Correlation Between Photoluminescence and Local Chemical States of Porous Silicon by Means of Electron Energy Loss Spectroscope

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Abstract

The correlation between photoluminescence (PL), microstructure and chemical states in porous Si (PS) has been investigated by means of PL measurement, transmission electron microscope (TEM) and electron energy loss spectroscope (EELS). The intense red PL with a peak at a wavelength of 640nm was measured by a PL-lifetime measurement system at room temperature for PS layers formed on p-type silicon wafers. The anodization was carried out in HF solution at a current density (I_a) of 100-350mA/cm^2 for 10 s, at room temperature. The intensity and lifetime of PL increase with the increase in the I_a. The cross sectional TEM reveals that the PS layers have a tree-like structure, and that the structure becomes finer with increasing the I_a. The EELS measurement on the PS layer clarifies that the shape of the appearance of Si^{4+} edge at 108eV energy loss in fine structure of Si-$L_{2,3}$ edge due to the change in chemical states of silicon from Si to SiO_2 and the intensity of Si^{4+} edges change with the depth from surface of PS layer and with the I_a as well. The counts ratio of Si^{4+} to Si^{0+} is correlated to increase in PL intensity. These results suggest that some kind of defects in SiO_2 and the defects in boundary of Si crystallites and SiO_2 structure are responsible for the light emission from PS layer.

1. Introduction

The recent observation of visible light emission from electrochemically anodized porous silicon (PS) layers at room temperature[1] has stimulated researches on the physical aspects of photoluminescence (PL) from nanostructures of semiconductors and its applications to advanced devices. Potential applications of PS is now considered to include optoelectronic integrated circuits, optical memories, and advanced display systems. 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], (4) surface chemistry such as siloxene derivatives[5] or SiHx[6]. No agreement has been attained yet, because many factors such as chemical states and structure are important for understanding the mechanism of PL. Although a great deal of work has been devoted to the preparation and the study of the optical and structural properties of PS, very few papers have been reported on the relation between these properties of PS. [7-9] 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.

On the other hand, the electron energy loss spectroscope (EELS) is proved to be an effective method to investigate the local chemical states of elements in compounds or alloys [7, 8]. In case when Si crystallites and Si oxide coexist in a bulk material, Si-$L_{2,3}$ edge in a EELS spectrum usually shows a changed fine structure. The changes in the fine structure should reflect different characteristics of each components. For PS, the investigation of the details in the fine structure of the differences between element edges or between different EELS spectra, and of the relation of them to other characteristics of PS may give hints for understanding the mechanism of PL for PS.

The present work describes the correlation between the intensity of the PL and elemental chemical states in PS by means of photoluminescence (PL) analysis, electron energy loss spectroscope (EELS) and transmission electron microscope (TEM). Especially the differences in the structure and the local chemical composition of PS layers were focused.

2. Experiment

PS samples were prepared by anodizing boron doped p-type Si (100) wafers with resistivity of 0.04-0.06 Ω cm. The solution for anodization was produced by mixing of 50wt% HF and C_2H_5OH in a rate of 1:1. The anodization was carried out for 10 seconds (t_a) at room

temperature (25°C), in fluorescent lamp, and by applying a constant current density (I_a) of 100, 200, and 350 mA/cm^2. A magnetic stirrer was used during the anodization to avoid bubbling on the surface of wafers. The as-produced samples were washed by deionized water and ethanol, dried under warm air blow (50-60°C). The PL spectra were obtained using a PL-lifetime measurement system with a streak camera (Hamamatsu C4780) at room temperature. Excitation source was a nitrogen laser (wavelength: 337nm, pulse width: 0.3ns, repetition rate: 10Hz, intensity: 70μJ/pulse). The samples were then made into cross-sectional TEM specimens by argon ion milling method, observed by TEM and analyzed by EELS. The TEM used was a JEOL ARM1000 operated at 1000kV, to which a post-column parallel detection EELS system with a resolution of 1.5eV made by GATAN is attached. The size of area where the EELS spectra were taken was about 100nm in diameter.

3. Results and Discussion

The PS layers anodized in three different I_a (100, 200 and 350mA/cm^2) were shown to be photoluminescent in red range with a peak wavelength around 640nm. Figure 1 shows a typical result of PL intensity data against wavelength and time (t) for a PS specimen anodized at 200mA/cm^2 for 10 s. At t = 0, a laser pulse introduced to the PS surface and stimulated PL. Then the PL began to emit in a wide range as shown in the figure. The strongest emission was detected near a wavelength of 640nm, but the emission periods in time becomes longer as wavelength increased. The tendency of the PS in other conditions are similar to that in Fig. 1. The peak wavelength dose not change, but the intensity of PL becomes stronger as the I_a increased.

Since the time dependence of emission of PL is an important property for the PL mechanism, the decay profile of PL at the peak wavelength of 640nm±10nm was analyzed to be fitted to exponential functions. Every PL decay profile was fitted as follows:

$$I = A\exp(-t/\tau) + I'$$

The first part in the above formula is the major part and the I' the minor part of the PL. The most important parameter to be related to the PL mechanism is τ which ranges from 10μs to 16μs. A plot of PL intensity, which is a sum of counts in a wavelength range of 640nm ±10nm, as well as lifetime τ for three different I_a is shown in Fig. 2. The PL lifetime τ increases slightly with the increase of I_a. This may correspond to the difference in the recombination paths of the photoexcited carriers in PS layers [9].

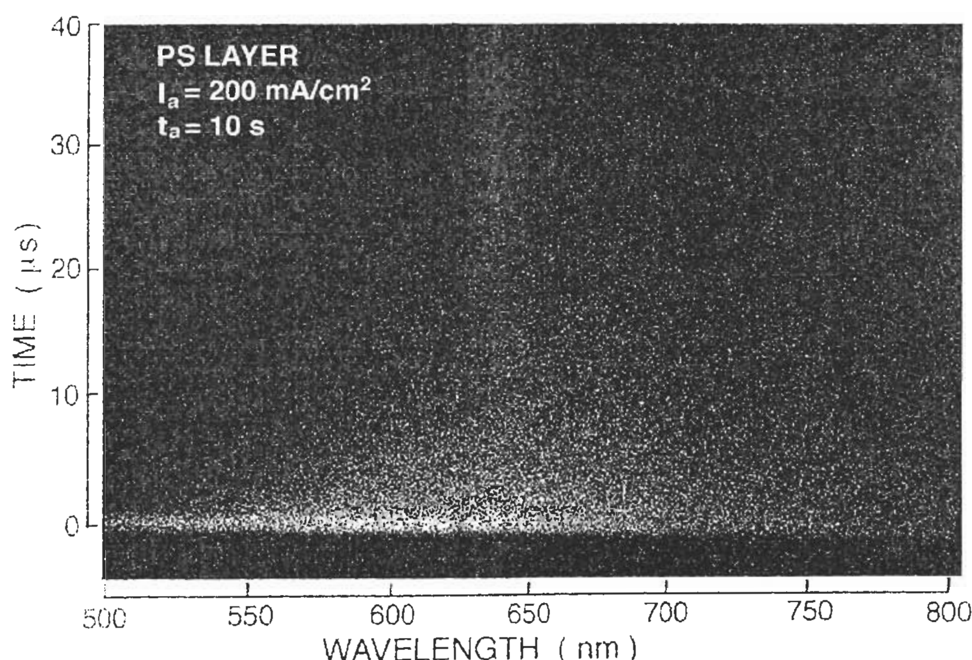

Fig. 1 Wavelength dependence of photoluminescence (PL) emission for a porous Si (PS) layer formed at current density (I_a) of 200mA/cm^2 for 10 s (t_a).

A cross sectional TEM micrograph of a PS layer anodized at an I_a of 200mA/cm^2 is shown in Fig. 3. The TEM revealed that the PS layers were in thickness of about 800, 1250 and 2200nm for I_a of 100, 200 and 350mA/cm^2, respectively, and possessed a tree-like structure along the direction from Si substrate to top of PS layer. The structure near the PS surface is finer than that near Si-substrate. Near the surface of PS layer, there is a sponge-like structure with thickness of about 200nm. Dark-Field images of TEM indicated that the black contrast streaks and spots were bonded to Si crystallites. The nearer to the surface of PS layer, the smaller the Si crystallite were found. In the sponge-like region, the Si crystallites could hardly be found. Comparison among the PS structures at all the conditions concluded that the tree structure of PS layer became finer also with the increase of the I_a, while the thickness of sponge-like structure did not change.

The specimens were then analyzed by EELS at corresponding points, of A to E in Fig. 3, to get depth profiles of local chemical states of Si elements in PS layers. Figure 4 shows the photodiode counts as a function of energy loss for a PS specimen anodized at I_a of 200mA/cm^2 for 10 s. 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, 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 SiO_2 (Si-O_4 tetrahedron) and Si crystals are shown by Si^{4+} (the energy loss ΔE=108eV) and Si^{0+} (ΔE=100eV) in the figure, respectively. The

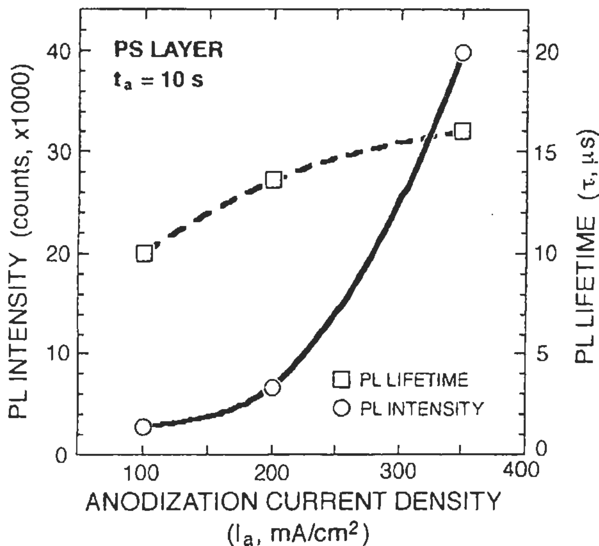

Fig. 2 The relation of photoluminescence (PL) intensity and PL lifetime τ with the anodization current density (I_a) for forming porous Si (PS) layers.

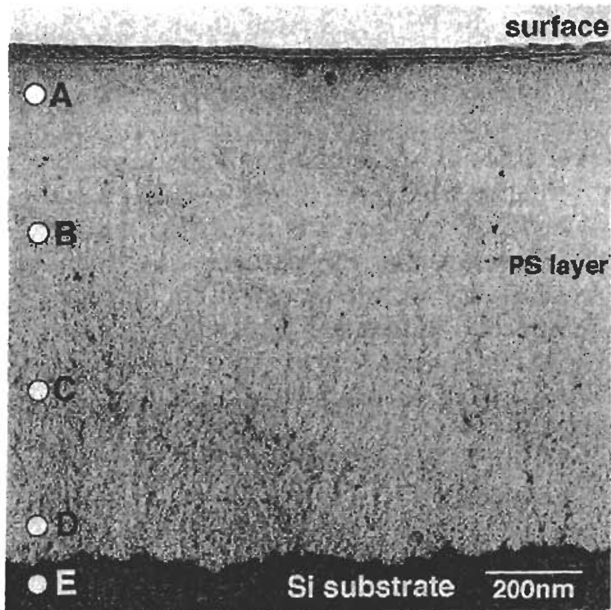

Fig. 3 A cross sectional TEM micrograph of porous silicon (PS) formed on a low resistivity p-type Si wafer at 200mA/cm^2 at room temperature, showing EELS analysis positions of A, B, C, D and E.

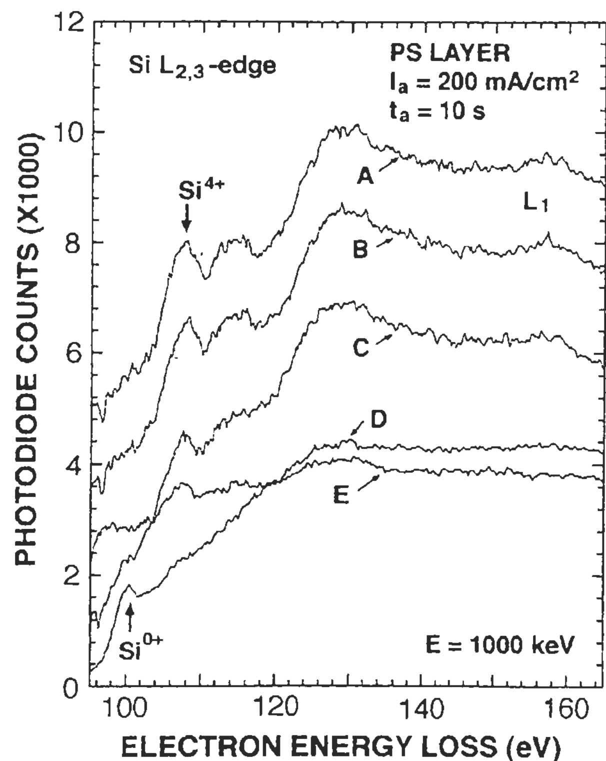

Fig. 4 The results of EELS analysis of porous silicon (PS) formed on low resistivity p-type Si wafer at 200mA/cm^2 for 10 s, showing Si-$L_{2,3}$ edges of Si^{0+} and Si^{4+}. A to E corresponds to the places shown in Fig. 3 by A to E.

Si^{4+} edge can always be seen in the spectra but its shape changes slightly between different spectra. The relative intensity of Si^{4+} edge becomes stronger as the analyzed points change from the Si substrate of PS to the surface of PS. The relative intensity of Si^{0+} edge, on the other hand, changes in a reverse direction comparing to the change of Si^{4+} edge. The EELS spectra taken from specimens formed at other conditions also showed the similar characteristics to that in Fig. 4, but the shape became blunter for PS formed at I_a of 100mA/cm^2 and sharper for I_a of 350mA/cm^2.
Since the photodiode counts in EELS spectra is strongly dependent on the detection conditions such as the thickness of specimen and the electron beam intensity, it is difficult to compare directly the counts between different spectra or different specimens. However, the counts ratio of definite edges attained from same portion of a specimen should reflect the relative content of relevant chemical components. 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) of EELS and the PL intensity of PS layers had been carried out. Figure 5 shows the correlation between R and PL intensity of PSs. The intensity of a edge in EELS spectra was calculated by summarizing the counts in range of edge position ±2eV. The R is an average value for analyzed points at depth less than half of the thickness of PS layer from PS surface. As shown in Fig. 5, the PL intensity changes with the R in a very similar way. These results suggest that the PL intensity is dependent on the relative content of SiO_2 over Si crystallites positively.
In the present work, the thickness ratio of PS layers for three different I_a of 100, 200 and 350mA/cm^2 have a rate of, approximately, 2:3:6. On the other hand, the PL intensity shown by photodiode counts attained in the range of 640nm±10nm have a rate of about 3:7:40. Even if it is assumed that the all amount of PS layer had contributed to the PL, it can be concluded that the difference in the PL intensity mainly resulted from the difference in characteristics of PS itself, not from the difference in thickness. From the results of TEM in Fig. 3, the PS layer formed in present work were in tree-like structure, but the structure became finer with the increase of I_a. The increase in PL intensity with the I_a suggests

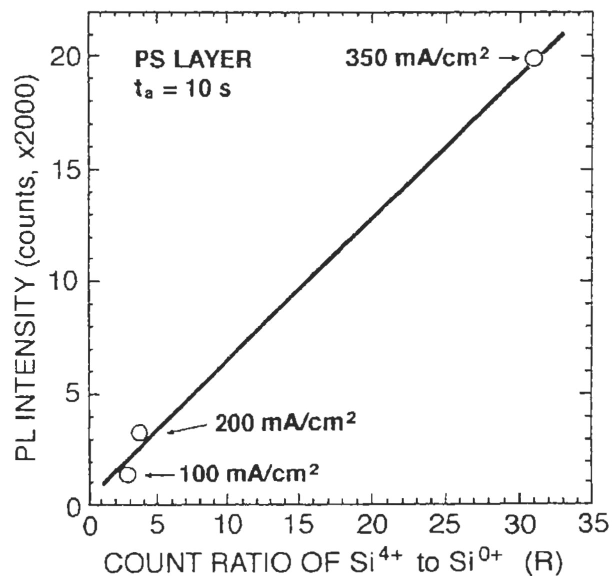

Fig. 5 A correlation of PL intensity and the relative intensity (R) of Si^{4+} edge to Si^{0+} edge of EELS for PS layers formed at 100, 200 and 350/cm^2 for 10 s.

that the finer tree-like structure is favorable for intense PL.
The fact that Si $L_{2,3}$ edge in EELS spectra from PS layers consists of Si^{4+} and Si^{0+} edges, which corresponds to the chemical states of SiO_2 (SiO_4 tetrahedron) structure and Si crystallites, respectively, means the coexistence of both Si crystal and SiO_2 substance in the photoluminescent PS. An R for a Si $L_{2,3}$ edge in an EELS spectrum from Si substrate, calculated in the same way as it was done for EELS spectra from the PS layers, was about 1.5. The R values in Fig. 5 are always far beyond 1.5, thus the SiO_2 corresponding to the Si^{4+} edge is considered to be mainly responsible for PL. However it should be noted from the previous study [10] that bulk SiO_2 itself has an energy gap of about 9.0eV, and has no PL in the red region. Therefore the coexistence of Si and SiO_2 is necessary for intense red PL in PS layer. It is reasonably anticipated that the defects in SiO_2 or at the boundary between Si crystallites and SiO_2 play an important role on PL emission.

4. Conclusion

The red photoluminescence (PL) from the porous Si (PS) layer formed on low resistivity p-type Si(100) wafer by anodization at current density (I_a) from 100 to 350mA/cm^2 at room temperature increases with the increase of I_a, and the lifetime increases slightly with I_a as well. The PS layer has a tree-like structure, and

the structure becomes finer with the increase of I_a. The finer tree-like structure is shown to be favorable for intensive PL. The EELS analysis reveals that Si crystal and SiO_2 (Si-O_4 tetrahedron) substances coexistent in PS layers, and that the PL intensity is dependent positively on the relative content of SiO_2 to Si crystallites or on the concentration of SiO_2 in PS. These results suggest that the micro-process of PL emission would be concerning with some kind of defects in SiO_2 and the defects in boundary of Si crystallites and SiO_2 structure as well.

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