

Energy Loss Spectroscopy and Electron Microscopy of Photoluminescent P-type Porous Silicon Treated with NaOH Solution

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Abstract

Porous silicon (PS) layers were electrochemically formed on p-type low resistivity Si (100) wafers and then etched with NaOH solution to resolve the Si-oxide in PS layer. The chemical conditions and microstructure of the NaOH solution treated as well as as-prepared PS layers were studied by means of electron energy loss spectroscopy (EELS) and transmission electron microscopy (TEM), and correlated with the red photoluminescence (PL). Etching by NaOH solution longer than 10 seconds suppresses PL of PS dramatically and meanwhile, the chemical conditions and microstructure of PS are also change apparently. The content of Si-O₂ chemical structure in PS decreases with increasing the NaOH etching time and the sponge-like structure near the surface of PS is shown to be etched much more than the inner structure of PS. These changes are consistent with the decrease of the PL from the PS layer. This result suggests that the Si-O₂ chemical structure relates to the PL and that the sponge-like layer on the surface of PS as well as on the surface of existing pores in PS contributes to the PL.

Introduction

Porous silicon (PS) formed electrochemically on crystalline silicon at room temperature is known to be visibly photoluminescent [1], and is thought to be a prospective material for optoelectronic devices. Many research works have been carried out on its photoluminescence (PL) mechanism [2-6] as well as applications [7,8]. The models proposed for the mechanism of PL are so far based on (1) quantum confinement effect in Si nanocrystals[1], (2) surface-confined states in nanocrystals[2], (3) oxide defects at the interface of nanocrystals or in the bulk amorphous [3,4], and (4) surface chemistry such as siloxene derivatives[5] or SiH_x[6]. However, little agreement has been attained yet. The actual PL of PS relies not only on the properties of base material and the condition of preparation [9,10], but also largely on the post-formation treatments, such as aging [11,12], and treating in chemical environment [13,14]. Electrochemically formed PS usually consists of Si crystallites and amorphous-like structure [15]. The chemical components in PS are thought to be Si, O, Si-O compounds and etc.. Post formation aging or treatment can affect both the microstructure and chemical components in PS. To clarify the effect of microstructure and chemical components of PS on the change in PL is definitely helpful to understand the mechanism of PL of PS.

Although a great deal of work has been

devoted to the preparation and the optical and structural properties of PS, few works have been reported on the relation between these properties of PS. Therefore, it is necessary for identifying the mechanism to correlate chemical state with other characteristics of PS such as the PL emission intensity and microstructure of PS. In the present work, The PS electrochemically formed on low resistivity p-type silicon wafers at room temperature were etched by NaOH hydro-solution, in order to resolve the Si-oxide layer on the surface of the PS layer [14]. The change in PL of the treated specimens has been correlated with the changes in local chemical states and microstructure of PS layer by means of electron energy loss spectroscopy (EELS) and transmission electron microscopy (TEM).

Experiment

PS samples were prepared by anodization of boron doped p-type Si (100) wafers with resistivity of 0.04-0.06 Ωcm. The anodization was conducted with a solution of 50wt% HF and C₂H₅OH in a rate of 1:1. The anodization was carried out for 10 seconds at room temperature (298K), in fluorescent lamp, and by applying a constant current density of 100, 200, and 350 mA/cm². A magnetic stirrer was used during the anodization to avoid bubbling on the surface of wafers. As-produced samples were washed by deionized water and ethanol, dried under warm air blow (323~333

K). They were further etched with a solution of NaOH:H₂O = 0.0005:1 for 5 to 120 seconds at room temperature. Etching steps were 0, 5, 10, 30, 60, and 120 seconds. The PL spectra were obtained using a PL-lifetime measurement system with a streak camera (Hamamatsu-photonics C4780) at room temperature. Excitation source was a nitrogen laser (wavelength: 337 nm, pulse width: 0.3 ns, repetition rate: 10 Hz, intensity: 70 μ J/pulse).

The as-prepared samples were made into cross-sectional TEM specimens by mechanical and argon ion milling methods. A thin chromium layer was evaporated to the surface of PS layer before preparing the cross sectional TEM thin film in order to protect the PS surface. After the preparation of the cross sectional TEM specimens, NaOH solution treatment was conducted similar to the specimens for PL measurement, in order to correlate the results of PL measurement with those obtained by TEM observation and EELS analysis. The TEM used in this study was a JEOL ARM1000 operated at 1000 kV, to which a post-column parallel detection EELS system with a resolution of 1.5 eV made by GATAN is attached. The size of area where the EELS spectra were taken was about 100 nm in diameter.

Results and Discussion

The PS layers anodized in different current density (100, 200 and 350 mA/cm²) were

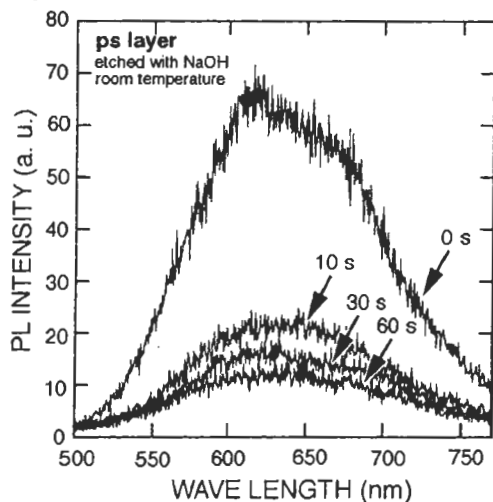


Fig.1 Photoluminescence (PL) spectra of NaOH solution treated porous silicon (PS) layer formed on low resistivity p-type Si wafers in current density of 350 mA/cm² at room temperature. The PL intensity decreases with the etching time.

shown to be photoluminescent in red range with a peak wavelength around 640 nm, with the intensity of PL increases with the anodization current density. Fig. 1 shows the effect of NaOH solution treatment on the PL spectra of PS layers formed on a silicon wafer in current density of 350 mA/cm². The PL decreased dramatically by NaOH solution etching for over 10 seconds treatment. The PL intensity decreases with increasing the treatment of time but the peak position remains at the same wavelength. The peak PL intensity in a wavelength range of 640 \pm 40 nm dropped to about 25% by 10 seconds NaOH solution treatment. The tendency of the PL behavior of PS obtained at lower current density is similar to that in Fig. 1, except for the lower absolute intensity of PL. It is interesting to point out that the relation of PL intensity to the NaOH solution etching is very similar to the relation of PL intensity to the anodization current density [15].

The as-prepared PS layers with their substrate were made into cross sectional thin film specimen for TEM observation and EELS analysis. The EELS measurement was carried out at consequent points, from the place near the surface to the place adjacent to Si-substrate in the PS layer. The depth profiles of the local chemical states of Si elements in PS layers are shown in Fig. 2 as photodiode counts versus electron energy loss for a PS specimen anodized at 350 mA/cm² before and after 60 seconds NaOH solution treatments. The spectrum A in the figure was obtained near the surface of PS layer, and B to E were obtained with the analyzed points located evenly in the PS layer from the surface to the Si substrate. Since the Si-L_{2,3} edge is known to be at an appropriate energy loss and is effective for characterizing the chemical states of Si element, the fine structure of Si-L_{2,3} edge was obtained by background subtraction technique. The fine edges in the Si-L_{2,3} edge corresponding to the Si-O₄ tetrahedron structure and Si crystals are shown by Si⁴⁺ (the energy loss $\Delta E=108$ eV) and Si⁰⁺ ($\Delta E=100$ eV) in the figure, respectively. The Si⁴⁺ edge can always be seen in the spectra but its shape changes slightly between different spectra at different positions as well as for different specimens before and after the NaOH solution treatment. As it was reported previously [15], the relative intensity of Si⁴⁺ edge becomes more intensive as the analyzed point moves from the Si substrate to

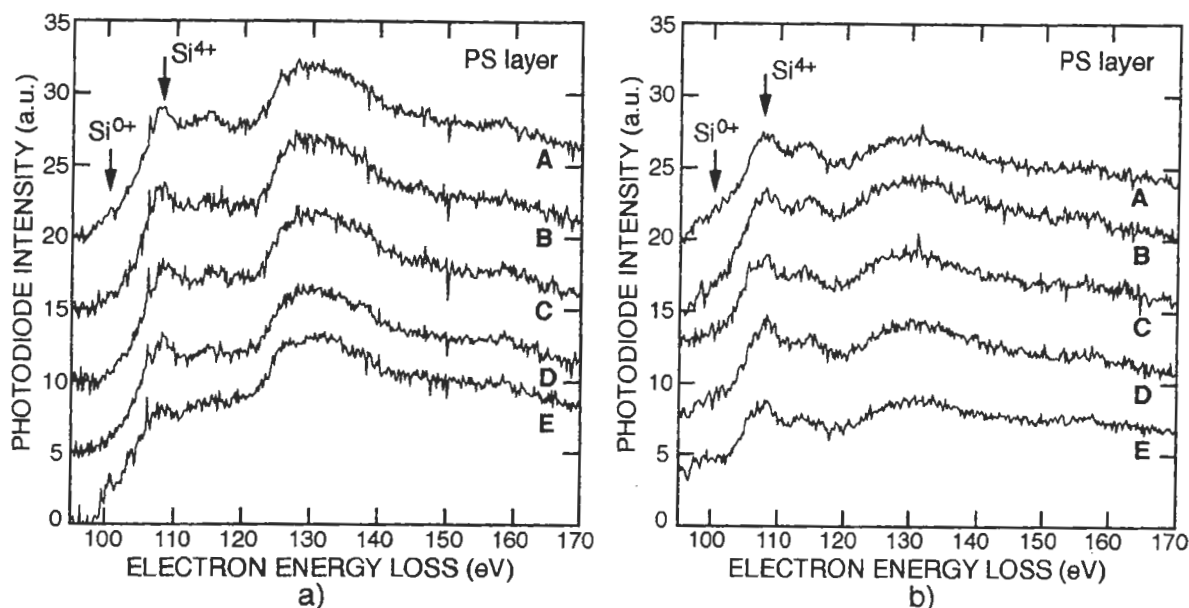


Fig.2 EELS spectra of NaOH solution treated PS layer formed in 350 mA/cm^2 . The spectra noted by A to E were obtained from consequent points from the place near the surface to the place adjacent to Si substrate. a) Spectra of as anodized specimen, and b) etched with NaOH solution for 60 seconds.

the surface of PS layer, while the relative intensity of Si^{0+} edge decreases. The Si^{4+} edge of the NaOH solution etched specimen as observed in Fig. 2b) seems to be broader comparing to that of the unetched specimen in Fig.2a), and the Si^{0+} edge looks also more apparent than that of the unetched specimen. The Photodiode intensity near the energy loss of 130 eV in the EELS spectra in Fig.2b) becomes much lower than that in Fig.2a).

The photodiode counts in EELS spectra are strongly dependent on the detection conditions such as the thickness of specimen and the electron beam intensity. However, the count ratio of definite edges attained from same portion of a specimen can reflect the relative content of relevant chemical components in a given position in different detection conditions. In order to get a relation between chemical states and characteristics of PL, the comparison of the ratio of Si^{4+} edge counts to Si^{0+} edge counts (shorted as R_0) of EELS and the PL intensity of PS layers had been carried out. The intensity of edge Si^{4+} and Si^{0+} are calculated by integrating the photodiode counts in range of edge position within $\pm 2 \text{ eV}$. The relative content of Si-O_4 structure for each analyzed position was obtained by R_0 (= integrated counts of edge Si^{4+} /integrated counts of edge Si^{0+}). An average of R_0 for the analyzed positions in PS layer was calculated. Fig. 3 shows the correlation between the average of

R_0 , noted by $\text{Si}^{4+}/\text{Si}^{0+}$, and PL intensity of the PS layer. The PL intensity of PS is a sum of the counts in a wavelength range of $640 \pm 40 \text{ nm}$ in a PL spectrum. As shown in Fig. 3, both of $\text{Si}^{4+}/\text{Si}^{0+}$ and the PL intensity decrease with the NaOH solution etching time. It suggests that the PL intensity is dependent on the relative content of Si-O_4 structure to Si element in Si crystallites positively.

As shown in Fig. 3, the count ratio $\text{Si}^{4+}/\text{Si}^{0+}$

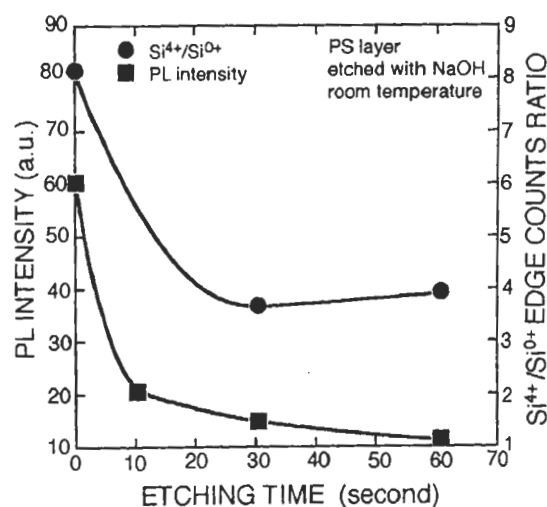


Fig.3 A correlation of PL intensity with the count ratio of edges $\text{Si}^{4+}/\text{Si}^{0+}$ in EELS spectra of PS layer formed in 350 mA/cm^2 . Both of them decrease with the NaOH etching time.

decreases quickly at the beginning of NaOH etching. After 30 seconds etching, it changes little. To the contrast, PL decreases continuously after 30 seconds etching, though the speed becomes much slower than that at the beginning. The resolving process of the Si-oxide and Si crystallites in PS may interpret this phenomenon. At the beginning of NaOH etching, the resolving of outer layer Si-oxide results in a quick drop in both the PL intensity and $\text{Si}^{++}/\text{Si}^{0+}$ value. With the increasing of the etching time, the outer layer of Si-oxide becomes thinner, and further more, the small Si particles might also be resolved with its surrounding Si-oxide. If the Si-oxide and Si are resolved in a similar speed, the $\text{Si}^{++}/\text{Si}^{0+}$ would be remain at about the same value. Since the Si-oxide is still being resolved by NaOH etching, the PL intensity would also be decreasing continuously, as observed in Fig. 3. The cross sectional TEM observation was carried out to reveal the structural change of PS layers after NaOH solution etching. Fig. 4 shows a set of micrographs of PS layer taken

in dark field mode. Fig. 4a) and c) were taken from the specimen unetched by NaOH solution and the same area after 30 seconds NaOH solution etching respectively. Electrochemically formed porous silicon in this work has been observed structurally to consist of sponge-like region near the surface of PS layer and tree-like region in inner part of PS layer [15]. The arrows in Fig. 4a) and c) indicate the interface of the two regions, near which the PS layer changes gradually from tree-like structure to sponge-like structure. The micrographs were obtained using one of the $\{111\}$ diffraction spots, so that the white dots in the micrographs correspond to Si-crystallites. It is easy to know from the micrographs, that there are little Si crystallites in the sponge-like region. The existence of small Si-crystallites is one of characteristics of the tree-like structure different from the sponge-like region of PS layer. The inner part of PS layer did not change much in structure by the 30 seconds NaOH solution etching, but the surface layer, i.e. the sponge-like region,

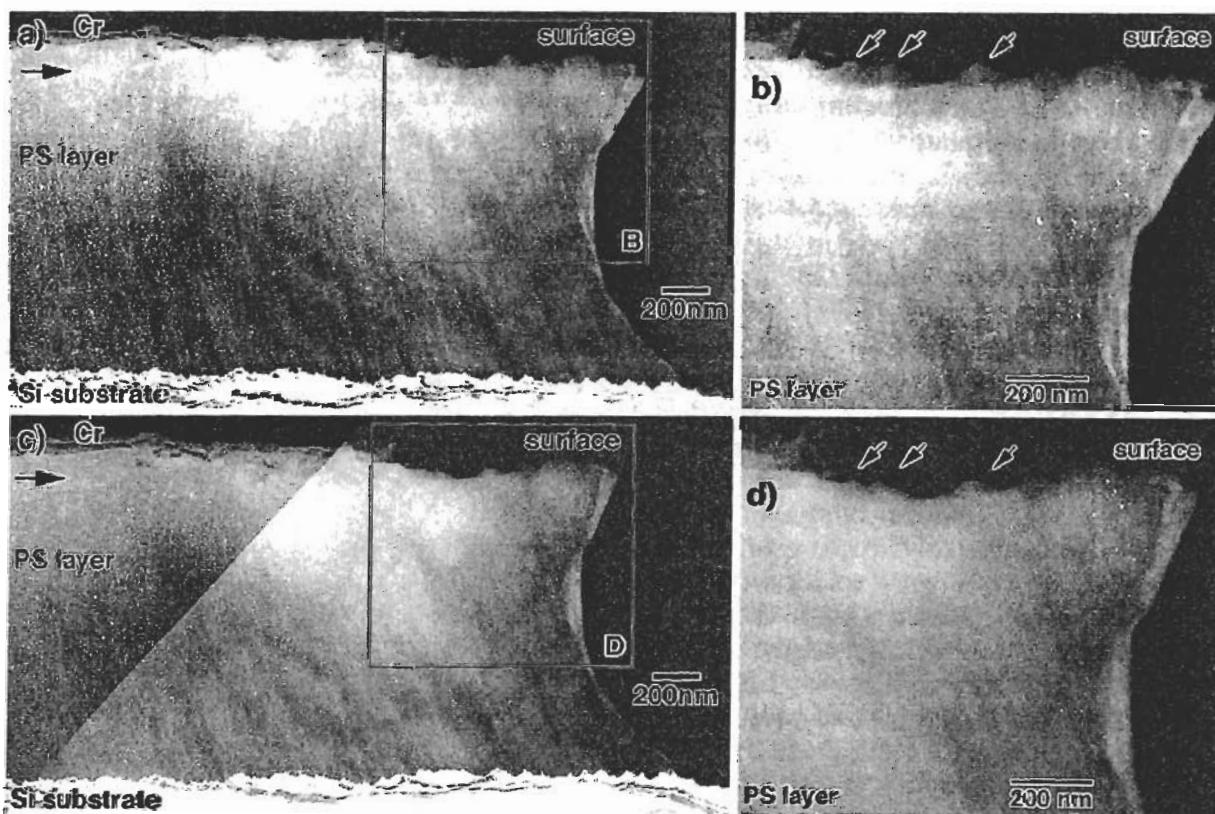


Fig.4 A series of cross sectional TEM dark field micrographs of PS layer formed in $350 \text{ mA}/\text{cm}^2$. a) As-prepared PS, b) the part B in a), c) etched by NaOH solution for 30 seconds. This figure is pieced together with two successive micrographs with different contrast. And d) the part D in c). The sponge-like region of PS was reduced apparently by a 30 seconds etching shown by arrows in b) and d). Cr layer was coated on the surface to protect PS.

changed apparently after the NaOH solution etching as observed in the figure. In the left part of Fig. 4a) and c), a thin Cr layer which was evaporated on the surface for protecting the PS covers the sponge-like layer, but the effect of NaOH etching on the PS can be seen in the right part of the figure. It can be observed more clearly in the Fig. 4b) and d), as shown by arrows. The protruding parts on the surface of the PS layer can be identified as belonging to the sponge-like region of PS and indicated by arrows. They became smaller as shown in Fig. 4d). The 30 seconds etching with NaOH solution decreased PL dramatically and also reduced the sponge-like region apparently. Obviously seen is the correlation of the reduction of the sponge-like region and the decrease in PL intensity for the NaOH solution etched PS layer.

The sponge-like region is located near the surface of PS. To this point of view, there should be also a similar surface at the skeleton structure of pores in PS layer, since the PS is known to have a pore structure morphologically [9,10]. The NaOH solution treatment has a same effect of resolving this layer. It should be responsible for the decrease of relative content of Si-O₄ structure in the inner part of PS and be correlated to the reduction of PL of PS layer.

In the cross sectional high-resolution

transmission electron microscopy (HRTEM), the sponge-like region is observed to have a amorphous-like structure. On the other hand, the nanoscale Si crystallites in size from 2~3 nm can be observed in the inner part, i.e. the tree-like structure region, in the specimens before and after NaOH solution etching. Fig. 5 shows a typical HRTEM of inner part in PS layer, which was not conducted the NaOH solution treatment. a) is the original micrograph, and b) is after the noise reduction using fast Fourier transformation (FFT). c) is the Fourier transformed pattern of a) and d) is the mask applied to b) to get d). Si crystallites are indicated by A, B and C in Fig.5a) and b) which are surrounded by amorphous. They can hardly be separated each other as seen in b) because they are in the same orientation and with irregular shapes. This orientation is also the same as to the substrate, which reveals that the crystallites are the remains of original Si substrate after anodization. The regular TEM and HRTEM mode observations made it clear that the tree-like structure of PS does not change apparently after NaOH solution treatment.

The present study reveals that the NaOH solution etching of PS layer resulted in a decrease of the Si-O₄ tetrahedron, and that this decrease correlated with the reduction of red PL of PS layer. These results confirm the

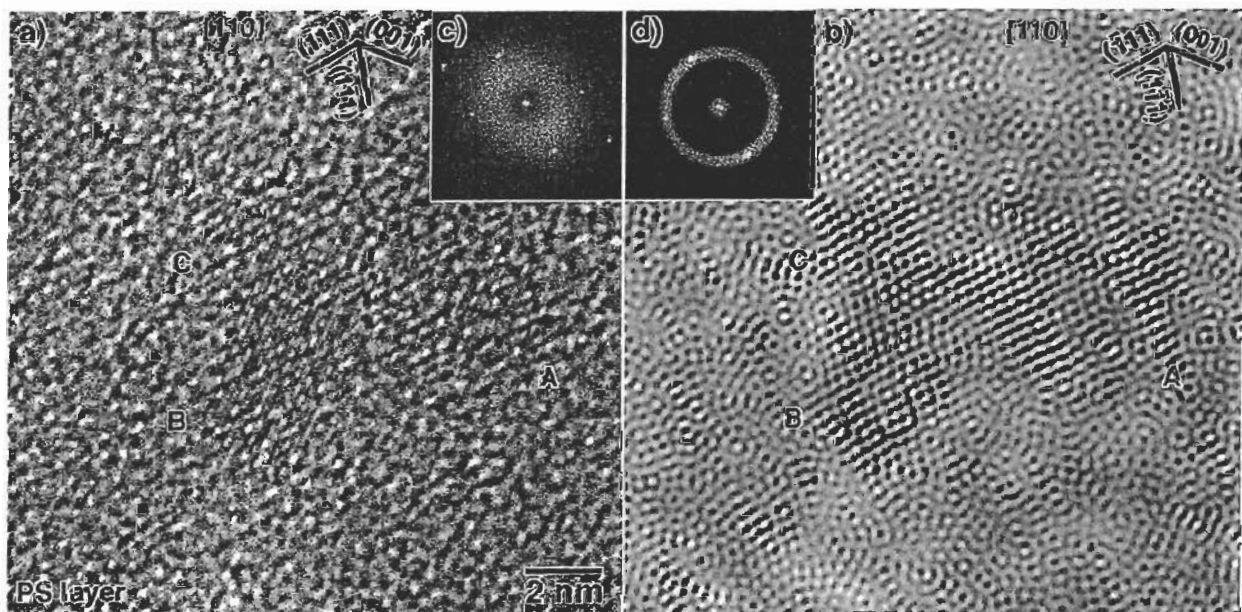


Fig.5 A high resolution cross sectional micrograph of an as-prepared PS layer formed in 350 mA/cm². Nanoscale Si crystallites in size from 2-3 nm are observed surrounded by amorphous. a) the original micrograph, b) noise removed image of a) with a fast Fourier transformation (FFT), c) a FFT pattern of a), and d) the mask used for getting image b).

relation between the red PL and Si-O₄ tetrahedron structure. Though the red PL intensity dropped to less than about 25% of the original intensity after 30 seconds NaOH etching, the morphological structure in inner part of PS, i.e. the tree-like structure, not changed apparently. It was difficult to clarify the difference of the tree-like structure of PS before and after NaOH solution etching by morphological observation such as TEM. On the other hand, the apparent reduction of the sponge-like region in PS is consistent with the decrease in Si-O₄ structure as well as in red PL intensity. This consistence suggests that the sponge-like region has a large content of Si-O₄ structure and contributes to the red PL largely. 1M NaOH solution (4% in content) treatment of n- and p-type PS layer was reported to have an effect of resolving the surface Si-oxide completely [14]. The NaOH solution in the present work was much dilute (0.05% in content) than the above one. Based on the results of the EELS measurement and morphological observation by TEM, the etching of PS layer with this NaOH solution has not resolved the Si-oxide completely, but it dose have an effect to reduce Si-O₄ structure and PL of PS layer. It is reasonable to conclude that the NaOH solution etching in present work has an effect to resolve a thin layer on the PS. This thin layer is the sponge-like region on the surface of PS layer, and is also probably a thin layer on a pore surface of the PS.

As it was analyzed above, the chemical state of the sponge-like layer may dominate by Si-O₄ structure, since their resolving correlates to the decrease of relative content of Si-O₄ structure. The Si⁴⁺ peak in X-ray photoelectron spectroscopy (XPS) was interpreted as the existence of SiO₂ [14,16]. However it should be noted from the previous study [17] that bulk SiO₂ itself has an energy gap of about 9.0 eV, and has no PL in the red region. Therefore the defects in SiO₂ or at the boundary between Si crystallites and SiO₂ should play an important role on PL emission.

Conclusion

The 0.05% NaOH hydro-solution etching has an effect to suppress the red photoluminescence (PL) of the porous silicon (PS) layer formed on low resistivity p-type Si(100) wafer by anodization at current density from 100 to 350 mA/cm² at room temperature. This

suppression of the PL is found to correlate to the decrease of relative content of Si-O₄ structure by the EELS analyses, and to the resolving of a thin layer (the sponge-like layer) on the surface of PS layer by TEM observation. The sponge-like layer dominates by Si-O₄ structure chemically and contributes to the red PL more than other part in PS layer. These results suggest that the PL would be concerning with some kind of defects in a thin Si-oxide layer both on the upper surface and pore surface of PS layer as well as the defects in boundary of Si crystallites and Si-oxide structure.

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