

Large blue shift of light emitting porous silicon by boiling water treatment

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(Received 8 September 1992; accepted for publication 4 January 1993)

A boiling water treatment of light emitting porous silicon can give rise to a large blue shift of its photoluminescence spectrum and meanwhile strengthen the skeleton of porous Si by filling up many pores with aqueous oxide. A stable blue-green light emission at the peak wavelength down to 500 nm is achieved. FTIR measurements show that the formation of Si dihydride on the sidewall surfaces of the Si rods is not responsible to the visible luminescence for the very thin Si wires.

Multicolor photoluminescence with external quantum efficiencies as high as 10^{-1} at room temperature was achieved recently from highly porous crystalline Si.¹ This striking phenomenon has been attributed to the formation of a surface-passivated Si quantum wire array, although the controversy about its mechanism still remains.² According to the quantum confinement mechanism, the peak wavelength of photoluminescent porous Si (PS) is closely related with the size of Si wires. To achieve short emitting wavelength, the diameter of Si rods in PS must be very small, in other words, the porosity of the sample should be very large. By using ordinary HF anodic etching, one can observe the light emission of PS in the red, orange, and yellow ranges. If the porosity increases further, the skeleton of PS becomes very fragile and could not be self-sustained. It has been found that some post treatments, such as oxidation in air and electrochemical oxidation under anodic bias could reduce the effective size of the Si rods, and thus, cause a blue shift of the luminescence spectrum.³⁻⁵ However, the oxidation of the sidewall surfaces of Si rods in PS samples will induce a large density of interfacial states, which will significantly affect the luminescence efficiency and finally cease the light emission. To date, the shortest emitted central wavelength of the PL spectrum is 530 nm, which is in the green color range and corresponds to the effective diameter of about 1.7 nm for Si wires. For full color displays, one requires blue emission, which is yet to be demonstrated.

In this letter, we found that a boiling water treatment can give rise to a large scale blue shift of the luminescence spectrum of PS, and meanwhile, sustain its fragile skeleton by filling many large pores in the PS film. A photoluminescence spectrum centered at the wavelength of 500 nm (blue-green region) was observed. To our knowledge, it is the shortest PL wavelength ever been reported.

The samples used were prepared by anodic etching of boron doped *p*-type (100) Si wafers with the resistivity of 20 Ω cm. By conventional room temperature electrochemically etching in HF solution at 5–30 mA/cm² for 1–10 min, the PS showed a PL spectrum with the peak wavelength at about 700 nm under the Ar⁺ laser illumination, as shown by curve (a) in Fig. 1. A large blue shift of the PL spectrum occurred after the PS sample was simply immersed in boiling deionized water. The PL peak wavelength changes as a function of water boiling time. After immersing for 10–30 min, the peak position eventually

shifts to 500 nm, as shown by curve (b) in Fig. 1, where the excitation source is the 253.7 nm line of a UV lamp. A blue-green color is observable by the naked eye in the dark, although its intensity is weaker than that of the red or yellow color emission. In Fig. 1, the integral intensity of curve (b) is smaller than that of curve (a) in a factor of about 2–5 as estimated by comparing the incident power densities of light sources and the luminescence intensities.

To explain the effect of water boiling, scanning electron microscope (SEM) observation has been performed. Figure 2 shows the surface morphologies of the PS sample before and after water boiling for 30 min. At the magnification of 5000, we can see many pores in the sizes of 0.5–2 μ m on sample surface. The density and diameter of these macropores reduced greatly through immersion into the boiling water. It seems that a portion of pores are sealed by boiling water treatment. We believe that the effect of water boiling is also a kind of oxidation, which forms some kind of oxide, most possibly the aqueous oxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), on the sidewalls of Si columns. The volume expansion of Si columns due to oxidation will reduce the size of macropores, fill up some micropores, and thus strengthen the Si skeleton. Further boiling treatment would consume the PS layer gradually. For example, the treatment for 1–2 h would result in no luminescence from the sample which might correspond to the entire oxidation of the PS layer.

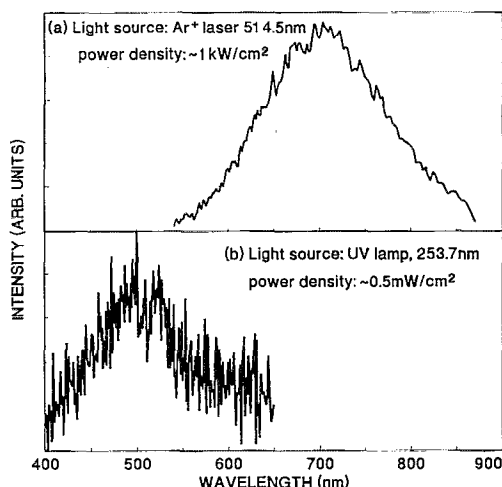


FIG. 1. Photoluminescence from (a) as-anodized porous Si and (b) after boiling water treatment.

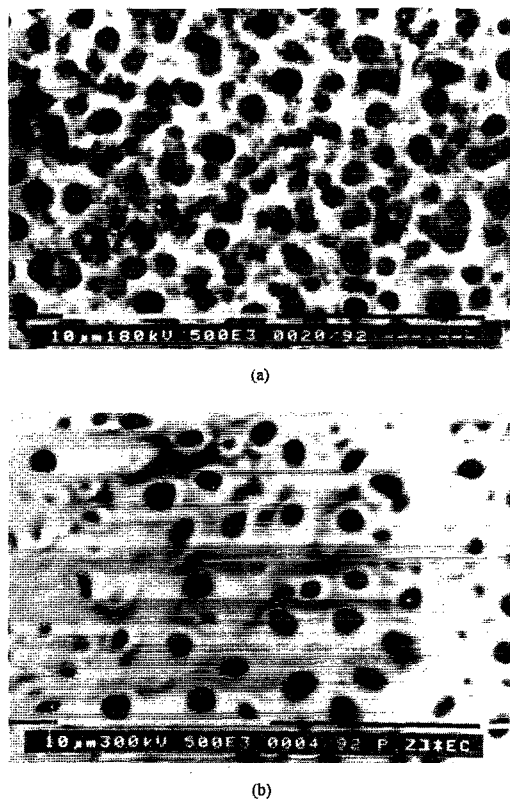


FIG. 2. Morphology of the porous Si (a) before boiling water treatment and (b) after boiling water treatment.

The boiling water oxidation does not increase the surface recombination velocity of Si wires very much. It is quite similar to the results of vapor oxidation.⁶ Tsai *et al.* have suggested that the silicon dihydride species play important roles in high efficient light emission of PS.^{7,8} With the sidewall surfaces of PS Si rods saturated by hydrogen atoms, the nonradiative recombination centers originated from the Si surface dangling bonds are greatly reduced. They concluded that the formation of dihydride species SiH₂ is crucial rather than monohydride SiH, as verified by the infrared absorption spectra. We did the Fourier transform infrared (FTIR) reflection spectra measurements of water boiling PS samples and found that the above statement might be true for thicker Si wires but not for thinner wires. Figure 3 shows the FTIR spectra of a PS sample treated with boiling water for different times. The corresponding luminescent colors are also indicated. Each spectrum was taken after drying the sample with gas flow N₂. Without the boiling water treatment, the PS emits a red light and there exist two stretching vibration modes of monohydride (2120 cm⁻¹) and dihydride (2080 cm⁻¹), as well as a scissor bending mode of dihydride (907 cm⁻¹) in the FTIR reflection spectrum. No signal related with oxygen is observed. With increasing the boiling time from 10

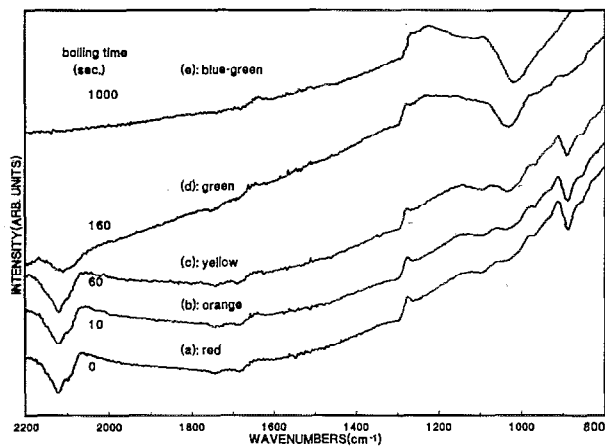


FIG. 3. Fourier transform infrared reflection spectra of the porous Si before and after boiling water treatment for the times indicated.

to 1000 s, the emission color changes from red to orange, yellow, green, and blue-green, sequentially, while the hydrides related peaks are gradually removed. An oxide absorption band around 1105 cm⁻¹ increases with boiling which suggests that the boiling water immersion is a kind of oxidation process. In addition, the curves (d) and (e) in Fig. 3 indicate that the dihydride is no longer responsible for the high efficiency of light emission in case of very thin Si wires. It seems that the Si hydrides formed by HF anodic etching are replaced by the aqueous oxide during the boiling water treatment. The latter aqueous oxide could also passivate the sidewalls of Si rods, although it is not as effective as the Si dihydride in terms of reducing the recombination velocity.

In conclusion, we have achieved a large blue shift of PL from PS by the boiling water treatment. A stable blue-green light emission at the peak wavelength of 500 nm is observed. The effect of water boiling is to reduce the size of Si wires and to strengthen the skeleton of PS by aqueous oxidation. It has also been found that the formation of SiH₂ on the sidewalls of Si is not essential to the visible luminescence from the thinner wires.

This work was partially supported by the National Natural Science Foundation of China.

- ¹ L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
- ² A. G. Cullis and L. T. Canham, *Nature* **353**, 335 (1991).
- ³ S. Shih, C. Tsai, K.-H. Li, K. H. Jung, J. C. Campbell, and D. L. Kwong, *Appl. Phys. Lett.* **60**, 633 (1992).
- ⁴ A. Halimaoui, C. Oules, G. Bomchil, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, and F. Muler, *Appl. Phys. Lett.* **59**, 304 (1991).
- ⁵ V. Lehmann and U. Gosele, *Appl. Phys. Lett.* **58**, 856 (1991).
- ⁶ R. R. Razouk and B. E. Deal, *J. Electrochem. Soc.* **126**, 1573 (1979).
- ⁷ C. Tsai, K.-H. Li, J. Sarathy, S. Shih, and J. C. Campbell, *Appl. Phys. Lett.* **59**, 2814 (1991).
- ⁸ C. Tsai, K.-H. Li, D. S. Kinosky, R. Z. Qian, T.-C. Hsu, J. T. Irby, S. K. Banerjee, A. F. Tasch, Joe C. Campbell, B. K. Hance, and J. M. White, *Appl. Phys. Lett.* **60**, 1700 (1992).