A Study on Visible Luminescence of Porous Silicon

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Since Canham reported that the porous silicon can emit efficient visible light, many research groups have been concentrating their work on the visible luminescence of the porous silicon. As silicon has an indirect band gap of only 1.1 eV, it is difficult to obtain efficient light emission from this system. Now, people want to push the frontier of the silicon-based material into the optoelectronics territory and achieve the entire silicon optoelectronic integration by using porous silicon. The very cheap efficient display device may also be made of visible light emitting porous silicon. The current-induced light emitting device of porous silicon and the highly sensitive photodetector of porous silicon have been fabricated in some laboratories. But the mechanism of visible luminescence from porous silicon is still under study. The main current point of view is the quantum confinement of the recombining electrons and holes in the one-dimensional quantum wires[1]. But some other research groups believe that the visible light is from the siloxene and its derivatites[2]. There are still some other points of view too. The exact origin of the visible light from the porous silicon is still a contentious subject. The photoluminescence spectrum of the porous silicon usually peaks between 600—700 nm with the full width at half maximum (FWHM) from 100 nm to 140 nm[3]. The Raman scattering spectrum of the porous silicon has a typical peak near 510 cm^{-1}[4]. The depth of the anodized layer of porous silicon is at micrometer scale. In this note, we report the photoluminescence (PL) experiments on the porous silicon fabricated with the standard anodization method and the obtainment of the fluorescent powder from the surface of the porous silicon. The PL spectrum of the fluorescent powder shows a similar peak position, a similar shape and a similar FWHM to those of the porous silicon wafer. And the powder cannot be dissolved in water, alcohol, acetone and some other common solvents. The fluorescent powder can also emit the efficient visible light after further grinding. The microstructure study of the SEM and the composition study of the XPS suggest that the efficient visible light from the porous silicon comes from the fluorescent powder formed during the process of anodization.

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1 Experiment

1.1 *Preparation of the Samples*

Silicon wafers used in the experiments were n-type single crystalline silicon (2.4—3.6 Ω·cm in the resistivity) with a mirror surface and an unpolished reverse side. The fabricating condition and process of the porous silicon were similar to those indicated in Ref. [3]. During anodization the surface of the silicon wafer was illuminated uniformly by a 250-W infra-red lamp. The powder-like fluorescent material was brushed down directly from the surface of porous silicon. The manual grinding to the fluorescent powder was fulfilled in an agate mortar.

1.2 *Spectral Measurement*

1.2.1 PL measurements. The samples were excited by the 337-nm emission of a pulse width of about 10 ns from an N_2 laser. The peak power of the laser was several hundred kilowatts (KW). The luminescence of the samples was detected by using a Spex-1403 monochromator, an R-928 photomultiplier and a Parc-162 box-car integrator. All the data were input into a computer and the PL spectra were drawn out.

1.2.2 Raman spectrum measurements. The samples were excited by the 448-nm line of Ar^+ laser. The Raman scattering measurement was carried out using a JY-T800 laser Raman spectrometer.

All the spectral measurements were achieved at room temperature.

1.3 *Analyses of the Microstructures*

The SEM photographs of the sample's surface morphology, the sample's cross-section microstructure and the powder morphology were obtained using the 1000B SEM.

1.4 *Analysis of the Compositions*

The exact compositions of the fluorescent powder in the surface of the porous silicon wafer were carried out through the Escalab-MKII XPS apparatus.

2 Results and Discussion

The PL spectrum of the porous silicon is shown in Fig. 1-1. The spectrum peaks at 17260 cm^{-1} (580 nm) with an FWHM of 3600 cm^{-1} (122 nm). The Raman scattering spectrum of the porous silicon is shown in Fig. 2. The spectrum has a peak near 520 cm^{-1} with a width of 15 cm^{-1}.

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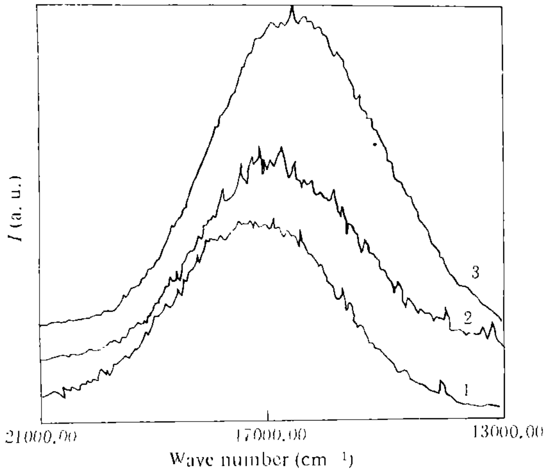

Fig. 1. The PL spectra of the porous silicon (1), the fluorescent powder (2), the porous silicon on unpolished surface (3).

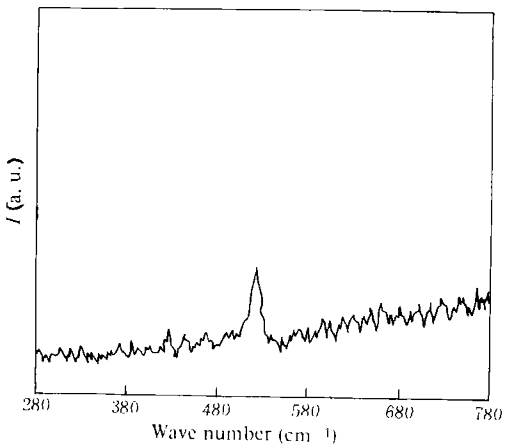

Fig. 2. The Raman scattering spectrum of the porous silicon.

The PL spectrum from the fluorescent powder is shown in Fig. 1-2. The spectrum peaks at 17,000 cm^{-1} (588 nm) with an FWHM of 3480 cm^{-1} (122 nm). Fig. 1-3 shows the PL spectrum of the porous silicon etched on an unpolished surface of the single crystalline silicon wafer. The spectrum peaks at 16,540 cm^{-1} (608 nm) with an FWHM of 3200 cm^{-1}. (118 nm).

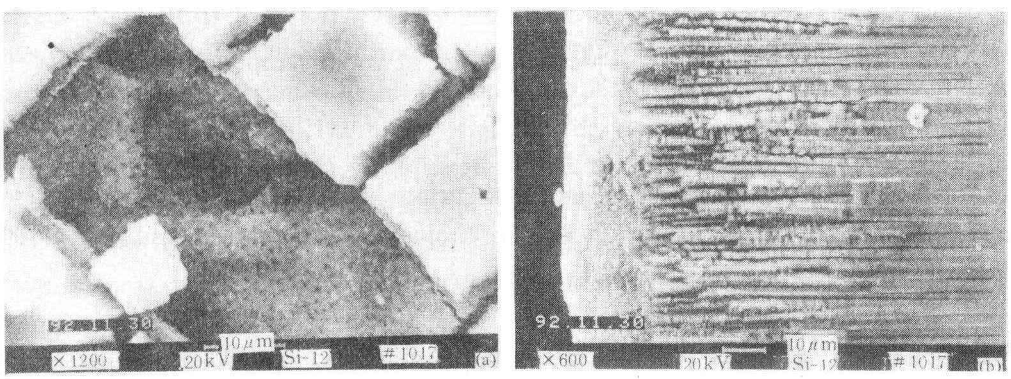

Fig. 3. The SEM observation of the surface and the cross-section of the porous silicon. (a) The surface morphology of the porous silicon observed with SEM; (b) the cross-section microstructure of the porous silicon observed with SEM.

Figure 3(a) is the SEM photograph of the surface of the porous silicon wafer. There are large numbers of micropores at the place where the surface layer has been dropped out. Fig. 3(b) shows the SEM photograph of the cross section microstructure of our porous silicon sample. The sample has three different layers: the surface layer, the porous layer and the single crystalline silicon substrate. The lengths of the clear micropores are nearly 100 μm.

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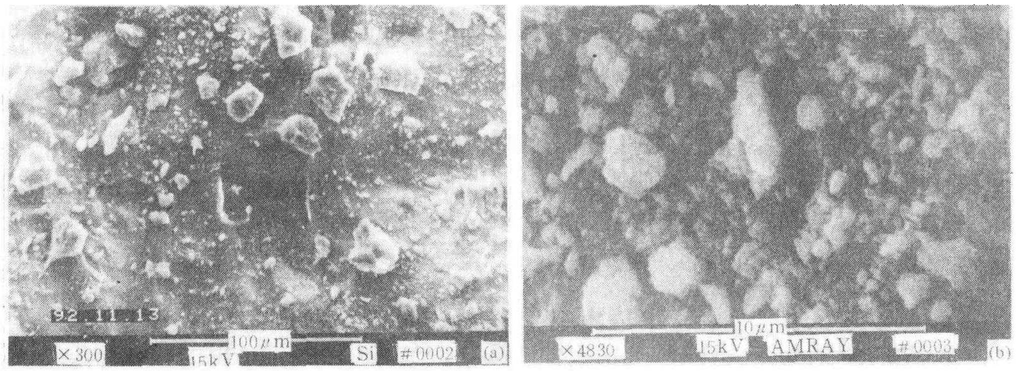

Fig. 4. The SEM observation of the fluorescent powder. (a) The SEM photograph of the morphology of the fluorescent powder before grinding; (b) the SEM photograph of the morphology of the fluorescent powder after grinding.

Figure 4 shows the morphologies of the fluorescent powder observed with the SEM. Fig. 4(a) shows the fluorescent powder before grinding. Fig. 4(b) shows the fluorescent powder which has been ground. Both the fluorescent powder in Fig. 4(a) and (b) show no pillar-like structures. The micropowder will agglomerate after grinding.

Figure 5 shows the result of the XPS study of the fluorescent powder in the surface of the porous silicon. The spectrum shows that the fluorescent powder is composed of many kinds of elements, such as Si, C, O, and F. The Si content is only 52.7% (the C content is 33.43%, the O content, 13.04%, and the F content, 3.26%, but element H is not counted in).

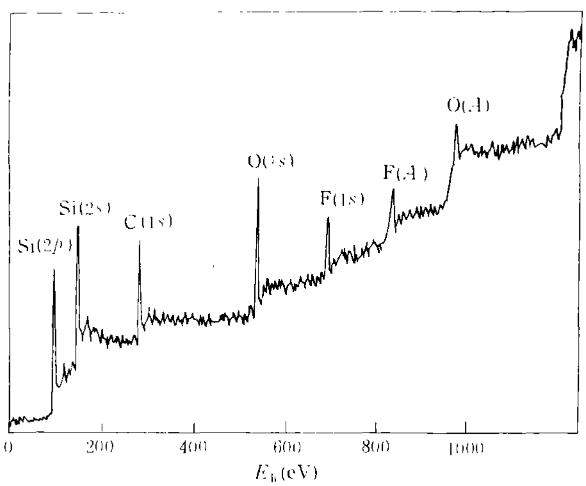

Fig. 5. The XPS composition study of the fluorescent powder in the surface of the porous silicon.

Considering that the PL spectra of the fluorescent powder and the porous silicon in Fig. 1 have a similar peak position, a similar shape and a similar FWHM, we suggest that the efficient visible luminescence is from the fluorescent powder in the surface of the porous silicon formed during the process of anodization. The PL spectrum of the sample fabricated on the unpolished surface of the single crystalline silicon wafer (Fig. 1-3) proves that the surface treatment (polished or not) has no effect on the

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photoluminescence of the porous silicon. The fact that the fluorescent powder can also emit efficient visible light after further grinding suggests that the powder is unlikely to be composed of one-dimensional crystalline silicon quantum wires. The observation of the cross section of the porous silicon suggests that the fluorescent powder is most likely formed in the surface layer over the porous layer. The study of the XPS also supports the point of view above and indicates that the composition of the fluorescent powder is complicated.

3 Conclusions

The visible light emitting porous silicon has three different layers: the surface layer, the porous layer and the single crystalline silicon substrate. The surface treatment (polished or not) has nothing to do with the fabrication of the visible light emitting porous silicon. The efficient visible luminescence from the porous silicon is from the fluorescent powder formed during the process of anodization. The composition and the structure of the fluorescent powder may be very complicated and are under further study now.

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References

1 Canham, L. T., *Appl. Phys. Lett.*, 1990, **57**(10): 1046.
2 Brandt, M. S. *et al.*, *Solid State Communication*, 1992, **81**(4): 307.
3 Nobuyoshi Koshida & Hideki Koyama, *Optoelectronics-Devices and Technologies*, 1992, **7**(1): 103.
4 Sui Zhifen, Leong, P. P. & Herman, I. P., *Appl. Phys. Lett.*, 1992. **60**(17): 2086.

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