

The Evidence of Quantum Size Effect from Photoluminescence of Low Temperature Oxidized Porous Si

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We examined the change in photoluminescence spectra of porous Si after several repetition of the set of chemical oxidation and deoxidation. We observed monotonous shift to higher frequencies of the photoluminescence peak as the repetition times increases. We also observe the shift to higher frequencies of the photoluminescence when it is oxidized using illumination of synchrotron radiation then deoxidized chemically. Raman measurement showed these shifts to higher frequencies are closely related to the quantum size effect.

1.Introduction

Intense photoluminescence from porous Si(PS) has recently received considerable attention.^{1,2)} Studies of PS have focused on its photoluminescence mechanism.^{3,4)} The size reduction of the width of PS strands is important to examine whether the photoluminescence from PS is caused by the quantum size effect. Oxidation of PS is general way to reduce the width of PS strands. During dry oxidation at high temperatures, however, surface diffusion of Si occurs and the width of PS strands increases.⁵⁾ Therefore, it is important to oxidize PS at low temperature. From this standpoint, we reduced the width of PS by oxidizing and deoxidizing chemically as well as by oxidizing using illumination of synchrotron radiation (SR) in this study. After each step, we measured the changes in photoluminescence spectra to investigate the photoluminescence mechanism. We found that the photoluminescence peak shifts to higher frequencies during these treatments. We also measured Raman spectra after each step and found the peak position shifts to lower energy when the photoluminescence peak shifts to higher energy. This indicates the photoluminescence of PS is caused by the Quantum size effect.

2.Experiment

The PS samples we used were made from (100) oriented, 9-11 Ω cm resistivity, p-type silicon

substrates. The anodization was performed in an HF solution at a constant current density of about 30mA/cm² for 20 min. We oxidized our PS samples by dipping them in 20wt% aqueous H₂O₂ solution at room temperature for about 15 min. We then deoxidized them by dipping them in 1.5 wt% aqueous HF solution for about 5 min. We repeated the set of these oxidation and deoxidation. An as-anodized PS was also oxidized by using SR illumination. SR was illuminated to the as-anodized PS in high vacuum in order to desorb hydrogen from the PS surface. Then oxygen was introduced in the chamber and adsorbed to the PS surface. The substrate temperature during SR illumination was less than 200 °C and oxidation at low temperature was performed. The power of SR at the illumination center is about 1 W/cm² and illumination time is 300 sec. We then deoxidized the sample by dropping a few drops of 1.5 wt% aqueous HF solution.

After each step, we measured photoluminescence at room temperature using Ar⁺ ion laser ($\lambda = 4880\text{\AA}$). We also measured Raman spectra in order to estimate the width of PS strands. In the case of SR illuminated sample, we measured photoluminescence and Raman spectra at the position about 2 mm far from the illumination center.

3.Results and Discussion

Figure 1 shows the change of PS photoluminescence spectra after several repetition of the set of chemical oxidation and deoxidation. Figure

1 (a) is for the as-anodized PS. The peak is centered around 800 nm (1.55 eV). Figure 1 (b) is for the sample for which the set of chemical oxidation and deoxidation was repeated 4 times. Although the width of the spectrum is almost the same, the photoluminescence peak is shifted to a shorter wavelength, 785 nm (1.58 eV). Besides this shift to a shorter wavelength, the integral of photoluminescence intensity increased. Figure 1 (c) is for the sample for which the set was repeated 8 times. The results show a further shift to higher frequencies of the photoluminescence peak to 770 nm (1.61 eV) accompanied by an increased integral of intensity.

Figure 2 shows the Raman spectra for these samples. Figure 2 (a) is for the as-anodized sample. Figure 2 (b) is for the sample of 4 repetition times. Figure 2 (c) is for the sample of 8 repetition times. The peak position of Raman spectra shifts to lower energy as the repetition times of the set of chemical oxidation and deoxidation increase. The reason for this Raman peak shift is considered to be due to the confinement of optical phonons.⁶⁾ The smaller the width of PS strands becomes, the smaller the energy the Raman peak shifts to. Therefore, the result of the Raman spectra indicates that the width of PS strands becomes smaller as the repetition times of the set of chemical oxidation and deoxidation increase.

This width reduction of PS strands is explained by the following. During chemical oxidation, oxygen prefers to attack and break Si-Si backbones rather than reacting with Si-H bonds on the outermost surface.⁷⁾ As a result, one Si surface layer is lost. During deoxidation, moreover, HF attacks and inserts hydrogen into the Si-Si backbones after the HF has removed the oxides.^{8,9)} This leads to hydrogeneration of the second-layer Si and the outermost Si surface is lost. Therefore, the set of these chemical oxidation and deoxidation reduces the width of the PS strands. Furthermore, the repetition of the set reduces the width of PS strands monotonously.

Taking account of this width reduction, the shift of photoluminescence peak position to shorter wavelength as the repetition times increase is considered to be caused by the quantum size effect.

Figure 3 shows the change of PS photoluminescence spectra after the oxidation using illumination of SR and subsequent deoxidation. Figure 3 (a) is for the as-anodized sample. Figure 3 (b) is for the oxidized sample using SR illumination. Figure 3 (c) is for the sample deoxidized with aqueous HF solution after the oxidation. A large shift to shorter wavelength is observed between the spectrum for the as-anodized sample and that for the deoxidized one. The Raman peak of the deoxidized sample shifts to lower energy than that for the as-anodized one. The width reduction mechanism is

considered to be similar to that in the case of chemical oxidation and deoxidation. Therefore, the photoluminescence peak position shift to shorter wavelength is considered to be caused by the quantum size effect.

4. Conclusion

We observed a shift to higher frequencies of the photoluminescence peak of PS after the repetition of the set of chemical oxidation and deoxidation. We also examined the change in photoluminescence spectra of PS when it is oxidized using SR illumination then deoxidized chemically. After these treatments, photoluminescence shifted to higher frequencies. Raman measurement showed these shifts to higher frequencies are closely related to the quantum size effect and we believe that photoluminescence of PS is caused by the quantum size effect.

5. Acknowledgements

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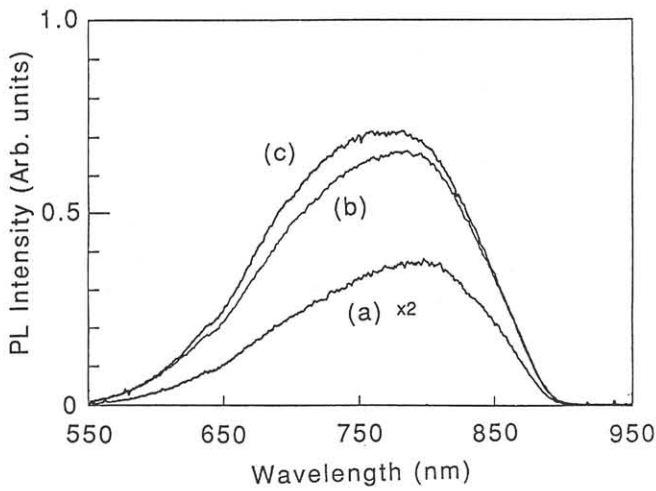


Figure 1 The change of porous Si photoluminescence spectra after several repetition of the set of chemical oxidation and deoxidation: (a) as-anodized, (b) 4 repetition times, (c) 8 repetition times

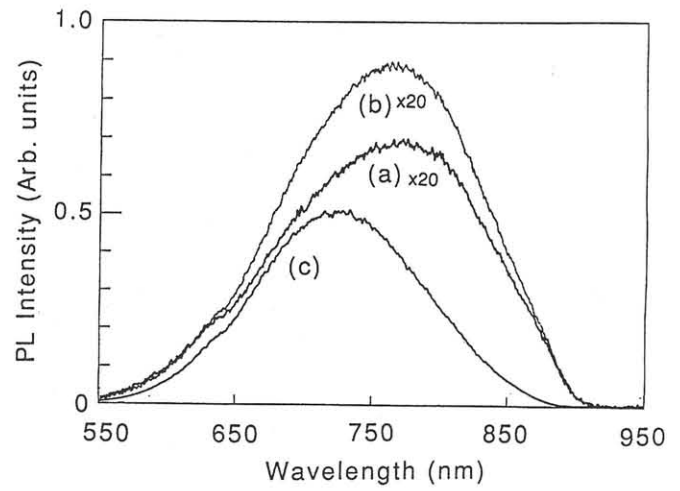


Figure 3 The change of porous Si photoluminescence spectra after oxidation using illumination of synchrotron radiation then deoxidized chemically: (a) as-anodized, (b) oxidized using illumination of synchrotron radiation, (c) deoxidized chemically after oxidation using illumination of synchrotron radiation

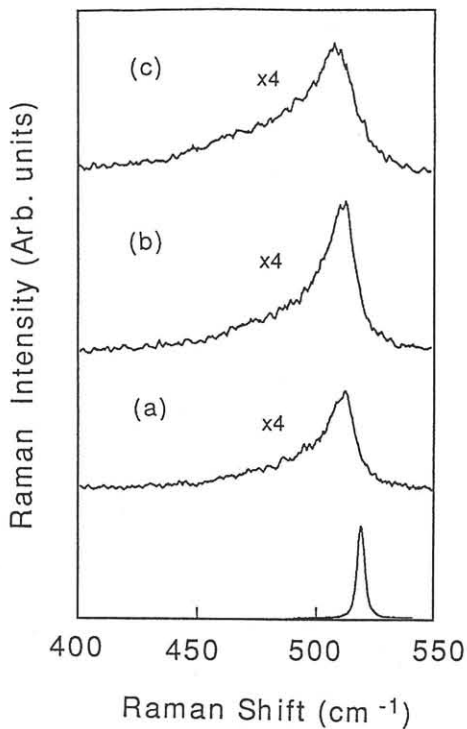


Figure 2 The change of Raman spectra of porous Si after several repetition of the set of chemical oxidation and deoxidation: (a) as-anodized, (b) 4 repetition times, (c) 8 repetition times, the spectrum of reference Si are also shown below.