

# The Effect of Chemical Etching of Porous Silicon: Photoluminescence Spectral Changes

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## ABSTRACT

We have investigated the effect of the chemical etching on the photoluminescence (PL) from porous silicon. The rinse in the mixture of HF acid and ethanol strengthens the PL intensity from porous silicon and then weaken it successively, accompanied by a blue shift. The close investigation and analyses of the PL spectra gave us an interesting fact that PL spectra consist of 3 Gaussian peaks. It suggests that the mechanism of PL emission from porous silicon can not be explained with a simple model.

**KEY WORDS:** porous silicon, photoluminescence, spectral variation, chemical etching

## 1. Introduction

Porous silicon is an attractive material for light-emitting devices. It is partly because porous silicon is a silicon-based material. Enormous researches have been devoted to realize light-emitting device using porous silicon and to unveil the mechanism of the light emission mechanism<sup>1)</sup>.

As for a model of photoluminescence (PL) from porous silicon, a quantum size effect is widely accepted for red-band PL. This model is interesting from the viewpoint of a nano-technology. Many researchers have pursued the evidence of the light emission based on the quantum size effect. On the other hand, some other interesting models have been also proposed. For example, siloxene or other related materials on the surface are the best known as an origin of the PL from porous silicon.

This is why it is important to study chemical states of the porous silicon surface: the chemical effects of methanol<sup>2)</sup>, ethanol<sup>3)</sup>, diluted HF acid<sup>4)</sup> or other solutions<sup>5,6)</sup>. In an early stage, electrochemically anodized porous silicon was often etched with a HF acid solution to enhance PL efficiency<sup>7)</sup>. Nevertheless, the effect of the chemical etching has not been

investigated closely for a long time. To investigate these effects is quite important because the chemical etching changes surface chemical modifications easily.

In this article, we have studied the PL spectral changes caused by the chemical etching. We report an interesting behavior of PL spectra and discuss the reason for the changes from a novel point of view.

## 2. Experimental details

We anodized a (100) oriented p-type silicon wafer with a conductivity between 1-10  $\Omega\cdot\text{cm}$  in the solution of HF acid (50 wt. %) : ethanol = 1 : 1. The current density and the time during the anodization were 20  $\text{mA}/\text{cm}^2$  and 30 min., respectively. No intentional irradiation of light was kept during the anodization.

The subsequent chemical etching was made for 120 s per one time by means of the immersion of the sample in the etchant of HF acid : ethanol : water = 1 : 2 : 1. The sample was rinsed in de-ionized water each time after the etching. The obtained sample was dried in blowing nitrogen gas. The PL measurement and the chemical etching of the samples were performed alternatively. We performed the chemical etching 16 times.

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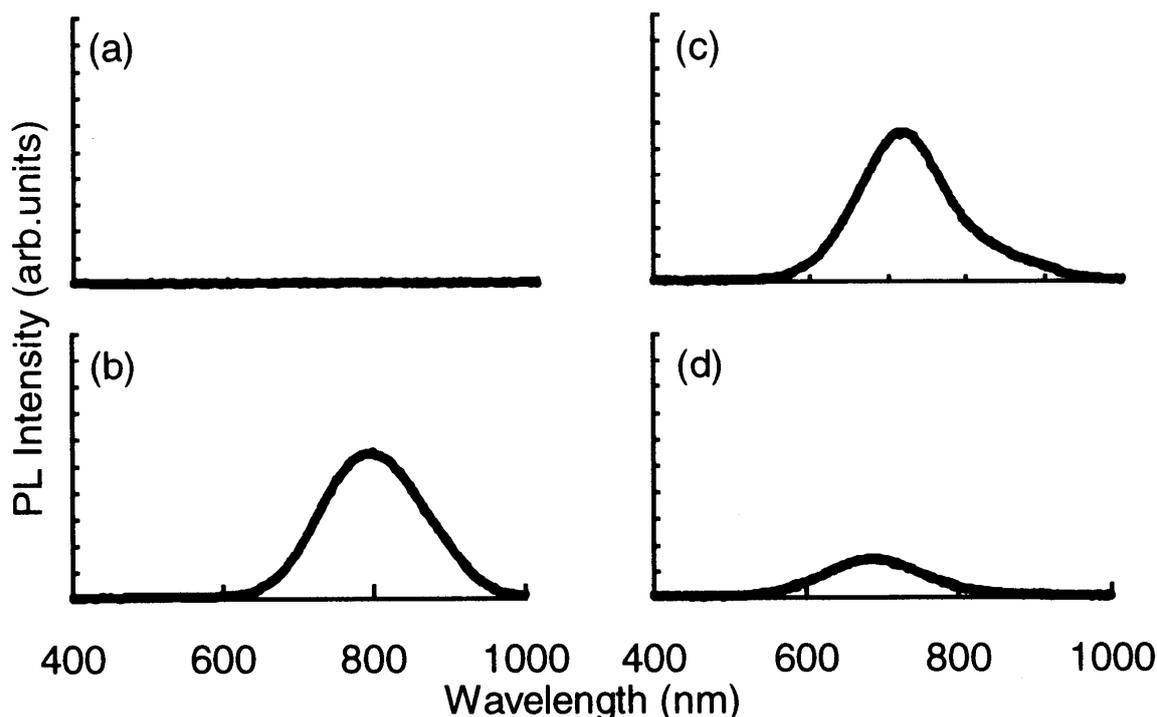


FIG 1. The PL spectra from porous silicon after chemical etching. The numbers of etching were (a) 0, (b) 5, (c) 10 and (d) 15.

The PL spectra were taken at room temperature with the exciting light (365 nm) from an ultraviolet lamp. The luminescent light was detected with a silicon photodiode in conjunction with a monochromator.

### 3. Results

We show PL spectra from porous silicon in Fig. 1. The number of etching was 0 (as-anodized), 5, 10 and 15, corresponding to (a), (b), (c) and (d), respectively. The axes of ordinates in Fig. 1 are in the same scale. An as-anodized sample gave no structure of PL spectrum. After 5-time treatment, a strong PL emission was observed at 800 nm. Figure 1-(c) shows the PL spectrum shifted to the shorter wavelength side and the structure became asymmetry. Further etching made the PL spectrum weak accompanied by a blue shift.

We show the variation of the PL intensity caused by the successive chemical etching in Fig. 2. It can be seen that the PL intensity was strong when the number of etching is around 8. In excess of this point, PL intensity became weakened instead. Figure 2 also shows the variation of the PL peak wavelength. It clearly shows that the peak wavelength was shifted from 860 to 680 nm.

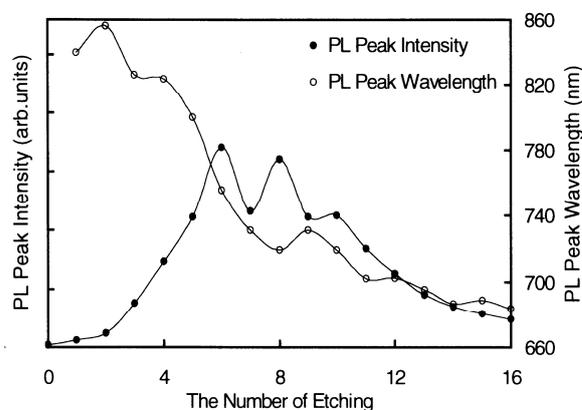


FIG 2. The PL maximum intensity variation owing to the chemical etching. Too many etching decreases the PL intensity. This figure also shows the dependence of the peak wavelength on the number of etching.

### 4. Discussion

The chemical etching effects have been reported before, but usually they exhibited monotonic changes. Our experimental results indicated how PL spectra varied by means of the successive chemical etching, which have not been known before.

At a glance, Fig. 2 tells us that PL structure simply showed a blue shift. It can hardly be accepted that the chemical

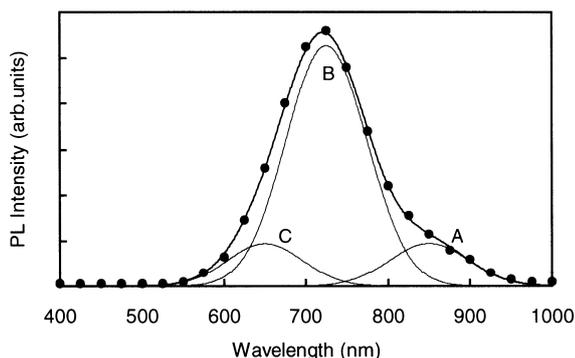


FIG. 3. The PL spectrum shown in Fig. 1-(c) is well decomposed to three Gaussian peaks situated at 850, 730 and 660 nm.

etching enhanced the oxidation that resulted in a blue shift based on the quantum size effect, because the PL intensity increased and then decreased. The behavior suggests more complicated conditions. It is incomprehensible based on the simple quantum size effect that the shape of the PL structure varied with the successive chemical etching as shown in Fig. 1. We recognized an asymmetrical tail in the right side in Fig. 1-(c), which is not seen in Figs. 1-(b) and 1-(d).

We then tried curve fitting using a least-square software assuming two or three Gaussian functions. We could not achieve a well fitting all 17 PL spectra with only two Gaussian functions. In order to obtain good fitting results, three Gaussian functions were needed. One example of the fitting results is shown in Fig. 3. We found that the all PL structure consisted of 3 fixed Gaussian functions: A (850 nm), B (730 nm) and C (660 nm).

We show the variation of the three peaks in Fig. 4. The PL structure can be explained with the composition of the peak A and B in the small etching number, while peak B and C are the main contribution where the etching number is more than 11. It is strongly suggested that three kinds of origins exist in light-emitting porous silicon. The quantum size effect cannot be suitable to explain the existence of the definite three peaks. The obtained evidences suggest that the PL derives from surface chemical states of porous silicon. The next interesting point is that the origin of the three kinds of PL peaks. In order to elucidate the origin, more sophisticated investigation is needed.

## 5. Conclusion

We investigated the successive chemical etching effect on PL spectra of light-emitting porous silicon and found that the

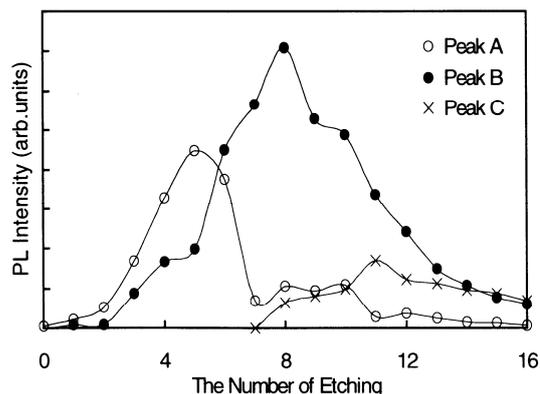


FIG. 4. The intensity variation of the three Gaussian peaks as a function of the number of etching.

variation of PL spectra was not so simple as to be explained by the quantum size effect. The PL intensity increased till the 8 times of the chemical etching and then decreased as the number of etching increased further. Since the shape of the PL spectrum was varied, it is difficult to comprehend that the blue shift is due to a change in size of nanocrystallites. We tried curve fitting using a least-square software and found that the PL spectra consisted of three Gaussian functions situated at 850, 730 and 660 nm. In order to clear the origin of each peak, an extensive study is expected.

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