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Stable blue light emission from oxidized porous silicon†

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Abstract. We have achieved production of porous silicon (PS) that emits blue light at a peak wavelength of 460 nm. On storing it in air for three months, or illuminating it with the 365 nm line of a uv lamp, its photoluminescence intensity and peak wavelength remain stable. With Fourier-transform infrared (FTIR) measurements, we have studied the surface chemical bonds of the PS emitting blue light, and compared its FTIR spectrum with those of the as-prepared PS emitting red–orange light, and those of the processed PS emitting no light. We consider that the blue light emission originates from the SiO_x layers covering nanoscale silicon units in PS.

Since Canham [1] first reported the photoluminescence (PL) of porous silicon (PS) at room temperature in 1990, many researchers have observed red, yellow, and green light, some of them [1, 2] attributing the PL to the quantum size effect. However, the blue light emission ranging from 4240 to 4912 Å is seldom observed in PS. To our knowledge, only Toshimichi Ito *et al* [3] and X Chen *et al* [4] have ever observed blue light, but not in detail. As we already know, blue light is one of the three primary colours in Nature (red and yellow being the other two); it is important for realizing a full-colour display. However, when the as-grown PS was illuminated or stored in air, its PL degraded with time [5, 6]. Afterwards, the stability of PL was given much attention by researchers. In this paper we report blue light emission at the peak wavelength of 460 nm, with both its intensity and peak energy stable. With Fourier-transform infrared (FTIR) measurements, we study the surface chemical bonds of the PS emitting blue light, and compare its FTIR spectrum with those of the as-prepared PS emitting red–orange light, and those of the processed PS emitting no light.

The samples used for the experiments were made from p-type (100) oriented silicon wafers, with a resistivity of 63 Ω cm, one side of which was deposited with aluminium. The electrolyser for fabricating PS was similar to that of [7]. An electrolyte ($\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}:40$ wt% $\text{HF} = 1:1:1$) was used, and the electrolysing current density and electrolysing time were 50 mA cm^{-2} and 8 min, respectively. The PS with a porosity of 69% was grown under illumination using a 250 W tungsten lamp at a distance of 20 cm from the PS; it then received a 350 °C thermal treatment (30 min) and a subsequent 550 °C thermal treatment (10 mins) in dry oxygen. The blue light spectrum was measured using a photoelectron multiplier, and the FTIR spectra were taken using a Nicolet-7000 with a resolution of 2 cm^{-1} .

The as-prepared PS samples emitted red–orange light. After oxidation in dry oxygen, the PS samples of a dark grey colour were emitting no visible light. We stored the PS

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samples in air for several weeks and measured their PL spectra again. To our surprise, under illumination with the 365 nm line of a UV lamp, the samples emitted blue light that could be observed by the naked eye. Further experiments demonstrated that the observed phenomenon was reproducible. Figure 1 shows a measured PL spectrum, with a peak wavelength of 430 nm. After a spectrum-response correction, the peak wavelength shifts to 460 nm. In order to study the stability of blue light emission, we illuminated the PS samples with the 365 nm line of a UV lamp and measured the PL intensity against illumination time. We found the PL intensity was stable under illumination which can be seen in the inset to figure 1. Even when the illumination time was increased to 4 h or so, the PL intensity was still unchangeable.

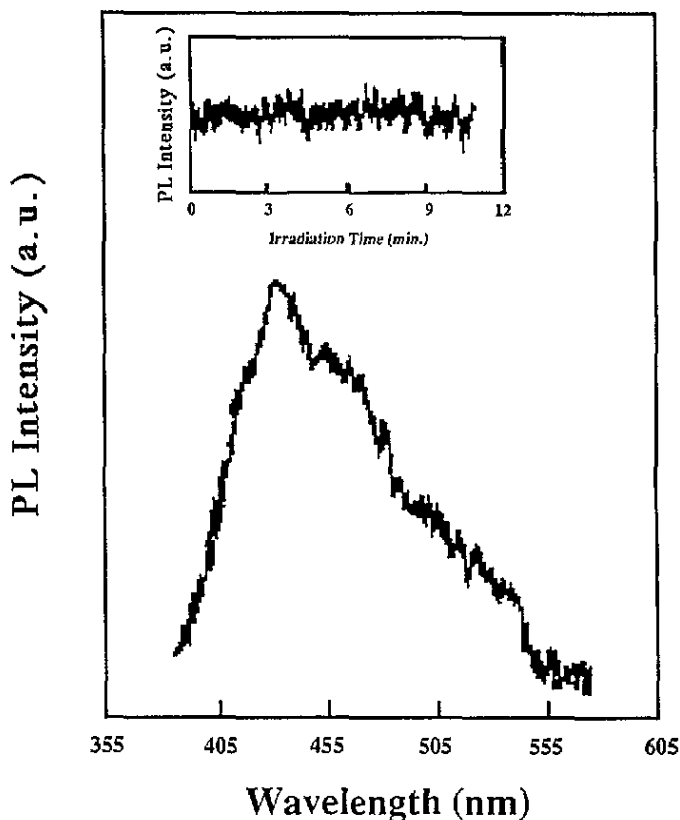


Figure 1. A PL spectrum measured under illumination from the 365 nm line of a uv lamp. The inset shows the PL intensity versus illumination time.

When PS samples began to emit blue light, we continually stored them in air and measured the PL spectra against storage time. Figure 2 shows the intensity and peak wavelength of PL as a function of storage time. We can see, during monitoring of three months, that the PL intensity fluctuates within 10%, which is probably caused by measurement error, and the PL peak position always locates at 2.7 eV. These results prove that the blue light emission of our PS is stable.

Using FTIR measurements, we have studied the surface chemical bonds of PS samples. Figure 3(a) shows the FTIR spectrum of an as-prepared PS sample with a PL peak wavelength

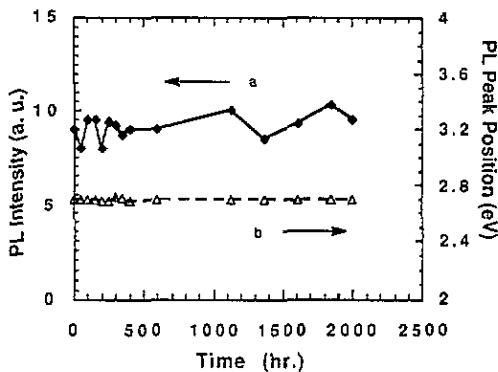


Figure 2. (a) the PL intensity versus storage time in air. (b) The PL peak position versus storage time in air.

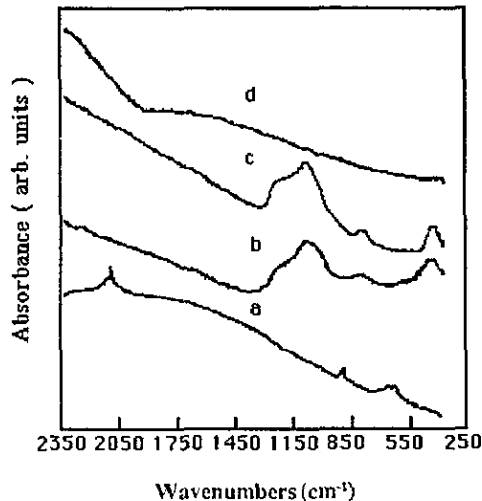


Figure 3. FTIR spectra for: (a), as-prepared PS sample; (b), oxidized after (a); (c), stored in air for 4 weeks after (b); (d), treated in HF for 30 s after (c).

of 680 nm, fabricated by the method mentioned above. We can see the 627 cm⁻¹, 667 cm⁻¹ peaks (SiH₂, SiH deformation mode [8]), the 907 cm⁻¹ peak (SiH₂ scissors mode [9]), and the 2116 cm⁻¹ peak (silicon hydrogen stretching mode [10]) in the spectrum, but the peaks related to oxygen do not exist. After the as-prepared PS sample received dry oxidation, as mentioned above, the processed PS sample emitted no visible light, and we measured the FTIR spectrum of this processed PS sample. The result is shown in figure 3(b), where we observe that all those peaks related to hydrogen disappear, but the 454 cm⁻¹, 800 cm⁻¹, 1090 cm⁻¹ peaks (Si-O-Si asymmetric stretching mode [11]) and the 1170 cm⁻¹ peak [12], all related to oxygen, appear. We stored the dry oxidation PS sample in air, where it began to emit blue light, and we measured its FTIR spectrum. The result is shown in figure 3(c). Obviously, there are no FTIR peaks related to hydrogen, and the peaks related to oxygen are nearly the same as those in figure 3(b). This means that neither the hydrogen- nor the oxygen-related bonds at the surfaces of nanoscale silicon units are responsible for the blue light emission. Finally, we dipped the PS sample emitting blue light in HF (wt 10%) for 30 s and found that the PS sample did not emit any visible light again. Figure 3(d) shows the FTIR spectrum of this PS sample. All the peaks related to oxygen have gone, and we can see no FTIR peaks related to hydrogen. SEM observations justify the existence of the PS layer after HF dipping although its thickness had been thinned to $\frac{1}{5}$.

Because a 2.7 eV (460 nm) band has been observed in silicas [13], we believe that the blue light emission originates from the SiO_x ($x \sim 2$) layers covering nanoscale silicon units in PS, and tend to think that the excited electron-hole pairs in nanoscale silicon units tunnel into the SiO_x layers and recombine through their luminescence centres [14]. As for the reason that processed PS samples do not emit blue light until after several weeks' storage in air, we think this is probably because the formation of luminescence centres in SiO_x layers of PS needs time.

In summary, we have found a way to produce PS emitting blue light at a peak wavelength of 460 nm, and on illumination with the 365 nm line of a UV lamp, or storing it in air, both its PL intensity and peak position were unchangeable. Using FTIR measurements on the PS

samples which emitted blue light, we found on their surface that the chemical bonds related to oxygen were strong, and all those related to hydrogen did not exist. FTIR studies indicate that neither the hydrogen- nor the oxygen-related bonds at the surface of nanoscale silicon are responsible for blue light emission. The SiO_x layers at the surface of nanoscale silicon units are essential for the stability of blue light emission from PS.

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