahara Y and Takeda K 1992 *Phys. Rev. B* **46** 15 578
- [14] Koyama H 1980 *J. Appl. Phys.* **51** 2228
- [15] Pio F, Guzzi M, Spinolo G and Martini M 1990 *Phys. Status Solidi b* **159** 577
- [16] Cullis A G, Canham L T, Williams G M, Smith P W and Dosser O D 1994 *J. Appl. Phys.* **75** 493
- [17] Chen Qianwang, Zhu Jingsheng, Li X-G, Fan C G and Zhang Y H 1996 *Phys. Lett.* **220A** 293