Evidence that blue luminescence of oxidized porous silicon originates from SiO$_2$

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We have analyzed red and blue luminescence from porous silicon as a function of oxidation parameters and feature dimension determined with an atomic force microscope. We have found correlation between blue luminescence intensity and the increase in feature size caused by oxidation. We have further shown that blue luminescence, is identical, with respect to spectrum and fast decay, to that of high microelectronic quality SiO$_2$ grown on crystalline silicon using dry oxygen plus an organic chlorine compound. Thus, we conclude that blue luminescence originates from SiO$_2$ film rather than from the silicon nanocrystals in the porous material. Intensity enhancement, as compared to SiO$_2$ on crystalline wafers, comes from the gigantic surface area of porous silicon.

Recent literature[1-6] has provided evidence that porous silicon can luminesce in two distinct bands: the originally discovered "red" band[7] 0.65 to 0.8 μm (1.5–1.9 eV) and the newly identified high energy "blue" band 0.43–0.48 μm (2.6–2.9 eV). The blue luminescence requires ultra violet excitation, thus, it was not observed in the vast majority of previous photoluminescence (PL) studies which used visible range excitation.

Red and blue luminescence are both affected by oxidation of porous silicon, however, in a different way. The blue band appears after oxidation[4-6] while the red luminescence exists in as-prepared material and increases in oxidized material, but tends to vanish after heavy oxidation.[6,8] The bands are also distinguished by slow and fast luminescence decay falling into 10 μs and 10 ns range for the red and blue bands, respectively.[2,4,5]

In this work we report luminescence characteristics of oxidized porous silicon excited with an excimer laser. Emphasis is given correlation with surface morphology which is studied with an atomic force microscope (AFM) taking advantage of the recently introduced "tapping" mode.

Porous silicon films on p-type $\langle 100 \rangle$ silicon wafers with resistivities of 3–10 Ω cm were prepared by anodic etching in ethanol:HF mixture (C$_2$H$_5$OH with 25 wt % HF). For a typical current density of 20 mA/cm^2, the film porosity was 71$\pm$1%. The thickness of porous layers was about 20 μm. Further treatment involved annealing in a rapid thermal processor (RTP) in a dry oxygen ambient and in dry nitrogen.

Figure 1 shows PL spectra of porous silicon films excited by 0.193 μm (6.4 eV) pulses of an ArF excimer laser. The films were subjected to 10 s RTP oxidation at different temperatures. The appearance of the blue band after RTP is evident in Fig. 1. It is significant to note that the peak position of the blue band (0.435 μm) remains unchanged while the intensity grows by two orders of magnitude. Under high photon energy excimer laser excitation, the blue band is a dominant one with the peak intensity (normalized to spectral response of the PL system) being about 40 times larger than that of the red band. The blue band could not be detected in films RTP annealed in a nitrogen ambient.

In PL measurements, 30 ns laser pulses with repetition rate of 4 Hz gave an estimate incident energy of 1 mJ over a spot size of 2 mm in diameter. The room-temperature PL was analyzed with a resolution better than 0.4 nm using an optical multichannel analyzer consisting of a dual port 0.5 m grating monochromator and a linear diode array system equipped with a microchannel gated intensifier. The measurements were performed with the gate width of 100 μs suitable for monitoring both fast and slow decaying blue and red band, respectively. Several delays preset by a digital delay generator, were used for evaluation of the decay time. The PL image was focused on the quartz optical fiber and transferred to the monochromator. Scattered laser light was cut off by the UV filter in front of the fiber.

The red band in Fig. 1 is positioned at 0.68–0.72 μm. Using 0.5145 μm Ar laser excitation, we have found that the same red band is peaked at 0.77 μm. The shift is in agreement with previous data. As shown in Ref. 9 this shift results from differences in the excitation depth (which results in luminescence from different film regions) and also from differences in excitation energy.
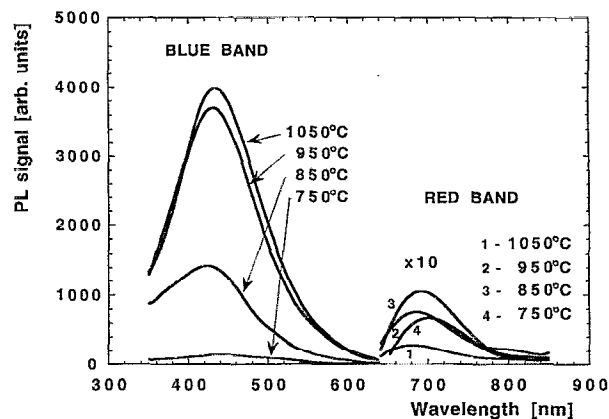

FIG. 1. The effect of RTP annealing in dry oxygen on porous silicon PL excited by on excimer laser.
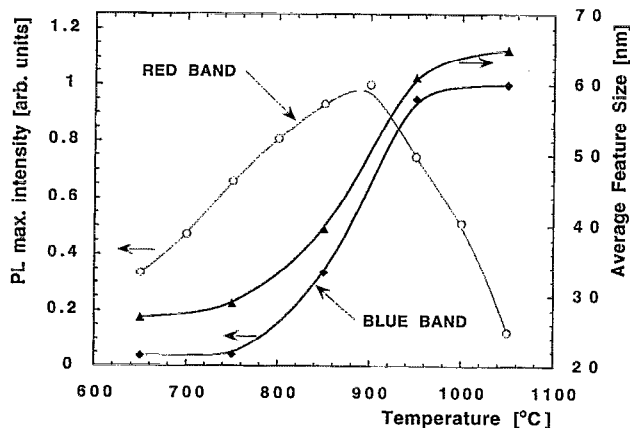
FIG. 2. Porous silicon PL intensity vs RTP oxidation temperature for two distinct bands and corresponding size increase of the surface features caused by oxidation.

The PL intensity versus RTP temperature is given in Fig. 2 for 10 s annealing in a dry oxygen. The 750 °C threshold temperature for the blue band intensity increase is similar to a thermal oxidation threshold for Si in O_2 ambient.[10] It is known however that thermal oxidation of porous Si proceeds much more rapidly than that of crystalline Si.[11] A large intensity increase takes place between 850 and 950 °C. Above 1000 °C the intensity tends to saturate, which may corre-

spond to the oxidation limit imposed by small dimensions of Si features in porous Si.[12] A post-RTP removal of oxide in buffered HF always resulted in an elimination of the blue band or, at least, a drastic reduction of its intensity.

The red band exhibited different behavior. Consistent with previous publications we have observed this band before oxidation and also after oxide removal by HF dip. Extensive oxidation, therefore, is not a necessary condition, but some oxidation is essential for enhancing the red band intensity. As shown in Figs. 1 and 2, the red luminescence intensity exhibits a maximum at RTP temperatures of about 900 °C. In fact, the annealing in oxygen at 800–900 °C is often used to enhance and stabilize the red-band luminescence. RTP above 1000 °C can eliminate the red luminescence completely.[6,8]

Fourier transform infrared (FTIR) spectroscopy revealed in RTP-oxidized porous Si characteristic oxygen-related bands identical to those reported in the literature. Accordingly, our sample can be considered representative for RTP-oxidized porous Si.

Changes in surface morphology of porous silicon caused by RTP in a dry oxygen are shown in Fig. 3 by surface images obtained with an AFM. RTP changes sharp features characteristic for as-anodized porous silicon into spherelike objects with sizes increasing with increasing oxidation temperature. AFM images were obtained with silicon-etched tips operating in tapping mode using the Nanoscope III Multi-
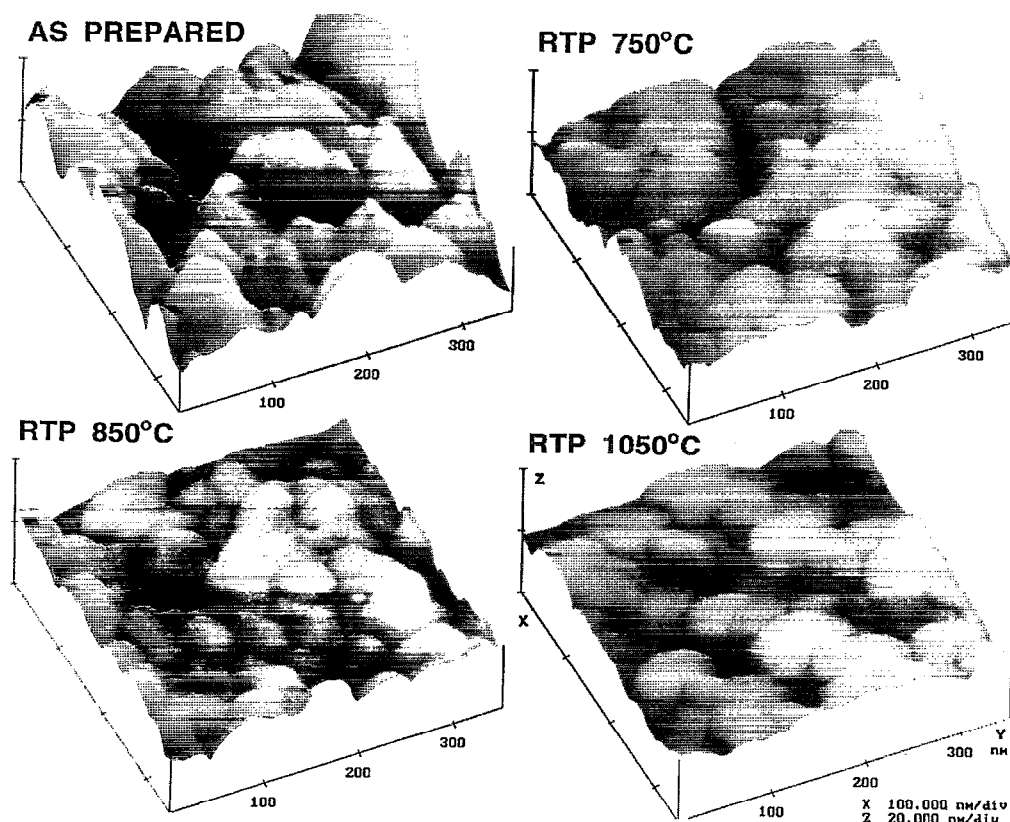

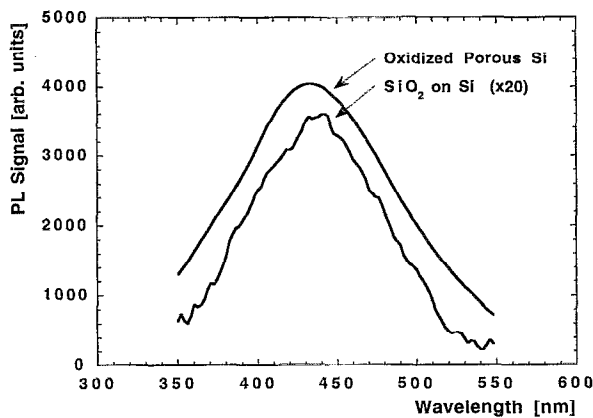FIG. 3. AFM images of porous silicon surface after RTP oxidation at different temperatures.

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FIG. 4. Spectral characteristic of the blue luminescence bands from RTP oxidized porous silicon and from 900-Å-thick SiO_2 grown on crystalline silicon in an O_2 ambient containing organochlorine. Both spectra were measured under identical excimer laser excitation and 100 ns gate delay.

mode AFM system. In this mode, the vibrating probe actually strikes the surface in each cycle and the decrease of amplitude due to tapping is used to track the sample topography. Tapping mode reduces capturing of the tip and dragging it along the surface, which offers a major advantage in AFM mapping of porous Si.[13]

Fourier transform of images was used for determination of the lateral dimensions of porous silicon features. The average feature dimension is given in Fig. 2 versus RTP temperature. The dimension increased, from about 28 nm in as-anodized silicon to a saturation value exceeding 60 nm in films oxidized at 950 and 1050 °C. One should note from Fig. 2, that the growth of the blue luminescence intensity follows very much the growth of surface feature dimensions. The increase of porous Si features is consistent with a volume expansion caused by oxidation of silicon by a factor of about 2.3.

To clarify the origin of the blue band in oxidized porous Si we have carried out luminescence measurements on oxidized single crystalline silicon wafers. Of a series of different oxides we have identified the process which gives the blue luminescence spectrum shown in Fig. 4. The spectrum is identical to that of oxidized porous Si. Both spectra in Fig. 4 were measured under identical excitation conditions. We have also found that the blue PL decay was for both cases very fast. With 100 ns gate delay (or an effective 70 ns delay considering 30 ns laser pulse width) we found blue luminescence reduction to unmeasurable levels in both instances. This gives an estimate of the luminescence decay constant of about 10 ns or less.

The fast decay is important for distinguishing oxidized porous Si from defect-related luminescence in silicon and quartz.[4] Blue PL (2.6–2.9 eV) is known to occur in silica and quartz, but not in thermally grown oxide. This luminescence is characterized by 50 ns decay, which is about 5 times longer than that in porous Si and also than that in presently studied thermal oxide on crystalline Si. A defect-related 2.7 eV band has also been observed in a-SiO_2,[14] however with a decay time of 5 ms, i.e., over 5 orders of magnitude larger

than that of the presently observed blue band.

The blue luminescing oxide was grown at 1000 °C in oxygen ambient with a 2% (volume) addition of organochlorine. One can notice that the presence of carbon- (ethanol during anodization and organochloride during oxidation, respectively) and halides (formed by fluorine during anodic etching and chlorine during the oxide growth, respectively) are the commonalities between porous Si and the blue luminescing oxide. We are therefore inclined to suggest that the blue luminescence may result from creation of carbon or halogen-related defects in silicon dioxide. Luminescence enhancement in porous Si with respect to that in SiO_2 may originate from the gigantic surface area of porous Si.

The suggested blue-band origin is very much different than the quantum confinement model of red luminescence involving band-to-band radiative recombination[7] or the interface state recombination.[15] It is difficult not to notice the incompatibility between these models and the experimental characteristics of the blue luminescence.

The involvement of defects, similar to a nonbridging oxygen hole center in silica fibers, has recently been proposed to explain the red luminescence of porous silicon.[16] It was suggested that these centers are located at the silicon-oxide interface. Our results indicate that the increase in the blue luminescence is similar to the increase in the size of oxidized features, therefore, one might expect that the defects involved are located in the oxide rather than at the interface. Finally, we find it very unlikely that the origin of blue luminescence can be explained in terms of the siloxene model proposed for red luminescence.[17] In our FTIR measurement we found no evidence of hydrogen in oxidized samples.

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