Blue Light Emission from Rapid-Thermal-Oxidized Porous Silicon

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The hydrogen-passivated surface of porous Si is converted to stable silicon oxides by a rapid-thermal-oxidation process. At a high oxidation temperature (Tox) above 800°C, blue photoluminescence (PL) with a peak of about 400nm was observed. On the other hand, at a low Tox, the PL peak remained about 700 nm which is similar to that of as-anodized porous Si. From FTIR spectra, we found that the PL spectra is sensitive to the surface-termination conditions of porous Si.

Porous silicon (PS) with a strong photoluminescence (PL) attracts much interest. A great deal of research effort has been focused on understanding the structure, elucidating the mechanism of a strong PL and fabricating light emitting diodes. Recent studies show that luminescent PS consists of Si nanocrystallites whose surface is covered with silicon hydride (Si:H) or silicon oxyhydride (Si:O:H) and that the efficient PL is closely related to a hydrogen passivation of the surface.¹⁻⁴⁾

More recently, some attempts have been made to convert a H-terminated surface to an oxidized one.⁵⁻¹³⁾ The oxidized PS is interesting for both physics and device applications from the following reasons: The H-terminated surface is unstable at room temperature, and many studies have been reported on the PL degradation in PS.^{14,15)} The PL degradation is a fatal drawback for device applications. Thus, a stable alternative surface passivation is strongly desired. Also, since the PL characteristics is sensitive to the H-terminated surface, investigating the PL by means of controlling the structure of the internal surface of PS helps us understand the PL mechanism which remains unclear. Moreover, a few papers have been published that oxidized PS shows a blue-green light emission (a peak wavelength is about 500nm)^{11,12)} which has not been observed for H-terminated PS yet. Obtaining a blue light emission is of great importance for both comprehending the PL mechanism and realizing a full color display.

In general, oxidation has had a detrimental effect on PL intensity. Both photoinduced oxidation and low temperature thermal oxidation have been shown to degrade the radiative efficiency. However, the PS with a high quality oxidized surface is reported to show a strong PL.^{7-9,12,13)} One of the most promising methods for providing a high quality oxide on the internal surfaces of PS is rapid-thermaloxidation (RTO), because the process time less preserves than a minute the Si nanocrystalites.^{12,13)}

In this work, we have converted the Hpassivated surface of PS to stable silicon oxides by a RTO process. We have clearly observed a blue PL with a peak of about 400nm for the PS oxidized at a temperature higher than about 800 °C. This is the first time to obtain a blue light emission with a peak of 400nm.

PS layers were formed on p-type (100) crystalline Si (c-Si) wafers whose resistivity was $3.5-4.5 \Omega$ cm. Thin Al films were evaporated on

the back of the wafers to form a good ohmic contact. The anodization was carried out in HF-C2H5OH solution (HF:H2O:C2H5OH=1:1:2) at a constant current density of 10 mA/cm² for 5 We used a commercial RTO apparatus. min. The RTO process was performed as follows: First of all, to substitute oxygen for air, the furnace was evacuated into vacuum, and then O2 (100%) was introduced. Immediately after the anodization, samples were carefully set in the RTO apparatus so they would be exposed to as little air as possible. The heating rate was 200°C/sec, and the samples were kept for 35 sec at the oxidation temperature (Tox) ranging from 480 to 1200°C. The cooling rate was about 100°C/sec. During the RTO process, the flow rate of O2 was kept at 100cc/min.

PL spectra from RTO-PS were measured in a vacuum with 325 excitation light from a He-Cd laser. To get the information about the internal surface of RTO-PS, we measured the FTIR spectra. The picosecond initial PL decay measurements, which are a powerful tool for investigating the origin of the PL, were performed using a synchroscan streak camera



Fig.1 PL spectra of RTO-PS as a function of Tox. The excitation light source is He-Cd laser (325nm).

and a pulse with a wavelength of 240nm and a width of 200-ft from the fourth harmonic of a cw-mode-locked Ti:Al2O3 laser.

Figure 1 shows the PL spectra from RTO-PS under 325 excitation at room temperature as a function of Tox. In RTO-PS oxidized at low Tox below 800°C, the PL peak is around 700nm, which is similar to that of as-anodized PS. On the other hand, at higher Tox above 800°C, the strong blue PL near 400nm appears, and the red PL near 700nm disappears. We did not observed the PL with an intermediate wavelength.

Figure 2 shows the dependence of FTIR spectra on Tox. In as-anodized PS, the absorption peaks due to Si-H and Si-H2 are observed near 900 and 2100cm⁻¹. After oxidation these two peaks disappear. At low Tox below 800°C, an absorption band due to O-H is observed near 3400cm⁻¹, however at Tox higher than 800°C, this broad absorption band also disappears. As raising Tox, three peaks near 1100, 800 and 450 cm⁻¹, which are characteristics of thermally grown SiO2, monotonically increases. The FTIR spectra strongly suggest that the surface of Si nanocrystallites is covered with O-H and SiO2 for the RTO-PS samples at a Tox

lower than 800°C, and that is covered with only SiO2 for those at a Tox higher than 800°C. From Figs. 1 and 2, we found that the oxidation temperature at which the blue light emission is observed corresponds to that at which the change of the surface termination occurs.



Fig.2 FTIR spectra of RTO-PS as a function of Tox.

Figure 3 shows picosecond initial decay of PL. (a) refers to the PL decay at 400nm for RTO-PS at Tox of 880°C, and (b) the PL decay at 700nm for RTO-PS at Tox of 580°C. From Fig.3 the picosecond decay time constant τ is estimated to be 680ps and 80ps for curve (a) and curve (b), respectively, which indicates that τ of the blue PL at 400nm is larger than that of the red PL at 700nm. However, the multiexponetial PL decay in the range from μ sec to msec, which is seen in the red PL, is not observed in the blue PL. These results suggest that the origin of blue PL is different from that of red PL.

From these results, we think the surface layer of nanocrystallites plays the most essential role in a strong PL.¹⁶⁾ Therefore, the peak of PL suddenly shifts from 700 to 400nm at a Tox of about 800°C which corresponds to the temperature where the change of the surface condition occurs, and the properties of blue PL is different from those of red PL.

In conclusion, we have succeeded in fabricating PS with a blue light emission (a peak wavelength is about 400nm) by a RTO process. Our study suggests that the surface-termination conditions of PS plays the most important role in a visible strong PL.



Fig.3 Picosecond PL decay. (a) refers to the PL decay at 400nm for RTO-PS at Tox of 880°C, and (b) the PL decay at 700nm for RTO-PS at Tox of 580°C. (a)

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