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Optical properties of n-type porous silicon obtained by photoelectrochemical etching

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Abstract

The optical studies of n-type porous silicon prepared by the photo-assisted chemical etching are reported here. The optical properties of samples obtained under different conditions have been investigated by photoluminescence and Fourier transform infrared absorption measurements, and they are compared with that of p-type porous silicon. Our results clearly demonstrate that the blue emission in porous silicon originates from surface compounds. From the infrared absorption measurement, we point out that the surface compounds are Si–OH complexes. This conclusion is further supported by a recent calculation which shows that Si–OH complexes can emit the photon energy in the range observed here. We show that the optical properties of the n-type porous silicon are more stable than that of the p-type porous silicon. The result provides the evidence to support the fact that the n-type porous silicon is a better candidate for the application in optoelectronics. © 1999 Elsevier Science Ltd. All rights reserved.

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Silicon is the main material of microelectronics at present, but it is not widely used in optoelectronics. The reason is due to the inherent nature of the indirect transition in the band-edge emission. When the visible photoluminescence (PL) of electrochemically etched porous silicon was reported by Canham [1] in 1990, the material [2–5] has been extensively studied to clarify luminescence mechanism and to investigate its possible use as a new material for the optical device application. Despite of a large amount of research, the mechanism underlying the visible luminescence is unclear. The two most widely discussed mechanisms are the quantum confinement model and the surface model. Recently, an improved model, including both the effects of quantum confinement and surface state, has been proposed [6,7]. In our recent reports, we suggested that the lower energy emission (~1.8 eV) originates from the quantum confinement effect and the higher energy emission is dominated by the surface-state recombination [8,9]. Unlike most of the previous reports concentrated on the studies of p-type porous silicon, in the paper, we present the optical studies of n-type porous silicon prepared by the photo-assisted chemical etching. The obtained results will be compared with that of the p-type porous silicon. We clearly demonstrate that the blue emission in porous silicon originates from surface compounds. From the infrared absorption measurement, we point out that the surface compounds are Si–OH complexes. Our result is further supported by the recent calculation, which shows that Si–OH complexes can emit the photon energy in the range observed here. In addition, we show that the optical properties of the n-type porous

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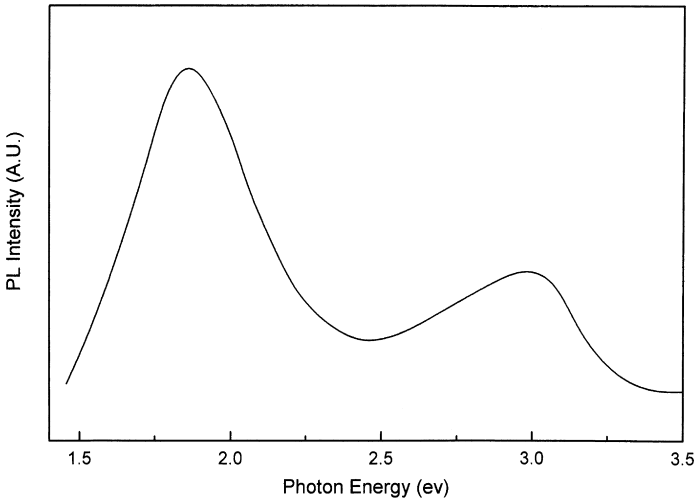

Fig. 1. Photoluminescence spectra of the n-type porous silicon prepared by the photo-assisted etching.

silicon are more stable than that of the p-type porous silicon.

Porous silicon samples were prepared by an electrochemical anodization method. The silicon wafers were n-type P-doped with resistance of 0.005–0.01 Ω cm and (111) orientation. Anodization was carried out using 60 mA/cm^2 in a solution of HF (40%):C_2H_5OH (1:1) for 25 min. A 100 W bulb was used for illumination from a 15 cm distance [10]. Samples were rinsed in running deionized water and blown dry by nitrogen gas immediately after electrochemical etching. The photoluminescence spectra were recorded by a SPEX 0.85 m double spectrometer, and a photomultiplier tube. The sample was placed inside a closed-cycle He cryostat. A He–Cd laser working at 325 nm was used as the excitation source. The infrared absorption spectra were measured using a Nicolet ZDS Fourier transform infrared spectrometer at room temperature.

The reaction involved in the anodic dissolution of

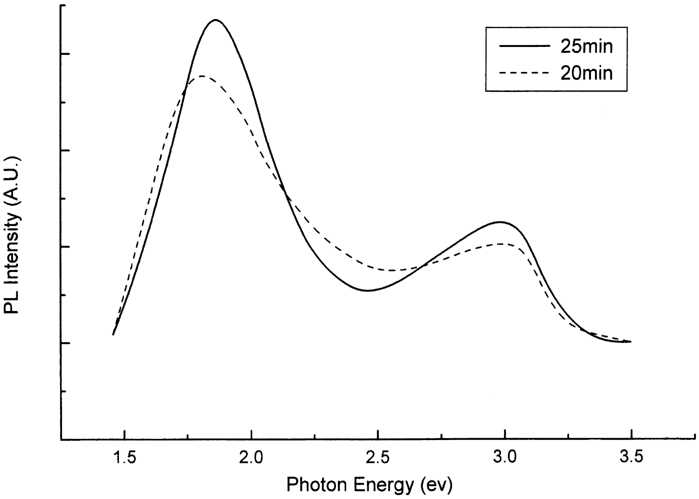

Fig. 2. Photoluminescence spectra of the n-type porous silicon prepared by different etching time.

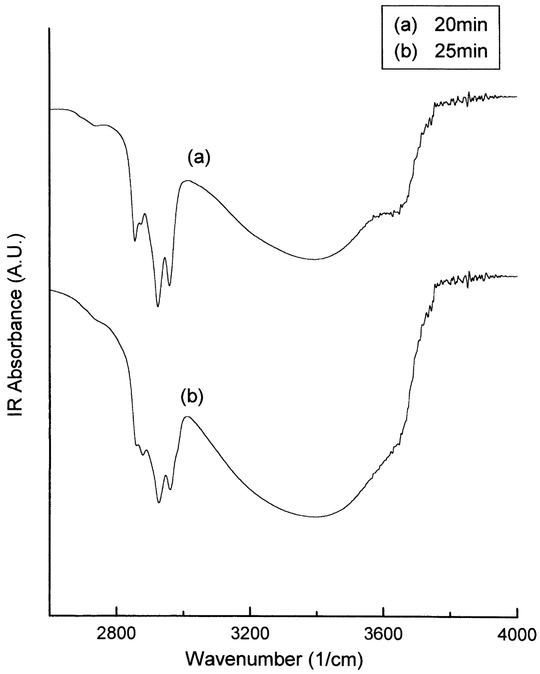

Fig. 3. Infrared absorption of the n-type porous silicon prepared by different etching time.

siliconin HF solution can be expressed by Eqs. (1) and (2) [10,11]

$$\mathrm{Si} + 4\mathrm{HO}_{ad}^{-} + \lambda \oplus\!\rightarrow \mathrm{SiO}_2 + 2\mathrm{H}_2O + (4 - \lambda)e^{-}$$
$$(\lambda \leq 4)\mathrm{SiO}_2 + 6\mathrm{HF} \rightarrow \mathrm{H}_2\mathrm{SiF}_6 + 2\mathrm{H}_2\mathrm{O} \qquad (1)$$

$$\mathrm{Si} + 2\mathrm{F}_{ad}^{-} + 4\mathrm{HF} + \lambda \oplus\!\rightarrow \mathrm{H}_2\mathrm{SiF}_6 + \mathrm{H}_2 + (2 - \lambda)\mathrm{e}^{-}$$
$$(\lambda \leq 2) \qquad (2)$$

in which HO_{ad}^{-} and F_{ad}^{-} are the adsorbed ions, and $\oplus$ and e^{-} represent hole and electron, respectively. According to these equations, the etching of the n-type porous silicon is very difficult, because the reaction needs holes to react. In order to overcome this problem during etching, we illuminated the sample with a 100 W bulb to produce more hole carriers. Similar photoelectrochemical etching of the n-type porous silicon has also been reported [12,13]. Quite surprisingly, the as-grown sample reveals a blue color as seen by the naked eye. Fig. 1 shows the PL spectrum of the as grown n-type porous silicon. Note that without the assistance of light illumination during etching, the as-grown n-type porous silicon does not have a detectable PL signal. As we are aware, p-type porous silicon, after annealing in an oxygen environment at 500°C for 1 h, can exhibit a similar spectrum as shown in our previous report [9]. However, here we show that the appearance of the blue emission in the n-type porous silicon does not need the annealing procedure.

Fig. 2 shows the PL spectra of different etching time of the n-type porous silicon. We can see that the 1.8 eV peak has a blue shift when the etching time increases, while 2.9 eV peak remains at a fixed position. This behavior is indeed consistent with our previously proposed model [8,9], in which we suggested that the 1.8 eV emission originates from the quantum confinement effect, and the 2.9 eV blue emission is dominated by the surface recombination. According to this model, when the etching time increases, electrons are confined in a narrower region, as a result the 1.8 eV peak is blue shifted. Because the 2.9 eV peak originates from surface complexes, its peak position is not influenced by the effect of quantum confinement, and remains fixed as the etching time is varied.

To explore further the origin of the surface complexes, we measured the infrared absorption spectra for porous silicon prepared by different etching time. It is found that the blue emission correlates very well with the absorption band centered around 3400 cm^{-1} as shown in Fig. 3. We can see that the infrared absorption intensity becomes stronger as the etching time is longer. Besides, we also observed that the absorption intensity around 3400 cm^{-1} of the sample prepared by the photo-assisted etching is much stronger than that of the sample prepared without light illumination. According to the reported result on porous silicon as well as other studies [14–16], the absorption band around 3400 cm^{-1} can be attributed to the vibration mode of Si–OH complexes. We, therefore, suggest that the active microstructures of the blue emission are Si–OH surface complexes. Further evidence to support our suggestion here can be also found in a recent theoretical calculation [17].

It is known that due to its unstable structure, porous silicon is subject to a significant evolution with time,

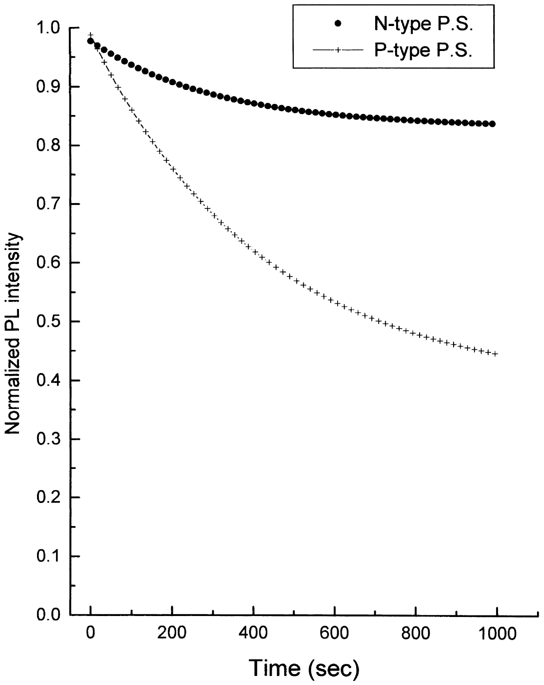

Fig. 4. The normalized PL decay intensity as a function of illumination time for the n-type and the p-type porous silicon.

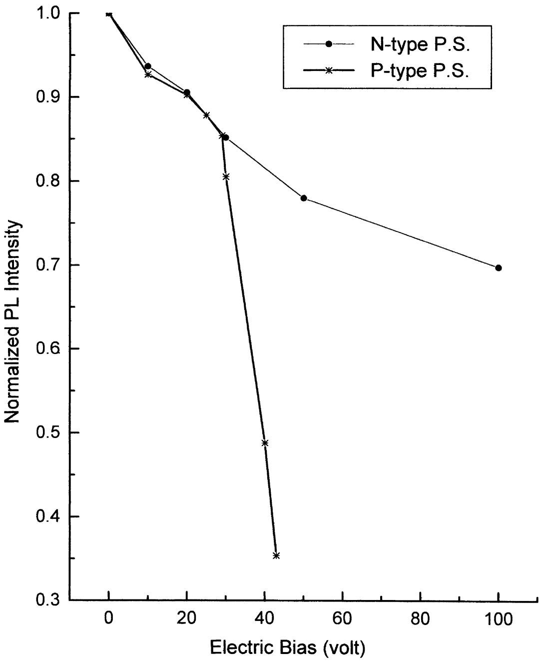

Fig. 5. The drop of the PL peak intensity versus applied lateral voltage for the n-type and the p-type porous silicon.

which directly affects its luminescent properties [18,19]. This behavior is quite true for the p-type porous silicon as shown in Fig. 4. We can see that the PL intensity of the p-type porous silicon suffers a significant degradation under illumination. However, under a similar condition, the PL intensity of the n-type porous silicon decays much slower than that of the p-type porous silicon as shown in Fig. 4. This implies that the structure of the n-type porous silicon is more resistant to external illumination. A further test of the stability of the n-type porous silicon was conducted under an external bias. In Fig. 5, we can clearly see that under the same condition, the PL intensity of the p-type porous sample reduces by about 65% when the bias is 40 V, while that of the n-type porous silicon decreases only by about 15%. We, therefore, conclude that the structural stability of the n-type porous silicon is better than that of the p-type porous silicon.

In conclusion, we reported an investigation of optical properties of the n-type porous silicon prepared by the photo-assisted etching. We found that the as-grown porous silicon can exhibit a blue emission at room temperature. We confirmed that the blue emission originates from the surface Si–OH complex, and the lower energy 1.8 eV peak results from the quantum confinement. We also demonstrated that the structural stability of the n-type porous silicon is better than that of the p-type porous silicon. This property indicates that the n-type porous silicon is a better candidate for the application in optoelectronics than the p-type porous silicon.

Acknowledgements

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