Intense Luminescence from Thermally-Oxidized Porous Silicon

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Introduction

The visible light emission from porous Si(PS) [1, 2] has stimulated our great interest in the silicon nanostructure. The optical properties have so far been interpreted in terms of quantum confinement effects in the Si nanostructure. The formation of luminescent siloxene derivatives such as $Si_6O_{3+n}H_{6-m}$ in a PS layer has also been suggested as a possible origin of light emission [3]. Hydrogen termination of porous Si surface is thought to be a crucial factor to reduce the nonradiative surface recombination and to obtain the visible light emission [4, 5]. In this paper, we report on the strong visible luminescence from PS whose surface is passivated with SiO₂ instead of hydrogen.

Experimental

P-type Si(100) wafers with a resistivity of $2\sim4\Omega$ cm were anodized in a 50% HF solution with a current density of 25mA/cm². Anodization under these conditions for $3\sim15$ min leads to the formation of $6\sim30\mu$ m-thick PS layers. Subsequent chemical etching in a diluted ethanoic HF was carried out for $1\sim3$ min to obtain the luminescent PS. The PS layers were subsequently oxidized in a $10\% O_2 + N_2$ gas mixture at $800\sim1000^\circ$ C for $1\sim30$ min.

Results and Discussion

The photoluminescence (PL) spectrum of a PS layer chemically etched for 1min exhibits a peak at ~1.6eV with a full width at half maximum of ~0.35eV as shown in Fig. 1. When this PS layer is thermally oxidized, the light emission with a peak energy of ~1.5eV is observable. The PL intensity after 20min oxidation becomes 20 times larger than that of PS chemically etched for 1 min. This maximum intensity at ~1.5eV is as intense as the case of a conventional PS layer which is obtained by 3min chemical etching of an as-anodized specimen and exhibits a 1.74eV peak. The oxidation for less than 20min causes a red shift of about 0.1eV in the PL spectrum, and further oxidation results in a little blue shift. This suggests that such visible luminescence is not simply due to the excitonic recombination associated with the quantized states but presumably due to the radiative recombination through the localized states which are not well identified yet. Even for an as-anodized PS which shows no visible-light emission at room temperature, the thermal oxidation induces the similar intense photoluminescence. An FT-IR analysis of the PS layers before and after the oxidation has shown that only 1min oxidation leads to the complete desorption of hydrogen bonds and the formation of ultra-thin SiO₂ layer on the PS surface as represented in Fig. 2. Furthermore, x-ray diffraction peaks for PS oxidized for 30min become broad and shift toward the lower angle side with respect to those for the c-Si substrate as shown in Fig. 3, indicating the existence of ultra-fine crystalline Si structure with a lattice spacing elongated by about 0.02%. Regarding the stability of the PL intensity, a hydrogen-terminated conventional PS layer exhibits the rapid degradation in air under irradiation of a 488nm line from an Ar⁺ laser with 20mW/cm², and after 30min irradiation the intensity is decreased to about one third of the initial value as shown in Fig. 4. In contrast to this, the thermally oxidized PS shows no PL degradation even after 1hr irradiation.

In conclusion, we have succeeded in the ideal passivation of the PS layer with oxide. The PL intensity is as strong as the case of hydrogen-terminated PS and exhibits no degradation even under the laser illumination in air. This intense PL from the oxidized PS with no trace of bonded hydrogen excludes a possibility of luminescent siloxene-derivative formation in the PS layer. The PL red-shift caused by the progressive oxidation suggests that the visible light emission occurs through the unidentified localized states rather than the excitonic

recombination associated with the quantized states.

References

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Fig. 1 Room temperature PL spectra for PS layers chemically etched for 1min and subsequently oxidized at 1000°C. The spectra for PS layers chemically etched for 1min or 3min are also shown as references. A 488nm line from an Ar⁺ laser was used as an excitation source.



Fig. 3 X-ray diffraction peaks for porous Si oxidized at 1000°C for 30min are compared with those for a c-Si(100) substrate. Ni-filtered CuKα radiation (1.5405Å and 1.5443Å) was utilized for this measurement.



Fig. 2 Infrared absorption spectra for PS before and after oxidation. The Si-O-Si stretching absorption band at ~1080cm⁻¹ is so strong that the transmittance is nearly zero at this wavenumber range.



Fig. 4 PL intensities at 1.5 and 1.74eV for porous Si oxidized at 1000°C for 30min are compared with the case of 3min chemically-etched PS as a function of 488nm light irradiation time with a laser power density of 20mW/cm².