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LETTER TO THE EDITOR

## Blue light emitted from porous silicon obtained by hydrothermal etching

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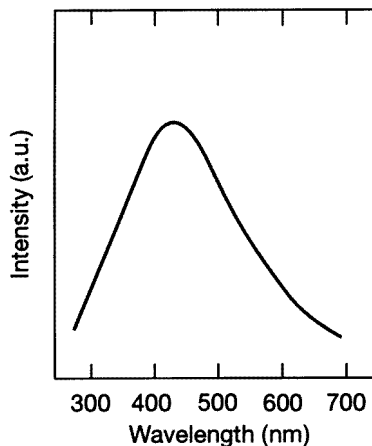
**Abstract.** Light emitting porous silicon (LEPSi) was prepared by hydrothermal etching of p-type single-crystal silicon. This sample preparation, which does not involve electrochemical etching followed by a rapid thermal oxidation (RTO) process in a dry oxygen ambient, yields blue light emission, the wavelength of the photoluminescence (PL) band peaking at 430 nm. The blue-emission porous silicon (PS) with high mechanical hardness is easily obtained by this technique. Our results are interpreted in terms of the currently suggested theories.

Since Canham found that porous silicon prepared by anodic etching can emit bright red luminescence at room temperature when illuminated with UV light [1], the possibility of using silicon as a light emitting material for optoelectronic applications has attracted much attentions. Recently, blue light emitted from LEPSi has been reported [2–7]. The main feature of the preparation technique is the anodic etching followed by treatment in boiling water [2] or rapid thermal oxidizing (RTO) in a commercial furnace for 30 s in a dry-oxygen ambient [8]. Some investigators have utilized light assisted anodic etching of Si and have produced this way a similar structure with blue light emission [6]. Mainly three possible models have been proposed for the blue emission from LEPSi: band-to-band recombination in silicon nanocrystals [9], emission from the oxide [10], and emission due to surface states [11].

This letter reports on an alternative technique for preparing porous silicon with blue luminescence. It does not utilize anodic etching, nor does it use RTO treatment. Finally, the microstructure and possible mechanism for the blue PL are discussed.

P-type (100) silicon wafers with resistivities  $0.5 \Omega \text{ cm}$  were fixed in a Teflon vessel. Solutions of  $0.3 \text{ mol L}^{-1}$  LiF in  $10.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  were added to the vessel until 60–70% of its volume was filled, then the vessel was placed in a stainless steel tank to perform hydrothermal treatment, which was carried out at  $140^\circ\text{C}$  for 2 h. After being etched, the samples were washed with distilled water several times and dried in air at room temperature. For a typical sample, the film porosity was  $72 \pm 1\%$ . The thickness of the porous layer was about  $10 \mu\text{m}$ , which was evaluated by means of a scanning electron microscope (SEM) image of cross-sectional PS.

In fact, the hydrothermal etching is recognized to be similar to stain-etching [12], with points on the Si surface behaving as localized anodes and cathodes. However, the



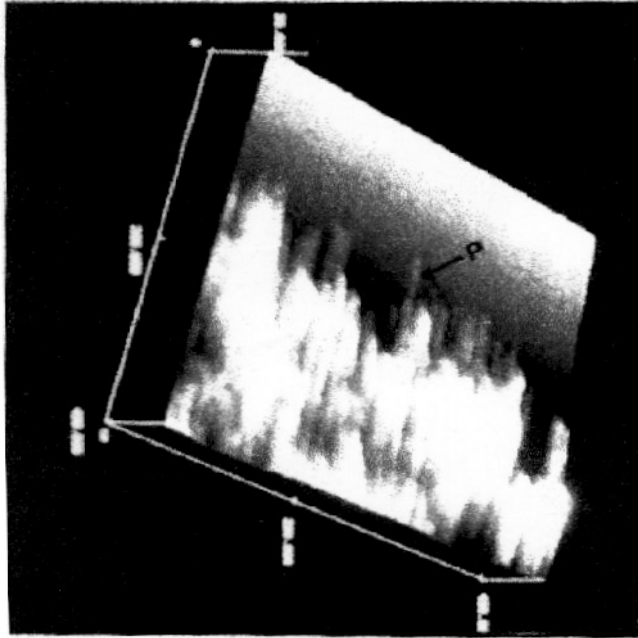
**Figure 1.** Room-temperature photoluminescence spectrum taken on porous silicon submitted to hydrothermal erosion in  $10.0 \text{ mol L}^{-1}$  nitric acid containing  $0.3 \text{ mol L}^{-1}$  LiF solution at  $140^\circ\text{C}$  for 2 h.

nonuniformity in sample etching due to the insulating effect of hydrogen bubbles that form on the wafer surface as a result of electrochemical etching can be avoided in the hydrothermal process due to the supercritical condition. Furthermore, blue-emission PS can be obtained directly by this technique without subsequent RTO treatment, while the stain-etch PS films display only red PL.

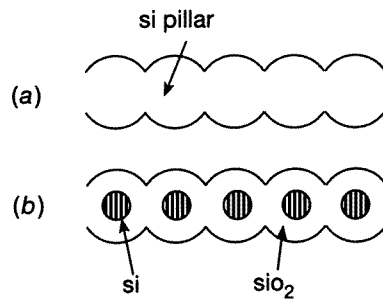
Figure 1 shows a typical PL spectrum of LEPSi excited with 256.6 nm radiation at room temperature. The PL spectrum exhibits a peak at 430 nm without a red component. The peak position is in agreement with that of samples obtained by electrochemical erosion followed by the RTO process [7].

The surface morphology of an as-prepared sample was examined using scanning tunnelling microscope (STM) observations. The typical image, as shown in figure 2, demonstrates that the PS layer consists of 5–8 nm columns (marked with P in the figure) with undulating width. Actually, the columns observed in the STM image are composed of isolated silicon nanocrystallites with size about 1 nm covered by amorphous silicon dioxide. This structural model, as shown in figure 3 ((a) and (b) are the pillars before and after oxidation, respectively), is confirmed by our recent small-angle x-ray scattering (SAXS) and high-resolution microscope (HREM) studies, which shows that there exist orderly dispersed silicon quantum dots in silicon oxide columns. The formation mechanism and further characterization will be discussed in detail in another paper [14]. Recent calculations suggest that the band gap is  $\geq 2.5 \text{ eV}$  for sizes below 2 nm [9]. Combining with the fact of the fast decay (ns) of blue emission [8], we tend to think that the blue emission is related to the silicon nanocrystallites with size about 1 nm embedded in amorphous silicon dioxide columns, which leads to both the opening of the band gap and surface states produced by Si–O bonds at the surface of the silicon nanocrystallites or the interface between the silicon nanocrystallites and the silicon dioxide. This also agrees with the observed correlation between the intensity of the blue-PL band and the intensity of the Si–O infrared absorption [6].

When the hydrothermal etching is carried out in a low concentration of  $\text{HNO}_3$  (with the same concentration of LiF as mentioned above), red-emission porous silicon can be

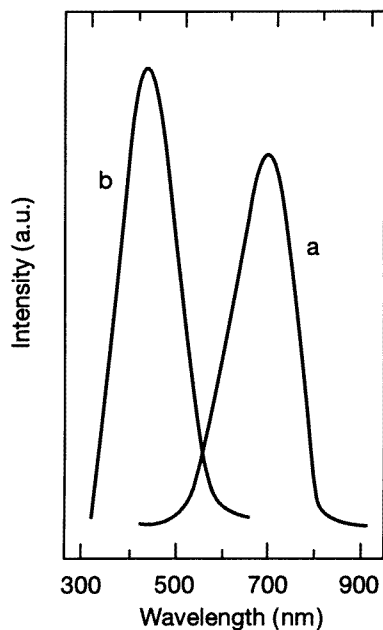


**Figure 2.** STM images of porous surface of freshly hydrothermally prepared blue-emission sample.

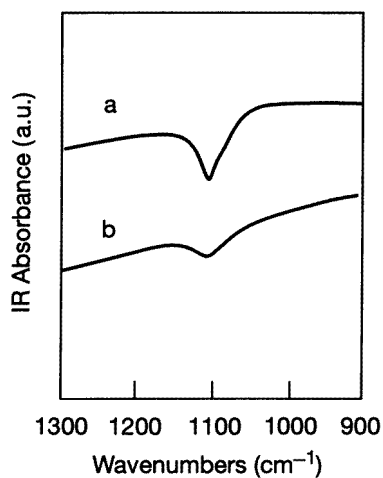


**Figure 3.** Structural model of pillars (observed in STM) before (a) and after (b) oxidation.

obtained. The PL spectrum for the PS layer prepared in a  $3.0 \text{ mol L}^{-1} \text{ HNO}_3$  solution (also  $0.3 \text{ mol L}^{-1} \text{ LiF}$ ) exhibited strong PL emission in the red with a peak at about  $690 \text{ nm}$ , as shown by spectrum (a) in figure 4. Fourier transform infrared (FTIR) absorption for both the red- and blue-PL samples hydrothermally prepared has a weak peak at  $1107 \text{ cm}^{-1}$  related to the asymmetric stretching vibrational mode of the Si–O–Si oxygen bridge in a configuration close to stoichiometry (figure 5). Thus, it is reasonable to suspect the origin of the blue band from  $\text{SiO}_2$  [7, 10]. Red and blue luminescence are both affected by oxidation of porous silicon, but, in different ways, the blue band appears after oxidation [7] while the red luminescence exists in as-prepared material and increases in oxidized material, but tends to vanish after heavy oxidation [7, 13]. This also makes us doubt the model where the blue luminescence comes from the  $\text{SiO}_2$ . Annealing of a red-PL sample at certain



**Figure 4.** Room-temperature photoluminescence spectra of porous silicon freshly hydrothermally prepared in  $3.0 \text{ mol L}^{-1}$  nitric acid containing  $0.3 \text{ mol L}^{-1}$  LiF solution at  $140^\circ\text{C}$  for 2 h (a) followed by annealing at  $950^\circ\text{C}$  for 30 s (b).



**Figure 5.** FTIR absorption spectrum of blue- (a) and red- (b) PL samples freshly prepared by hydrothermal etching.

temperatures (above  $600^\circ\text{C}$ ) can lead to blue emission peaking at 430 nm accompanied with the vanishing of the red band as revealed in figure 4(b). This may be because the subsequent thermal treatment causes the formation of isolated silicon nanocrystallites as shown in figure 3(b). While under hydrothermal conditions, the low concentration of nitric

acid solution ( $3.0 \text{ mol L}^{-1}$ ) has a weaker oxidation force, which does not lead to the formation of a silicon oxide layer thicker enough to isolate silicon pillars (the structure formation needs the undulating width for the original Si pillars).

As we mentioned above, the photoluminescence spectrum for the LEPSi prepared by hydrothermal etching does not contain two distinct bands, the originally discovered 'red' band, 650 to 800 nm, and the newly identified high-energy 'blue' band, 430 to 480 nm, at the same time. This is different from the case for the material prepared by electrochemical etching followed by the RTO process at temperatures from 750 to 1050 °C, which can include the two bands in the spectrum of same sample. This may be due to the difference in preparation conditions. Unlike the anodic etching process, which may lead to a wide size distribution of Si pillars due to nonuniformity in sample etching [15], the hydrothermal etching was conducted in an equilibrium way, and all the sample is in the same erosion conditions, which would lead to more uniform size of wirelike Si pillars. As a result, after oxidation (which can be conducted in the hydrothermal system or by subsequent annealing treatment in air) of the pillars the isolated nanocrystallites in each pillar will form in almost the same time (hypothesize that the PS layer consists of width undulating silicon pillars), then blue emission appears accompanied with the vanish of the red emission. In contrast, for anodic etching samples the isolated crystallites and Si pillars (covered by silicon oxide) may exist in a sample at the same time during annealing in air at certain temperatures [7], thus resulting in the coexistence of 'red' and 'blue' bands in its spectrum. This may be evidence that blue emission is related to the formation of the isolated silicon nanocrystallites.

One may argue if the blue-PL band in terms of the surface state related quantum confinement model, the PL spectrum and carrier lifetime should be very sensitive to the size of the crystallites [16]. Actually the size of crystallites usually obtained by transmission electron microscope (TEM), STM, or atomic force microscope (AFM) may be not the size of silicon nanocrystallites but its oxides with silicon nanocrystallites embedded. The true results should be obtained from XRD analysis. Furthermore, the temperature dependence of silicon nanocrystallite size variation with annealing temperature needs to be characterized systematically. Hence, the explanation of the blue-PL band in terms of the quantum confinement model ('pure' or surface state related) is unlikely due to the PL spectrum and carrier lifetime is not being sensitive to the size of the crystallites, this is still in dispute.

One more feature of the LEPSi obtained from hydrothermal erosion is that the blue PL is easily repeated and has better mechanical hardness than that of the anodic etching sample. These may be also due to the homogeneous erosion, and would promote the proceeding of use of this material.

In summary, it has been demonstrated for the first time that hydrothermal erosion of single-crystalline silicon in an LiF containing concentrated nitric acid solution yields a blue luminescence spectrum similar to that obtained by anodic etching followed by RTO treatment. The structure model of isolated silicon nanocrystallites embedded in an orderly manner in the amorphous silicon oxide pillars was proposed. The nanocrystallites result in the enlargement of the band gap of LEPSi and oxygen related states in the gap, which was suggested to be related to the blue photoluminescence.

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