

Blue-light emission from porous silicon induced by laser irradiation

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Received 11 January 2005; accepted 27 February 2005

Available online 31 March 2005

Abstract

Porous silicon coated with silica gel emitted light with higher energy after it had been irradiated by a Nd:YAG laser. SEM and XRD measurements demonstrate no crystal-to-amorphous transformation under the irradiation, which is presumably because of good protection of the material by silica coat. FTIR results show that the blue-light emission obtained is due to the formation of Si–C and Si–O–C surface bonds under the laser treatment.

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Keywords: Porous silicon; Laser processing; Blue light; Luminescence

1. Introduction

Numerous investigations have been carried out on the photoluminescence (PL) properties of porous silicon (PS) [1–4]. PS usually emits red–green light, and does not emit blue light even when the crystallite size drops well below 3 nm. This is explained by formation of Si=O surface bonds with a localized gap of 2.1 eV (green light) on exposure to air or oxygen [5]. A lot of effort has been made to obtain blue light by passivating surface and forming amorphous structure, but only low-intensity blue light has been achieved thus far [6–11].

Several studies reported on PL modification by laser irradiation on PS [12,13]. It was suggested that, provided appropriate laser treatment, PS surface conditions could be changed, thus resulting in formation of Si–O and Si–O–SiR surface bonds and emission of more intense and higher-energy light. However, the blue-light emission was never found by laser irradiation [12,13].

To prevent possible melting caused by high temperature under laser irradiation [14], in this work, we coated PS specimens with silica film prepared by sol-gel method. After laser irradiation, a relatively strong blue-light emission was

reached, which was shown by SEM, XRD and FTIR analyses to be due to the modified PS surface bonds rather than crystal-to-amorphous transformation.

2. Experimental procedure

Porous silicon was prepared by electrochemical anodization of polished p-type, B-doped (100) oriented Si wafers

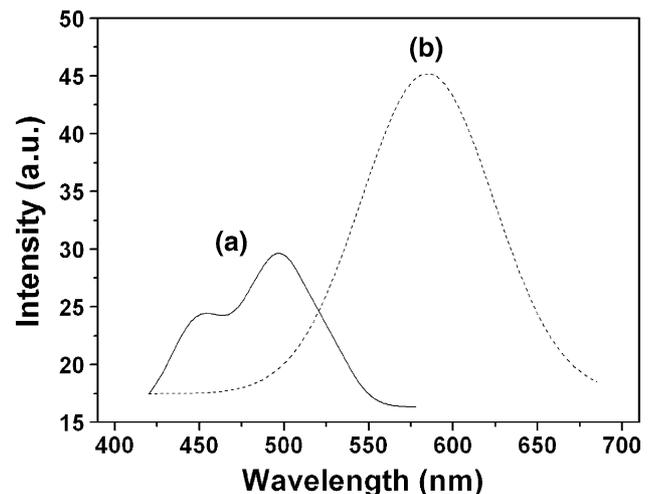


Fig. 1. PL spectra of samples 1 (a) and 2 (b) (Fitted with Gaussian curves).

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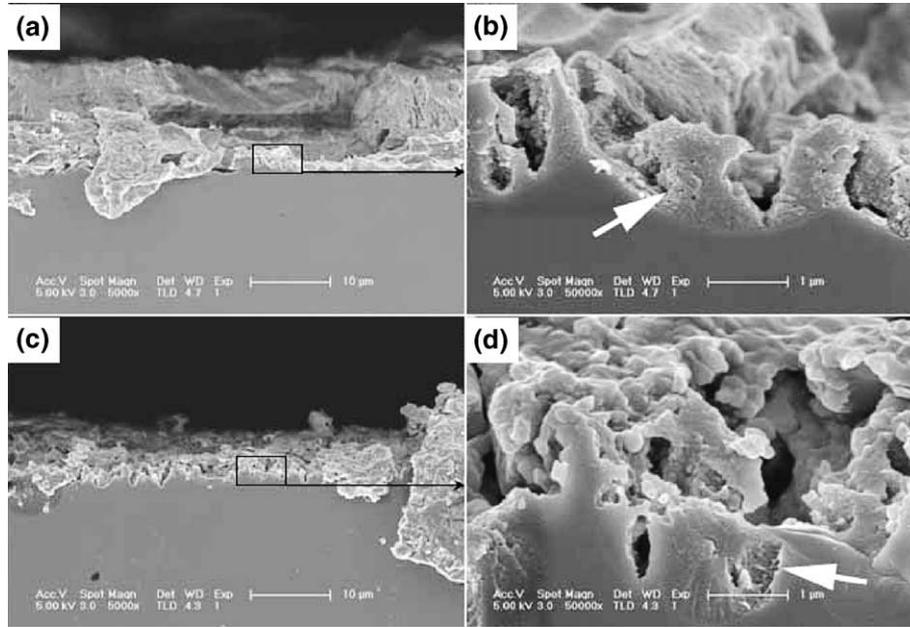


Fig. 2. Cross-section morphology of PS: (a) low-magnification image of sample 1; (b) high-magnification image of sample 1; (c) low-magnification image of sample 2; (d) high-magnification image of sample 2.

with a resistivity of 10–12 Ωcm. As an electrolyte a mixture of HF:C₂H₅OH:H₂O with the ration of 1:1.5:2 was used. The samples were anodized at current density of 30 mA/cm² for 30 min and then 20 mA/cm² for another 30 min. The silica gel was formed on PS layer by hydrolysis-condensation reaction of the solution mixture of Si(OC₂H₅)₄ (TEOS), C₂H₅OH, H₂O and C₃H₅(OH)₃ (volume ratio 1:1:1:1). Sample 1 was produced by pulsed-laser shock processing technique using a Nd:YAG laser. The laser used had the following parameters: energy density of 106 W/cm², wavelength of 1.06 μm, pulse width of 1.2 ms, and pulse frequency of 20 Hz. Its beam could be focused to provide a

spot diameter of 0.2 mm. For comparison, sample 2 was coated by silica gel with no laser treatment.

PL spectra were excited by the light of a Xe-150 lamp passing through a 365 nm filter. PS morphology was observed using FEI FP 6800 scanning electron microscope (SEM), and phase structure was determined by means of a Rigaku D/max 2500v/pc X-ray diffractometer. The infrared reflection spectra were collected by a Nicolet 560 Fourier transform infrared (FTIR) spectrometer.

3. Results and discussion

Fig. 1 shows the PL spectra of samples 1 (a) and 2 (b) fitted with Gaussian curves. The peak around 594 nm in sample 2 represents orange-light emission. The PL spectrum

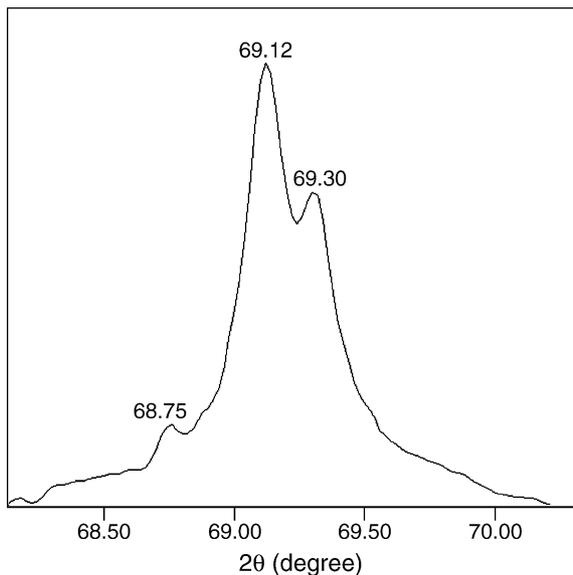


Fig. 3. XRD pattern of sample 1.

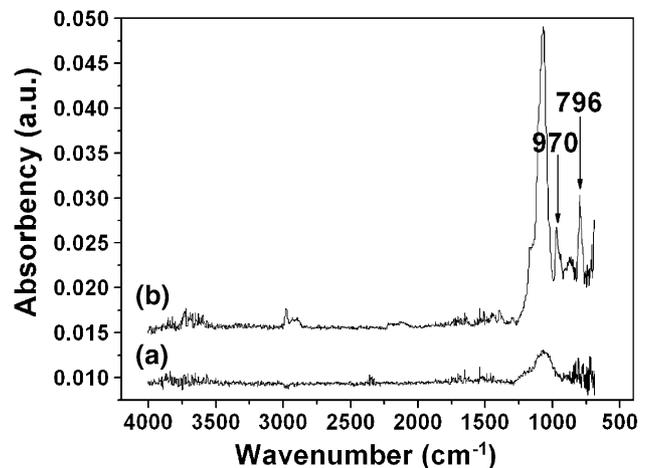


Fig. 4. FTIR spectra of samples 1 (a) and 2 (b) (The whole spectra).

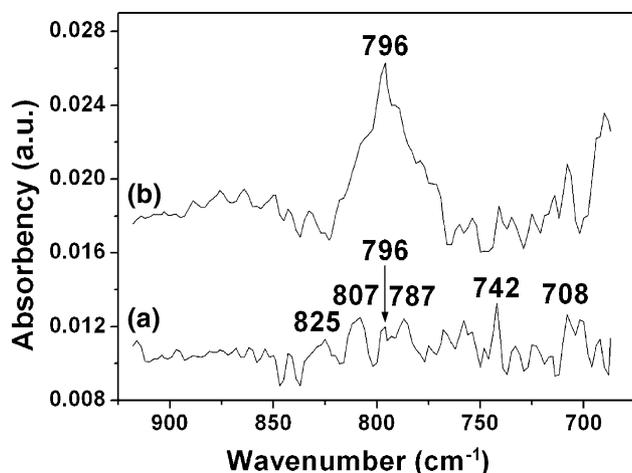


Fig. 5. Enlargement of Fig. 4 (Wavenumber range from 925 to 675 cm^{-1}).

changes significantly after laser irradiation, as two peaks are observed at 460 and 491 nm for sample 1. Although the peaks are slightly weaker than that in spectrum (b), this signifies that blue-light emission is occurring.

Two possible changes caused by laser irradiation could be responsible for the blue-light emission. One is the change in the PS crystal structure, and the other is the change in its bond structure. In order to find out the origin of the blue-light emission, SEM, XRD and FTIR analyses have been performed.

Fig. 2 shows the cross-section structure of porous silicon coated with silica after (a,b) and without (c,d) laser irradiation. For both samples, no obvious difference in PS structure is observed. In Fig. 2b and d, as indicated by white arrows, PS keeps loose state both after (b) and without (d) laser treatment, which proves no melting and compaction caused by heat effect due to laser irradiation of sample 1.

The XRD spectrum of sample 1 in Fig. 3 presents three diffraction peaks, the peaks at 69.12° and 69.30° being from the (100) plane of Si wafer, while the other peak at 68.75° from the nanocrystals in PS layers [15]. Based on the latter peak, we deduce that the PS in this specimen keeps crystalline structure, and no crystal-to-amorphous phase transformation occurred. Thus, all the above results suggest no change in the PS structure under the laser irradiation.

The FTIR results are shown in Fig. 4. It is seen that the broad peak at 1075 cm^{-1} and its shoulder at 1201 cm^{-1} , which are from Si–O–Si and Si–O bonds, respectively, [16,17] and very strong in spectrum (b), decrease dramatically for sample 1 (spectrum (a)). At the same time, the peaks around 970 and 796 cm^{-1} , which are mainly from TEOS [18], decrease seriously as well. The presence of the TEOS peaks in spectrum (b) indicates non-reacted TEOS in silica coating on sample 2. Fig. 5 is the enlargement of Fig. 4, where many weak peaks of sample 1 can be seen in more detail. The three peaks at 825, 807 and 708 cm^{-1} are due to Si–C bonds [19,20]; the peak at 742 cm^{-1} is ascribed to Si–O–C bonds [19]; and the peak at 787 cm^{-1} results from Si–H bonds [19].

The above results suggest that the change in PL properties is due to the change in its surface bonds. Namely, the Si–O–Si, Si–O and Si–H bonds in sample 2 are the origin of orange-light emission, their decrease causes disappearance of orange-light peak at 594 nm (Fig. 1). On the other hand, the Si–C and Si–O–C bonds formed during laser irradiation in sample 1, resulting in blue-light emission (Fig. 1, spectrum (a)) [21]. Moreover, the decrease of TEOS peaks suggests that the formation of Si–C and Si–O–C bonds is related to TEOS. Thus, we deduce the whole process of producing blue-light as follows: (1) under the laser irradiation, Si–H and Si–O–Si bonds broke, giving rise to H_2 and Si dangling bonds, (2) the dangling bonds are passivated by carbon atoms from TEOS which form Si–C and Si–O–C surface bonds responsible for blue-light emission.

4. Conclusions

Blue-light emission was successfully obtained from a porous silicon sample coated with silica gel and then irradiated by laser. The blue-light emission is suggested to result from the formation of Si–C and Si–O–C surface bonds under the laser treatment. Such a porous-silico-based material modified by laser irradiation can have potential applications in future integrated optical devices because of its more steady structure compared to that of porous silicon with finer nanocrystals.

Acknowledgements

This work was partially supported by the Natural Science Foundation of China (grant # 50402010), Natural Science Foundation of Tianjin City (grant # F104012), and Tianjin University (Project 985).

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