

## Blue emission of porous silicon intensified by boron deposition

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Porous silicon (PS), which is fabricated by anodic etching in HF acid solution, has been extensively investigated because of its intense luminescence in the visible spectral range [1]. Though red and green light emissions have been easily obtained by using suitable anodized conditions, blue emission is still difficult to observe in as-prepared porous silicon [2]. Several post-treatments have been developed to obtain blue emission from porous silicon, such as rapid thermal oxidation [3], high temperature thermal oxidation [4], boiling or vapor water treatment [5], ferroelectric materials filling [6], carbon-plasma-implantation [7], photo-assisted oxidation [8], and so on.

Even though a considerable progress has been achieved, many problems still exist for the application of porous silicon devices, such as low quantum efficiencies and short lifetimes. In recent years, many efforts have been devoted to the preparation of composites, which consist of porous silicon and nano-materials, which can emit light in visible range, such as CdS, ZnO, ZnS, CdSe and ZnSe [9–12]. It is believed that the composites can improve stabilization of the light emission, form new light emission bands and increase electroluminescence efficiency in porous silicon. Gokarna *et al.* [9] found that a passivated interface had formed between nanocrystalline CdS or ZnS and the surface of porous silicon after depositing ultra thin films of nanocrystalline CdS or ZnS on porous silicon. The stabilization of light emission in porous silicon, filled with CdSe or ZnSe nano-particles, was investigated by Belogorokhov *et al.* [10, 11]. Moreover, Elhouichet and Oueslati [12] found that the photoluminescence (PL) bands of porous silicon shifted towards high energy and the intensity became stable when dangling bonds on the surface were passivated by ZnO nano-particles. From this viewpoint, it is worthwhile to investigate the effect of more kinds of nano-particles on the light emission of porous silicon.

In this paper, the blue light emissions of the porous silicon before and after boron-particle coating were also investigated. It was found that the blue emission of the porous silicon was enhanced by boron-particle deposition.

The porous silicon was prepared by boron-doped (1 0 0) single crystal silicon with 1–10  $\Omega\text{cm}$  resistivity.

The anodic etching was carried out in a HF (40%) and ethyl alcohol (analytic pure) solution with a ratio of 1:2 in volume at room temperature. The anodization was carried out at a current density of 50 mA/cm<sup>2</sup> under a back illumination from a 50-W lamp mounted at a distance of 10 cm and the etching time 60 min. The anodized samples were rinsed with de-ionized water and dried at room temperature.

Then some PS samples were placed in the center of a horizontal tube furnace for collecting boron particles. The reaction chamber was pumped down to 20 Pa and heated under N<sub>2</sub> flow. As the temperature reached the scheduled temperature, the mixture gas of nitrogen, hydrogen and diborane with a flow ratio of 10:50:1 was allowed into the chamber. The holding temperature was 800 °C. Pressure in the chamber was kept at  $5 \times 10^4$  Pa. After deposition for 5 hr, the furnace was cooled down.

The PL spectra excited with 360 nm light were measured by means of a HITACHI F-4500 fluorescence spectrophotometer. The infrared absorption spectra of the samples were taken using a Bruker IFS 66v/S Fourier transform infrared (FTIR) spectrometer. The appearance observations were carried out using JSM-5610LV SEM. All the measurements were carried out at room temperature under ambient atmosphere.

Fig. 1a shows the structure of an as-etched porous silicon layer. Elements of the sample's surface are shown in the inset Energy Dispersion Spectroscopy (EDS) image of Fig. 1a. The microstructure consists of small pore channels with lots of interconnection. After the boron particles were filled is porous silicon (Fig. 1b), the shape almost does not change except the white slices consisting boron particles appear on the top of the porous silicon layer, which can confirm by the EDS image (the inset of Fig. 1b).

Fig. 2 shows the PL spectra of the porous silicon as-prepared and aged for two weeks. The blue emission centered at 450 in the PL spectrum of the as-prepared porous silicon can be observed. However, after two weeks the blue emission shifted from 450 to 420 nm, and a new emission band located at 550 nm was found.

Fig. 3 shows the PL spectra of the porous silicon coated by boron particles. The blue emission band, which was same as in the as-prepared porous silicon, was observed. In comparison with the as-prepared

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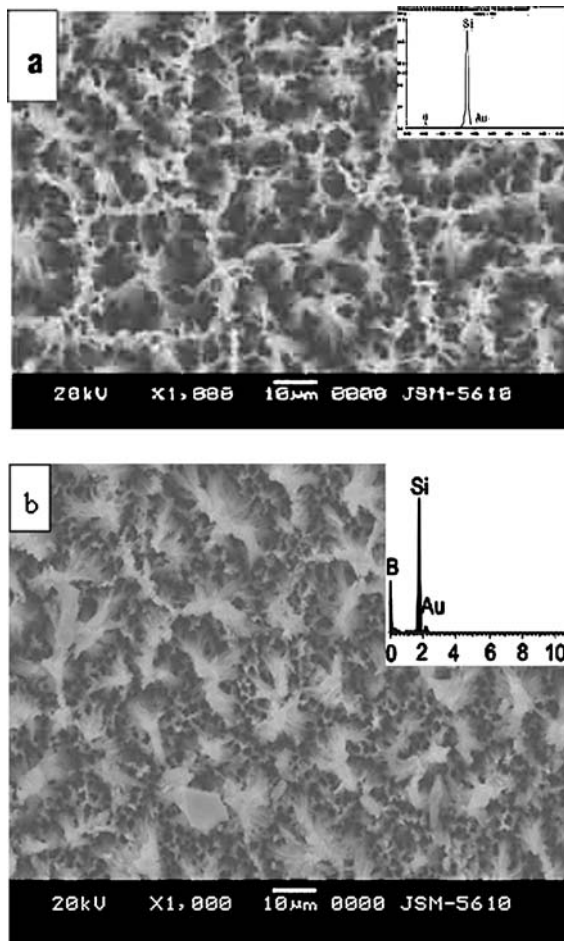


Figure 1 SEM images of the porous silicon as-prepared (a) and boron particle coated (b). Two EDS images are shown in inset.

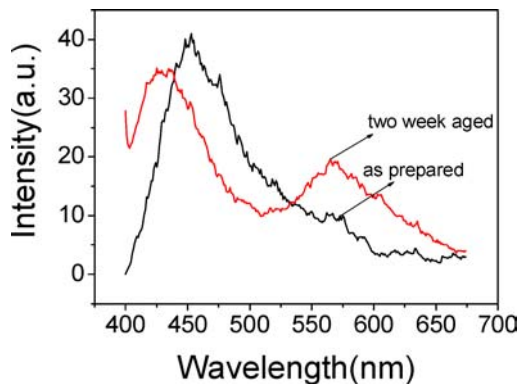


Figure 2 PL spectra of the blue light emission of the porous silicon as-prepared and aged for two weeks.

porous silicon shown in Fig. 2, the intensity increased strongly after coating. It is well known that boron particles do not emit light in the visible light spectra. Therefore, the blue emission in Fig. 3 should originate from the porous silicon and enhanced by coating boron particles. However, after two months, the emission intensity of the coated porous silicon samples decreased significantly (Fig. 3b).

As reported in the previous papers [3, 4], the blue emission in porous silicon may originate from the recombination of carriers and defects in the oxide layer coated on the wall side of porous silicon. Therefore, due to the normal oxidation on the surface of the as-prepared sample under ambient situation, the

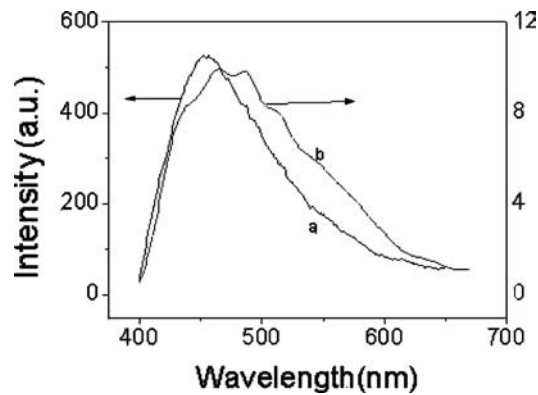


Figure 3 PL spectra of the blue light emission of the composite samples as-prepared (a) and aged for two months (b).

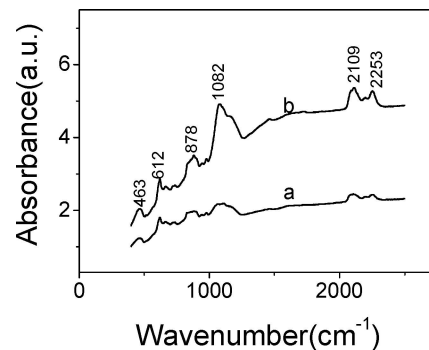


Figure 4 FTIR spectra of the samples (a): as-prepared porous silicon; (b): porous silicon aged for two weeks.

blue emission band centered at 450 nm was observed (Fig. 2). After aging for two weeks, the defect structures in the oxide layer might be changed due to the further oxidation in air, which resulted in shift of the blue emission at 450–420 nm and the observation of the new band at 550 nm. The FTIR spectra confirmed the oxidation of the porous silicon in air. As shown in Fig. 4, the intensity of 1082  $\text{cm}^{-1}$  peak related to Si–O–Si vibration mode increased after aging for two weeks. Moreover, the Si–H bonds located in 2109 and 2253  $\text{cm}^{-1}$  became higher after aging, which might be attributed to the adsorbed moisture in the atmosphere. Further work was needed to exploit the mechanism.

After coating boron particles, the intensity of the blue emission increased strongly (Fig. 3), indicating that the coated boron particles enhanced the blue emission. This might be due to annihilation of the non-radiation centers on the surface of the porous silicon during coating. However, the porous silicon could be continuously oxidized in air during aging for two months even if the porous silicon was coated with boron-particle layer. The oxidation could change or eliminate the defects that emitted blue light so that the intensity of the blue emission decreased, as shown in Fig. 3b.

The porous silicon, which emitted the blue light at room temperature, was prepared by anodic etching in HF acid solution. After the deposition of boron particles, it was found that the intensity of the blue emission was improved, which might be due to the elimination of the non-radiation centers on the surface of the porous silicon. Furthermore, after aging, the blue emission shifted in as-prepared porous silicon, and its

intensity decreased greatly in the coated porous silicon, which is attributed to the structural change or annihilation of the blue emission defects during oxidation.

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