

Stable and intense blue-green emission in porous silicon achieved by amine immersion and rapid thermal oxidation

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Porous silicon treated by amine immersion and then rapid thermal oxidation results in a photoluminescence peak shift from ~ 650 nm (red light) to a stable and intense ~ 520 nm blue-green light. The amine immersion may catalyze a process during rapid thermal oxidation that both reduces the sizes of Si cores and more effectively saturates the dangling bonds on the inner surfaces of the porous silicon. © 1997 American Institute of Physics. [S0003-6951(97)03010-6]

The highly porous silicon (PS) prepared by anodic etching in HF solution normally emits strong visible light in the red to yellow region of the spectrum. To reach shorter wavelengths such as those in the region of green and blue, the PS layer should possess a higher porosity such that the sizes of Si columns or clusters in the PS skeleton become smaller, this will result in an increase in the effective band gap caused by quantum confinement effect. The blue or green emission of PS is not effectively achieved using simple anodic etching, since the PS skeleton with such a high porosity is easily broken. A number of groups have achieved green or blue emission of PS by using different post-anodic treatments.¹⁻⁸ The basic idea is to make a light-emitting PS film with relatively low porosity first, and then to reduce the sizes of the Si cores by oxidation. This has the effect of shifting the luminescence peak from red to green or blue while still keeping the Si skeleton strong. Koch *et al.*¹ first reported a shift of the PL peak to the green region using rapid thermal oxidation (RTO). But the luminescence intensity was weak unless the oxidation temperature was higher than 800 °C. For blue band emission, Koch *et al.*¹ and later Tsybeskov *et al.*² observed a fast decay component in the blue in their time-resolved photoluminescence (PL) spectra for PS samples prepared by either thermal oxidation or chemical oxidation. Hou *et al.*³ first achieved a steady blue PL of PS using a boiling water treatment. The process was suggested to be a mild oxidation, but the size control of the PS cores seems quite critical so the reproducibility of achieving blue emission by such treatment is not satisfactory.⁴ Harris *et al.*⁹ also reported steady blue emission from PS, which was poorly reproduced and unstable. The blue emission observed by Calcott *et al.*⁷ and Loni *et al.*⁸ was believed to originate from SiO₂ rather than the PS cores since the samples were over oxidized by the treatments they used. In the work reported in this letter, a new method to achieve intense and stable blue-green emission from PS is developed. It uses amine immersion in combination with RTO; the process could be controlled in a wide temperature range with very good reproducibility.

Boron doped *p*-type single crystal Si (100) wafers with

the resistivity of 5–8.5 Ω cm were used as the starting materials. The samples were prepared by anodic etching in a solution of HF:ethanol=1:1 with the current density of 10 mA/cm². A 50 W halogen lamp was placed at a distance of 20 cm above the sample during the etching. The total etching time was about 20 min. After being cleaned by de-ionized water and dried by blowing N₂ over the wafer, the samples showed an orange color under UV illumination.

The amine treatment was carried out by dipping the sample in a mixed solution of (C₂H₅)₃N:C₂H₄(NH₂)₂=3:2 for ~ 15 min. Bubbles evolved from the sample upon reacting with the solution, and the sample was taken out from the solution after the bubbling had been stopped for about 5 min. The sample was then oxidized in a RTO furnace. The O₂ flux was 3–7 L/min. The heating rate and the cooling rate were about 50 °C/s.

The PL was excited by the 441.6 nm line of a 20 mW He–Cd laser with a light spot on the sample surface of ~ 1 mm². A Fourier transform-infrared (FT-IR) 5DX infrared spectrometer and an ER 200D-SRC electron paramagnetic resonance spectrometer were used for spectral measurements.

The PL spectra of the samples treated by amine immersion plus RTO (AIRTO) at different temperatures and oxygen fluxes were measured. Typical PL spectra are shown in Fig. 1. Curve a is the spectra of the as-etched sample. After the sample was treated by amine immersion at room temperature for 15 min, the PL spectrum (curve b) does not show a significant peak shift. With RTO only at 660 °C for 30 s, the PL peak of the as-etched sample shifts to the blue-green region but the intensity is very weak (curve c). For the sample treated with the amine immersion at room temperature for 15 min followed by the RTO at 660 °C for 30 s, a blue-green emission is observed as shown by curve d. The blue-green emission is so strong that it could be observed by the naked eye under daylight conditions. The durability of the blue-green emission is demonstrated by curve e which is taken from the AIRTO treated PS sample after being stored in dry atmospheric air for 160 days. Only minor change of the PL intensity occurs after this extended time exposure.

It was found that the different oxygen fluxes (3–7 L/min) and different RTO time (30–120 s) give only a minor influence on the PL characteristic of the treated samples. On the other hand, the resistivity of the starting materials is an important factor in achieving the blue-green emission. For

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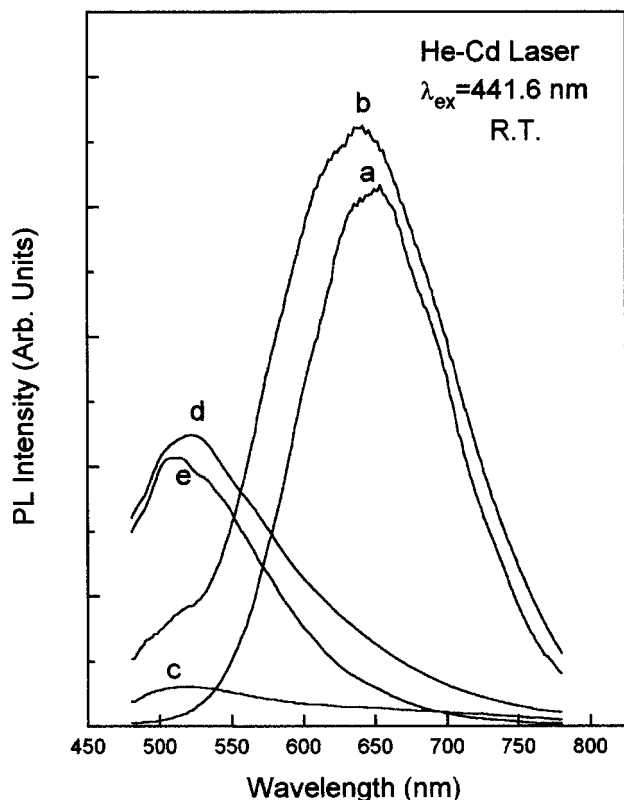


FIG. 1. PL spectra of the samples. (a) as-etched, (b) with amine immersion at 300 K for 15 min, (c) with RTO at 660 °C for 30 s, (d) with both amine immersion at 300 K for 15 min and RTO at 660 °C for 30 s (AIRTO), and (e) sample (d) stored in dry atmospheric air for 160 days.

PS samples with a substrate resistivity of less than 1 Ω cm, no blue-green emission was observed after the same AIRTO treatment mentioned above.

Plotted in Fig. 2 are the dependencies of the PL peak wavelength (curve a) and the peak intensity (curve b) versus the RTO temperature. The relationship between the RTO temperature and the PL peak intensity is quite similar to that reported by Koch *et al.*¹ for the PS samples treated by RTO only. On the other hand, the peak shift in our experiment does not depend on the RTO temperature within the range of 400–900 °C. Thus by properly choosing the starting materials, blue-green emission could be achieved with about 70%

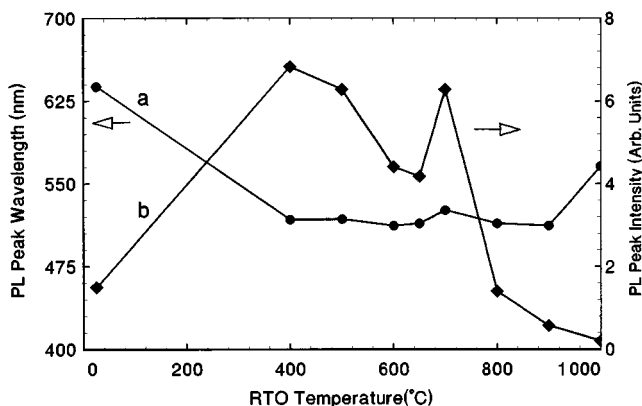


FIG. 2. (a) PL peak wavelength and (b) PL peak intensity of the AIRTO treated samples as a function of RTO temperature.

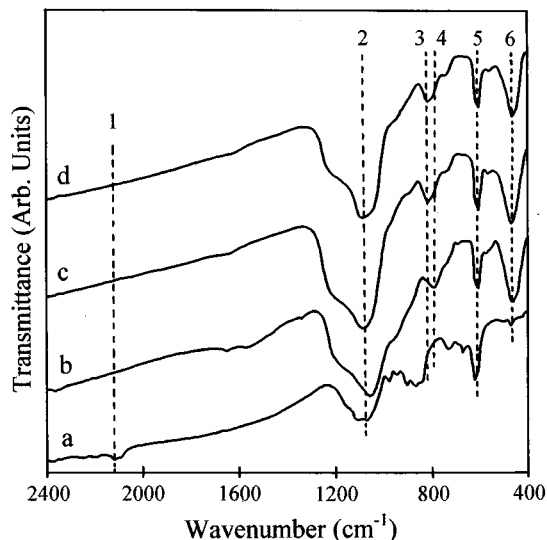


FIG. 3. FTIR spectra of the samples: (a) as-etched, (b) with amine immersion at 300 K for 15 min, (c) with RTO at 660 °C for 30 s, (d) with both amine immersion at 300 K for 15 min and RTO at 660 °C for 30 s (AIRTO), and (e) sample (d) stored in dry atmospheric air for 160 days.

reproducibility in an appropriate RTO temperature window.

The FTIR absorption spectra of the samples are shown in Fig. 3. The samples were stored in dry air ambient for one day prior to the measurements. Curve a corresponds to the as-etched sample. It mainly consists of three peaks 1, 2, and 5. Peak 1 at ~ 2110 cm^{-1} is related to the Si–H stretching mode^{10,11} and peak 2 at ~ 1110 cm^{-1} is related to the Si–O–Si asymmetric stretching mode.^{10,11} Peak 3 at ~ 620 cm^{-1} can originate from either Si–H wagging mode or Si–Si bulk vibrations.¹² Since peak 3 does not change following the RTO treatment for temperatures above 600 °C (at which time the Si–H bonds should have been broken with all H fully desorbed^{13,14}) it is reasonable to assign peak 3 to the Si–Si stretching mode.^{10,15} The peaks in the ranges of 978–837 cm^{-1} and 725–668 cm^{-1} are related to Si–H_x ($x \geq 1$).¹¹ Curve b corresponds to the sample treated by dipping in the amine solution for 15 min only. Four main peaks are discernible. Peaks 2, 4, 5, and 6 are related to the vibrations of SiO₂, Si–CH₃ bond (~ 790 cm^{-1}), Si–Si bond, and SiO_x (~ 460 cm^{-1}), respectively.¹⁰ No Si–H_x peaks are detected in the sample. It implies that the Si–H bonds on the inner surfaces of the sample may be replaced by –O and –CH₃ species. Curve c is the spectrum of the sample treated by RTO at 660 °C for 30 s only. In addition to peaks 2, 5, and 6, a new peak (peak 3) emerges at ~ 818 cm^{-1} which may be related to the vibrations of Si–N–O species or Si–O bonds because it can be removed by dipping the sample briefly into an HF solution. Curve d is the spectrum of the AIRTO treated sample, and it is almost the same as curve c. In the 400–4000 cm^{-1} wave number region, no organic substance or H-related vibrational peak is detected in both curves c and d (the spectra in the region of 2400–4000 cm^{-1} are omitted in Fig. 3). This is understandable because the boiling points of (C₂H₅)₃N and C₂H₄(NH₂)₂ are 89.7 °C and 117.1 °C, respectively. Both of them will volatilize during the RTO process.

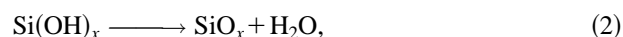
The strong luminescence intensity of AIRTO sample is

believed to be related to the enhanced passivation of the surface dangling bonds on the surfaces of PS skeleton. Our electron spin resonance (ESR) measurements (to be reported in more detail elsewhere) estimate the spin densities, which in our case should correspond to the densities of surface dangling bonds. The spin densities of the as-etched sample, the RTO sample, and the AIRTO sample are 4.0×10^{13} , 9.0×10^{14} , and $2.9 \times 10^{13} \text{ cm}^{-2}$, respectively. Thus the AIRTO sample has the lowest density of dangling bonds. The very high spin density of the RTO sample implies that the surfaces of PS skeleton are not passivated sufficiently at a temperature of $660 \text{ }^\circ\text{C}$. Since the surface dangling bonds serve as the nonradiative recombination centers, their enhancement results in a weak luminescence peak as shown in curve c of Fig. 1. Although the spin density of AIRTO sample is slightly lower than that of the as-etched sample, the total volume of Si cores in the former sample is reduced by the oxidation, so the PL intensity of AIRTO sample is expected to be not as strong as that of the as-etched sample as shown by curves a and d in Fig. 1.

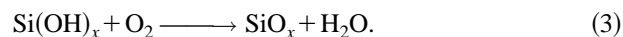
The above results are believed to be caused by the combined effect of amine immersion and RTO. One possibility is that amine could act as a catalyst. In this model, the SiH_x species in PS are hydrolyzed into Si(OH)_x species:



During the RTO treatment, Si(OH)_x species are decomposed or reacted with oxygen to form silicon oxides by the following reactions:



or



The decomposition temperature of Si(OH)_x is much lower than that of SiH_x , thus the oxidation could be carried out at lower temperatures with an effective reduction of the core size of the nanocrystals in the PS.

In conclusion, amine immersion followed by rapid thermal oxidation is found to be a simple and effective post-anodic treatment for light-emitting porous silicon. This treatment results in stable and intense blue-green luminescence with very good reproducibility.

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