

Depth Directional Variation of Photoluminescent Spectra from Porous Silicon

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ABSTRACT

We investigated the depth directional variation of photoluminescent spectra from porous silicon in such a way that we measured each spectrum after successive lapping. We observed a main peak at 830 nm with a sub peak at 650 nm in the spectrum from as-formed porous silicon. The sub peak vanished after the first lap. On the other hand, the main peak decreased gradually in intensity, which was caused by the successive laps, accompanied by a blue shift of the peak to a shorter wavelength side. The behavior of the main peak implies the existence of structural variation in the depth direction where the sub peak is strongly related to a surface state at the same time.

KEY WORDS: porous silicon, photoluminescence, spectral variation, depth profile.

1. Introduction

Porous silicon has drawn the attention of the scientific community as a light emitting material in the past.¹⁻³⁾ A number of studies have been done on this material from various perspectives. Silicon nanocrystallites and Si/Ge systems are well known as silicon-related materials that are capable of light emission.⁴⁾ However, porous silicon has an advantage in its cost-effective performance based on the simplicity of its formation process. Nowadays, various aspects of porous silicon are studied such as the evolution of the microstructure during annealing⁵⁾ and the effects of chemical etching of porous silicon.⁶⁾

In order to study the optical properties of porous silicon, we frequently take photoluminescence (PL) spectra that are surely the fundamental characteristics. We typically use ultra violet light as the exciting light. The analytical depth is limited to the absorption length of the exciting light: around 1 μm or less. The typical thickness of the porous silicon layer is in the order of ten μm . Therefore, the PL characteristics are determined at the very surface region of the porous silicon.

The inner structures of porous silicon have been well

studied in the past. The photoluminescence of porous silicon was discovered in 1990. However, few reports have been published on the inner structures from the viewpoint of photoluminescence (PL).^{7,8)} The inner structures of porous silicon are important, to electronic transport properties for device applications.⁹⁾ Our interest is in the variation of the direction of depth. We studied PL spectra with successive grinds for the surface removing. The change in PL spectra with the successive grinds can provide information about the inner structure of porous silicon.

2. Experimental details

We anodized a (100) silicon wafer of a p-type (Boron doped) which had a resistivity of 1-10 $\Omega\text{ cm}$. The solution was HF (50 wt.%) / ethanol (1 : 1) of 100ml. We used Pt wire as a counter electrode. The current density and the anodization time were 52 mA cm^{-2} and 75 min, respectively. An anodized area was as large as 1.54 cm^2 . We did not perform light irradiation during the anodization. We treated the anodized samples in a solution of HF (50 wt.%) / ethanol / water (1 : 2 : 1) for 120 s to enhance PL efficiency. The samples were rinsed in deionized water and then dried by blowing of nitrogen gas to suppress a surface oxidation.

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PL spectra were measured with an ultra violet lamp at 365 nm (3.4 eV) as an exciting light source. The PL light was monochromated with a single monochromator and detected with a silicon photodiode. In order to enhance S/N ratio, a lock-in amplifier was used with a mechanical chopper at 80 Hz chopping the exciting light. The analyzed area was around 1 mm² at the central part of the porous silicon.

We lapped the porous silicon with a water diluted aluminum abrasive of 3 μm. We performed the laps seven times. Each lap removed a surface layer of 9 μm. The thickness of the removed layer was estimated from the total thickness change (63 μm) before and after the successive laps measured with a micrometer. When we measured PL spectra after each lap, we carefully rinsed the samples with deionized water and dried by blowing nitrogen gas.

3. Results and discussion

The anodized samples exhibit little PL efficiency. The PL efficiency is drastically enhanced by the chemical treatment. The porous silicon prepared in this way provides PL strong enough to be seen by the naked eye. Characteristically PL spectra from porous silicon consist of one broad peak situated in a red or infrared region.

In our experiment, we obtained PL spectra of one main peak at 830 nm with a sub peak at 650 nm. Some other researcher also reported multi-peak PL spectra.¹⁰⁻¹³⁾ Although the origin of multi-peak PL spectra has been discussed, it has not been clarified yet. It is even difficult to reproduce the reported results at this stage.

The surface layer removal by the lap decreased PL intensities. The changes in PL spectra by the lap are shown in Fig. 1. Since PL intensity was too small after the fourth lap, we only show the four spectra: as formed and from one- to three-times lapped samples.

It should be pointed out that the sub peak at 650 nm disappeared completely after the first lap. On the other hand, the main peak at 830 nm gradually reduced in intensity along with each successive lap. The peak position of the main peak shifted to the left at the same time. Figures 2 and 3 show the PL intensity and the peak wavelength as a function of the number of laps, respectively. The three-time laps induced the intensity reduction to one ninth and the blue shift by 75 nm.

Matsuda et al. reported a cross sectional PL image of a porous silicon and its intensity variation along a depth direction only at 600, 700 and 800 nm.⁷⁾ Based on their

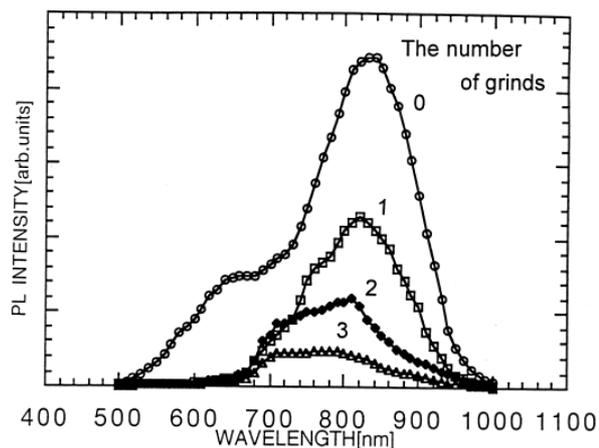


Fig. 1. The changes in PL spectra by a successive lapping of porous silicon.

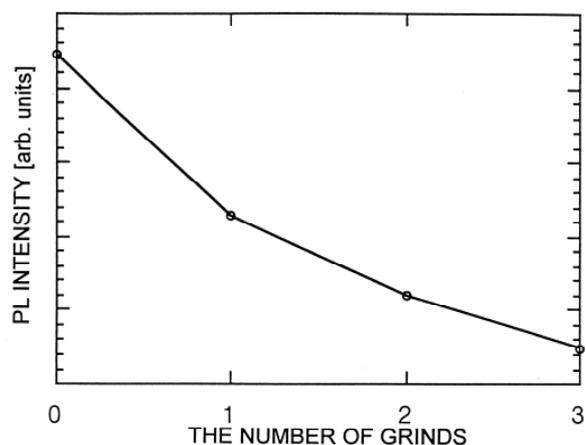


Fig. 2. The intensity variation of a main peak along with the number of laps in PL spectra.

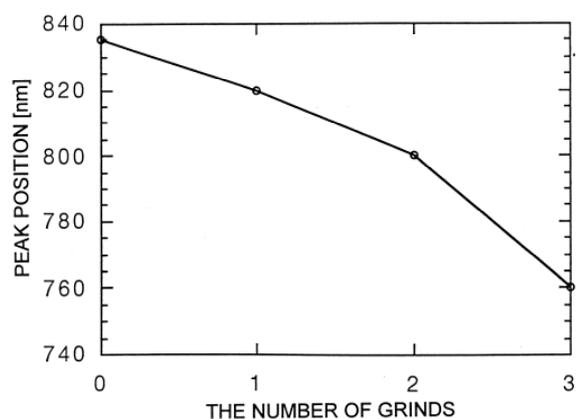


Fig. 3. The wavelength variation of a main peak along with the number of laps in PL spectra.

results, the PL at 600 is the stronger at the top surface where the PL at 800 is the stronger at the bottom. This is inconsistent with our results that PL peak shifts toward the shorter

wavelength with more number of laps. It is partly because the observed PL in our experiment is the light emitted perpendicular to the Si wafer surface, where they observed the PL emitted perpendicular to the cross section of the porous silicon.

It is interesting to note that the PL spectra (from the surface) reported by Matsuda et al. have two structures at 650 and 800 nm.⁸⁾ The features of the PL spectra are similar to our data with the exception of the intensities. The peak at the longer wavelength in Fig. 1 is stronger than the other peak while the peak at 650 nm is the stronger in their spectra. Both PL peaks in their spectra decrease in intensity gradually as moving to the depth direction. On the other hand, the peak at the shorter wavelength in our data only came from the surface.

Li et al. reported two PL bands at 2.5 eV (499 nm) and 1.8 eV (688 nm).¹⁴⁾ They explained that the PL at 2.5 and 1.8 eV were attributed to silicon nanocrystallites and a luminescent center in oxide, respectively. Zhang et al. also reported two PL bands at 2.5 and 1.9 eV.¹⁵⁾ They discussed that the PL band at 2.5 eV was due to the existence of SiO₂ or siloxene. The PL structure from siloxene was also reported to be at 500 nm by Stutzmann et al.¹⁶⁾ The PL band at 2.5 eV was not observed in our experiments.

Winton et al. observed a PL band at 620 nm and concluded that the band is due to passivated silicon nanocrystallites.¹⁷⁾ However, the PL emission at 620 nm may be, based on the report by Li et al.,¹⁴⁾ related to a luminescent state in the oxide that acts as a passivating agent. Cooke et al. report PL structures at 805, 747 and 680 nm, which were due to amorphous SiO₂.¹⁸⁾ Since more than one peak was observed, it is hard to acknowledge that light emission occurs across a fundamental band edge. Some luminescent centers in amorphous silicon play important roles for luminescence.

With the help of the discussions above, the observed PL structure at 650 nm is suggested to be due to a luminescent center in oxides. The oxides were only formed at the surface layer of porous silicon. The extinction of the sub peak tells us that the PL mechanism for the sub peak should be related to a surface state.

As for the main peak the intensity and the position was changed gradually along the number of laps, which indicates the gradual variation in the porous structure in the depth direction. The decrease in PL intensity with the laps can be explained by the removing of the nanocrystalline surface part of porous silicon. On the other hand, the shift of the PL peak

toward the shorter wavelength in depth was derived from the spatial variation of porous structures in the way that the deeper part from the surface consists of crystallites with a larger size.

The effect of mechanical stress and contamination by an abrasive can be excluded from the discussion above because the variation of the PL characteristics continued after the first grind. The origin of the intensity decline cannot be clarified now. It would be interesting to perform a close investigation on this topic in the future.

4. Conclusion

We studied the depth directional variation of a PL structure from porous silicon with the help of successive laps to remove the surface layer. In PL spectra, we observed a main peak at 830 nm and a sub peak at 650 nm. From the fact that the sub peak completely vanished after the first lap, we can conclude that the peak is due to the surface states which act as luminescent centers in the surface. On the other hand, the main peak gradually decreased in intensity along with the successive laps together with a blue shift. This peak is due to a quantum size effect. It was also suggested that there is a gradual variation in the depth direction from the viewpoint of PL spectra.

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