Critical conditions for achieving blue light emission from porous silicon

Xun Wang, G. Shi, F. L. Zhang, H. J. Chen, W. Wang, P. H. Hao, and X. Y. Hou
Surface Physics Laboratory, Fudan University, Shanghai 200433, China

By observing the luminescence micrographic images and measuring the decay behaviors of photoluminescence spectra, it is found that the blue light-emitting porous silicon obtained by boiling water treatment behaves very similarly to the red light-emitting sample. It is thus believed that the blue light emission is originated from the porous silicon skeleton rather than impurity contaminations. The achievement of blue light emission requires the proper control of the size of the Si nanostructures, effective passivation of the internal surfaces of porous silicon layer, and keeping a mechanically strong Si skeleton. A theoretical estimation and the experiments show that the simultaneous fulfillment of these conditions is quite critical, which explains the poor reproducibility of achieving blue emission experimentally.

The recent discovery of visible light emission from highly porous silicon (PS) has made the realization of all-Si based optoelectronic integration possible.[1] Full-color all-Si displays would require blue emission, which has been demonstrated for the first time in our previous work by using the water boiling as a postanodic treatment.[2] However, a strong suspicion may arise concerning the reality of the blue emission, that is, whether the blue light comes from the PS itself or from other contaminated species. One of the reasons that causes the suspicion is its reproducibility. We have tried the boiling water treatment for more than 150 times. Statistically, the probability of success was about 20%–30%. In this letter, we present further evidences on the behaviors of blue emission and conclude that the blue light most likely originates from the PS skeleton rather than other contamination. On the basis of a theoretical calculation of the energy gap of PS versus its size of nanostructures, the condition of forming a blue light-emitting PS structure is found to be very critical.

The procedure of sample preparation has been described in the previous letter.[2] After boiling water treatment, the PS sample showed a blue color under the illumination of an ultraviolet (UV) lamp. The luminescence efficiency of blue sample is about a factor of 5 smaller than that of red one, as determined by measuring the integrated photoluminescence (PL) intensities and the incident power densities of light sources.

It has been known that many organic compounds could emit blue light under the excitation of UV light. Thus people may wonder whether the PS sample was contaminated by some sort of organic compounds due to the possible impurity of de-ionized (DI) water or other materials used in the experiments. We did try this possibility by boiling the PS sample in tap water instead of de-ionized water to intentionally introduce surface contamination on the PS sample. In such cases, it is very easy to get blue color, which we believed is actually caused by the impurity contamination, since even a bare Si single crystal wafer could emit blue light after the tap water boiling. But we found two experimental facts that illustrate that the luminescence mechanisms for these two samples (DI water treated and tap water treated) are significantly different. First, we took the luminescence micrographic observation

by using an Olympus photomicrographic system. The micrographic pictures for these two samples are shown in Fig. 1. For the tap water treated sample, there are many bright white spots in the dimension of several μm distributed randomly on the sample surface. While for DI water treated PS sample, Fig. 1(a) shows that the whole surface of the sample consists of many domains with the dimension of several μm, each domain shows blue color uniformly. Figure 1(b) is the photoluminescence micrographic picture of a red light-emitting PS sample. The differences between Figs. 1(a) and 1(b) are the color and the shape of domains. Both of them are minor points in regard to the luminescence mechanism, while the difference between Figs. 1(a), 1(b), and 1(c) is essential. The luminescence morphology of Fig. 1(b) illustrates that the red light is emitted by the Si skeleton. The similarity between Figs. 1(a) and 1(b) provides evidence that the luminescence mechanism of the blue emission sample might be the same as that of red emission sample. While the luminescence morphology of the tap water treated sample surface does not show any domain structure. The bright spots in Fig. 1(c) are attributed to the contaminated species, while the remaining parts of the sample surface do not luminesce at all.

Another experimental fact is the time dependence of the PL spectrum. As shown in Fig. 2, under the illumination of Ar$^+$ laser, a PL peak red shift accompanied by an intensity decay occurs, which is known to be the common behavior of light-emitting PS. The PL spectra were taken by using the 457.9-nm line of Ar$^+$ laser as the excitation source, so that the PL peak energies have already shifted to around 515 nm. The excitation power density was about 3 kW/cm^2. The data acquisition time for each spectrum was 3 min. The PL signal becomes weaker and weaker after repeated scans. For the tap water treated sample, this phenomenon was not so significant. Shown in Fig. 2(b) are the time dependences of the PL intensities at 520 nm for two samples under the laser beam illumination. After 5 min illumination, the PL intensities drop down to about 15% and 80% of their initial values for the blue emission sample and the tap water treated sample, respectively.

Since in our case the possible contamination source if existed was mostly related with water, but the above evi-
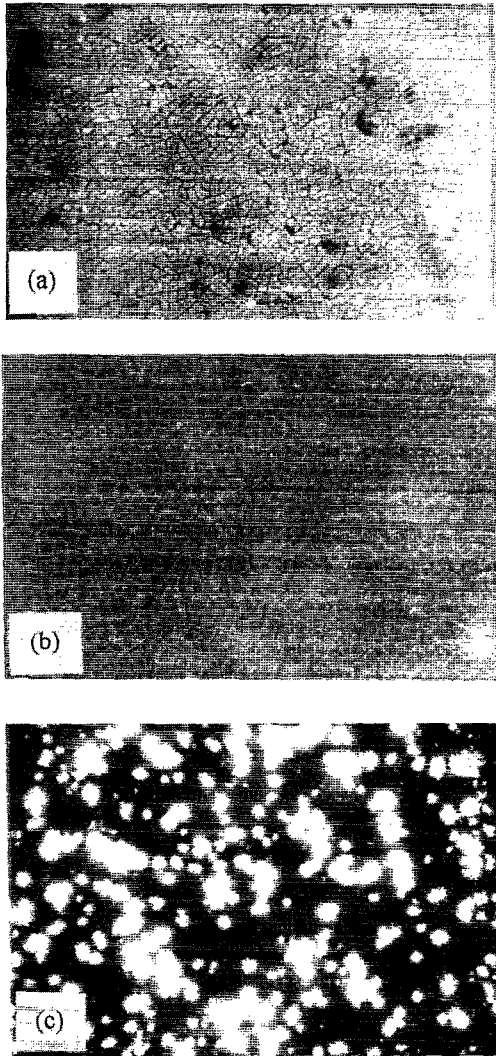
FIG. 1. Luminescence micrographic pictures of (a) blue light-emitting PS sample, (b) red light-emitting PS sample, and (c) tap water treated sample.

FIG. 2. (a) Photoluminescence intensity decay of a blue light-emitting PS sample. (b) PL intensity at 520 nm vs laser illumination time.

dence show that the luminescence behaviors of the intentionally introduced impurity contamination are quite different from that of the blue emission PS sample. It seems that the impurity of water is not likely the origin of blue emission from our PS sample. It is then lead to the second question why its reproducibility is rather poor.

To make a qualitative analysis, we believe that the blue emission could not be reached unless the following requirements are all fulfilled: (1) the size of Si nanostructures should be controlled properly, (2) the internal surfaces of PS should be passivated effectively, and (3) the Si skeleton should be mechanically strong enough to make it sustained on the substrate.

For analyzing how difficult is to make a Si skeleton with proper size of rods or dots but still strong enough, we
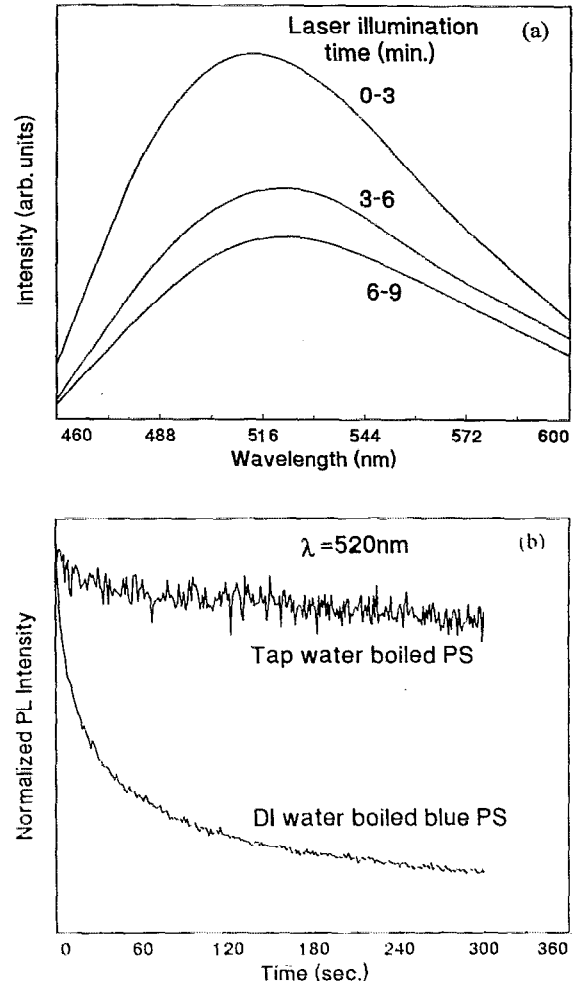
use the results of energy gap calculations by Fu et al.[3] The skeleton of PS was simulated by an assembly of clusters, in which the Si atoms sited at the lattice points of a diamond-like crystal. The dependence of energy gap on the diameter of cluster has been derived. During the anodic etching process, the Si atoms on the outmost shells of Si nanostructures would be peeled away layer-by-layer, then the diameter of cluster would change discontinuously. The band gap energies at discrete cluster sizes are listed in Table I. Since it is suggested that the recombination process of PL is most likely through the surface states rather than the

TABLE I. Calculated energy gap vs Si cluster size [from Fu et al. (Ref. 3)].

No. of shells	No. of atoms	Diameter of cluster (Å)	Eg (eV)	Corresponding luminescence color
5	47	11.8	3.08	blue
6	71	13.3	2.80	green
7	87	14.1	2.63	yellow
8	99	15.3	2.39	orange
9	123	16.1	2.31	red
10	147	17.2	2.16	red

interband transitions,[4–8] thus the PL peak energy would not be equal to the energy gap. From our previous study,[4] we estimated that the PL peak energy is smaller than the gap energy by a value of about 0.4–0.5 eV. The luminescence colors corresponding to the gap energies are also listed in Table I. The discontinuous change of the energy gap and the peak energy of PL spectrum has been proven to be true at least qualitatively in our previous experiments[4] and also by Zhang et al.[9] It means that the blue emission corresponds to the Si dots with only a certain value of dimension but not a range of sizes. Thus the size control should be very critical. According to Table I, only the cluster with five atomic shells but not four or six shells could emit blue light. Many authors calculated the dependence of the energy gap versus the size of Si nanostructure.[10–17] The results are somewhat different but the trends are similar. If the size discontinuity is taken into account, the above argument is still conceptually correct.

Furthermore, we would estimate the strength of Si skeleton. If we assume that the Si clusters with dimension of d are arranged into a cubic array with the distance between centers of nearest neighboring Si clusters equals L, for a red emission sample ($d = 17.2$ Å) which has a porosity of larger than 65%, L is estimated to be > 19.7 Å. If d is further reduced by anodic etching to 11.8 Å (blue color) keeping L unchanged, the porosity is then increased to > 89%. It seems quite difficult to self-sustain the blue emission films. Although the above estimations may not be correct quantitatively, it still could give us a rough idea to evaluate the difficulties in realizing a strong PS skeleton with proper nanostructure size.

As we pointed out in previous letter,[2] the water boiling treatment is actually a kind of oxidation, which reduces the size of Si nanostructures and passivates their surfaces with some sorts of silicon hydroxides. Meanwhile, the expansion of the nanostructure volumes due to oxidation makes the Si skeleton much stronger. All these effects are in favor of achieving blue emission.

On the other hand, the boiling water treatment will induce large strain between the PS film and the substrate. This will cause the crash or loss of PS films, especially for those high porosity samples. Actually, it has been found in experiments that most of the unsuccessful examples are caused by the loss of PS films during water boiling. Even the water boiling treatment is carried out for red emission sample, it is still not easy to handle with. Over oxidation causes the fully removal of Si cores. Starting from too thick Si nanostructures will lead to the oxidation stopped at improper size (the PS still emits red or orange color). Introduction of high density of nonradiative surface states will make the blue emission not visible. Inducing a low lying radiative surface state in the energy gap will shift the PL peak towards long wavelength. All these situations have to be avoided but we really do not know how to do it during the process, since no *in situ* monitoring method is available up to now. That is why the reproducibility of achieving blue light emission by water boiling is not satisfactory.

In principle, it is possible to shift the PL color from red, orange to blue by using other oxidation techniques.

Actually, Koch et al.[18] observed in the nanosecond time-resolved PL measurement a luminescent peak at 490 nm by using rapid thermal oxidation to reduce the size of Si nanostructure. However, the blue emission peak could only exist in the transient PL spectrum. While in steady PL measurement, the shortest luminescent wavelength they obtained was in the green region. We believe that the rapid thermal oxidation carried out at the temperatures higher than 900 °C is a kind of strong oxidation that is more difficult to handle with to meet the above requirements for achieving blue emission.

In conclusion, by investigating the luminescence micrographic images and the decaying behaviors of PL spectra of boiling water treated PS samples, it has been shown that the blue light emission is most likely to be originated from the PS skeleton rather than surface contaminations. The conditions for achieving blue light need proper size of nanostructures, low surface recombination velocity, and mechanically strong skeleton. The water boiling treatment is a kind of mild oxidation, which reduces the size of Si cores, passivates the internal surfaces of PS layer, and strengthens the Si skeleton by shrinking the pores. But the fulfillment of these conditions is rather critical, resulting in the poor reproducibility in experiments.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] X. Y. Hou, G. Shi, W. Wang, F. L. Zhang, P. H. Hao, D. M. Huang, and X. Wang, Appl. Phys. Lett. **62**, 1097 (1993).

[3] H. Fu, L. Ye, and X. Xie, Phys. Rev. B (to be published).

[4] X. Wang, D. Huang, L. Ye, M. Yang, P. Hao, H. Fu, X. Hou, and X. Xie, Phys. Rev. Lett. **71**, 1265 (1993).

[5] F. Koch, V. Petrova-Koch, T. Muschik, A. Nikolov, and V. Gavrilenko, Mater. Res. Soc. Symp. Proc. **283**, 197 (1993).

[6] Y. H. Xie, W. L. Wilson, F. M. Ross, J. A. Macha, E. A. Fitzgenrald, J. M. Macaulay, and T. D. Harris, J. Appl. Phys. **71**, 2403 (1992).

[7] S. Miyazaki, K. Shiba, K. Sakamoto, and M. Hirose, Mater. Res. Soc. Symp. Proc. **283**, 269 (1993).

[8] T. Motsumoto, M. Daimon, T. Futagi, and H. Mimura, Jpn. J. Appl. Phys. **31**, 2619 (1992).

[9] S. Zhang, K. Ho, Y. Hou, B. Qian, P. Diao, and S. Cai, Appl. Phys. Lett. **62**, 642 (1993).

[10] A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott, and A. Qteish, Phys. Rev. Lett. **69**, 1232 (1992).

[11] F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).

[12] C. D. Sanders and Y.-C. Chang, Phys. Rev. B **45**, 9202 (1991).

[13] T. Ohno, K. Shirashi, and T. Ogawa, Phys. Rev. Lett. **69**, 2400 (1992).

[14] J. P. Proot, C. Delerue, and G. Allen, Appl. Phys. Lett. **61**, 1948 (1992).

[15] T. Takagahara and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).

[16] B. Delley and E. F. Steigmeter, Phys. Rev. B **47**, 1397 (1993).

[17] S. Y. Ren and J. D. Dow, Phys. Rev. B **45**, 6492 (1992).

[18] V. Petrova-Koch, T. Muschik, D. I. Kovalev, F. Koch, and V. Lehmann, Mater. Res. Soc. Symp. Proc. **283**, 179 (1993).