The Blue and Red Luminescences from Ambient Air Aged Porous Silicon

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This paper reports on photoluminescence (PL), luminescence decay curves, and compositional analysis of porous silicon (PS) which is aged under air ambient by Fourier transform infrared vibrational spectroscopy (FTIR) and by Auger electron spectroscopy (AES). Porous silicon which has been aged under air ambient yields two PL band structures, i.e. blue/violet PL and red PL. The evolution of a blue/violet band is pronounced, especially for thin PS film which is prepared in dilute HF solution The blue/violet PL band has been observed initially to increase rapidly with aging, then saturated with further atmospheric aging The ambient air aged PS exhibits a fast decay time of sub-nanosecond at room temperature and shows appreciably faster decay time than that at 20K. Atmospheric aging of this thin blue/violet luminescing PS yields non-stoichiometric oxide judging from the vibrational spectra of Si-O and AES analysis.

Key works: Blue, Luminescence, Porous, Silicon, Decay curves, Ambient, Aging

I. Introduction

Porous silicon which is obtained by electrochemical etching has attracted a large number of investigations not only to its PL and origin of luminescence but further to its application as an optoelectronic device. The large surface area of PS renders it difficult to delineate the mechanism(s) of a strong PL from PS. Anodic etching of silicon leads to a high efficiency room temperature PL usually in the orange-red part of the visible spectrum. In addition to the usual orange-red PL from PS, blue and green luminescences from PS have been observed. Thus, there has been much interest in the literature on the blue shifted PL from PS and from nano-crystalline silicon. The blue and green luminescence can be obtained in purified boiling water treatment, even though this method shows a some difficulty in reproducibility [1] The blue luminescence also emerges after rapid thermal oxidation (RTO) of PS above 800°C[2,3] and after RTO followed by storage in ambient air.[4] An alternate preparation technique, i.e. spark processed Si, also luminesces in the blue and green spectral region.[5-7] Interestingly, the blue PL can be observed when the PS contains one or another oxidized layer. It has been discussed in the literature whether or not oxide layers (SiO₂) may be responsible for the room temperature blue PL in anodically etched silicon.[3,7] Recent studies on the blue PL attributes its origin to the Si crystallites,[8] Si quantum wires,[9] silanol groups adsorbed in a SiO₂ network,[10] SiO₂ and oxide related species.[2]

The present paper reports some experimental results on the blue/violet luminescence of ambient air aged PS. In particular, the evolution of the blue/violet PL band, luminescence decay curves, IR spectra and Auger electron spectroscopy analysis will be given in order to clarify possible involvement of oxidized layers for the blue/violet PL in an ambient air aged PS.

II. Experimental Procedure

The porous silicon samples were prepared by electrochemical etching of boron doped p-type (100) wafers with 8~12 Ωcm resistivity. Anodization was conducted for 10 min under a constant current density of 1 mA/cm². The samples were anodized in a solution of 2:3 HF: ethanol, with and without UV illumination, respectively. Then, PL measurements were conducted at various ambient aging time intervals. Photoluminescences were performed by a conventional setup with voltage measurement techniques. Optical excitation was achieved by a pair of lenses after passing a long pass band filter which blocks scattered laser light. The cut on wavelength of this filter (50% transmission) was 348 nm and inserted between sample and monochromator. The

luminescence was dispersed by a 1 meter single grating monochromator and detected by a GaAs photo multiplier. The PL dynamics were obtained in a separate system using a 390 nm pulsed beam which was produced by the second harmonic generation of mode-locked Al_2O_3 : Ti laser pumped by Ar^+ laser. The pulse duration and instrumental resolution were 1.7 ps and 20 ps respectively. The FTIR spectra were taken on various types of oxides as well as on an ambient air aged PS in nitrogen atmosphere.

III. Results and Discussion

Fig. 1 compares the PL spectra (a) of PS prepared under a HF solution with concommital UV illumination with PL spectra of (b) PS prepared under concentrated HF solution without UV illumination. All of the series of PL measurements were conducted within 1 hour after sample preparation. The numbers in Fig. 1 represent the amount of etching time in min. Each curve is normalized to 1 for its PL maximum in order to compare the evolution of the blue/violet band among various samples. There exist several interesting properties of PL among these samples. First of all, it is interesting to note the two PL band structures, i.e. blue/violet and generally observed red PL from PS. The eminent blue/violet luminescence can be observed especially for short durations of etching time. Specifically, one can detect the highest blue/violet PL for the 5 min etched PS in Fig. 1
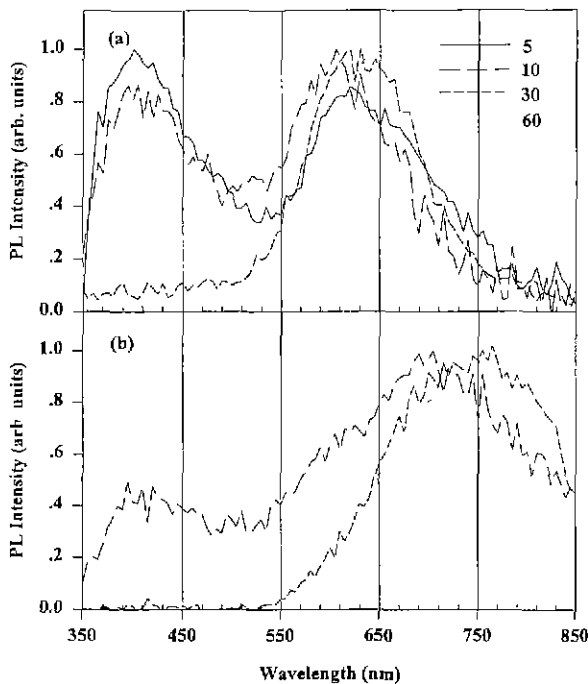
Fig. 1 Room temperature PL spectra of (a) photo-assisted anodic etched Si with 1:9 and (b) without photo-assisted anodic etched Si with 2:3 HF: Ethanol solution at a current density of 1 mA/cm² as a function of etching time. The numbers represent the amount of etching time in min.
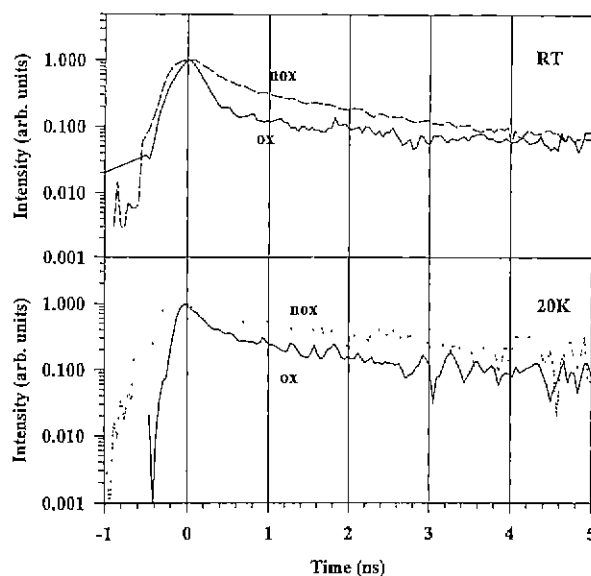
(a), whereas there is no appreciable blue/violet PL band for the 60 min anodically etched PS. Similar luminescence behavior is found for the PS prepared in concentrated HF solution as depicted in Fig.1 (b), but the blue/violet PL band is relatively weak compared to PS specimens prepared in dilute HF solution. Even after the especially short duration of etching time, the relatively strong blue/violet PL (even 1 hour after PS preparation) can be explained by the rapid atmospheric oxidation of this thin PS film. Thus, we can conclude that the shorter the etching time, the more prominent the blue/violet PL band becomes. The other interesting properties are as follows. The increased duration of etching time generally leads to a slight red shift of the red PL peak position. The further red shift of the red luminescence band was observed for the PS prepared in concentrated HF as depicted in Fig. 1 (b). The red shift of the red luminescence band for the longer duration of etching time as well as the PS prepared in concentrated HF solution can be explained by the formation of coarse porous structure namely, large crystals. Typically, the blue shift of the red PL band was observed for photo-assisted etched PS compared to dark etching under identical HF concentration similar to the reported results.[11,12] It is generally known that the formation of the porous structure is initiated from holes in silicon surface in HF solution. The photo-assistance is normally applied to enhance the amount of free carriers during the etching process, allowing holes to flow into the surface, otherwise already depleted porous structure. Thus the degree of porosity is higher and in consequence the dimensions of remaining Si nanostructures are smaller which in turn enhances quantum effect. We could also observe a blue shift to about 660 nm for photo-assisted etching of samples prepared in 40% HF solution compared to the PS prepared without UV illumination. Then, what would be the cause of this blue/violet luminescence from PS? In order to shed some light on this phenomenon, we have performed the PL measurements of PS with various intervals of ambient aging times. The relative intensity ratio between the blue/violet and red bands with aging time is depicted in Fig. 2. The blue/violet PL band is observed for short duration of etching time, namely thin film, and initially increases rapidly with aging, then finally saturates with a further increase in aging time. In contrast to this, thick PS (long duration of etching time) does not show any appreciable blue/violet PL band with atmospheric aging. These experimental results lead to the following conclusion that the blue band is more or less originated from surface and has some relation to the degree of oxidation. Therefore, the absence of the blue PL band for the thick PS seems to result from the fact that the volume fraction of blue/violet PL band which is related to the surface oxidation might be too small compared to that of the red PL band. There exist another interesting PL properties worthy of mention. The PL peak positions
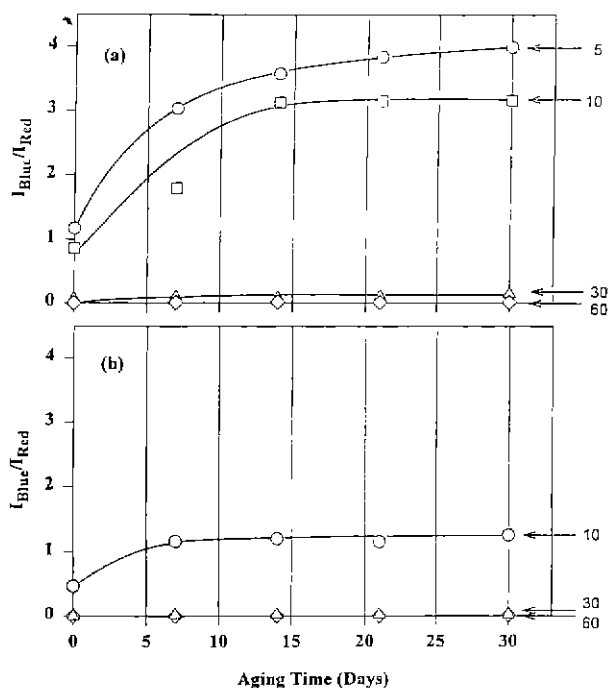
Fig. 2. PL intensity ratio between the blue and red bands of (a) photo-assisted anodic etched Si with 1:9 and (b) without photo-assisted anodic etched Si with 2:3 HF: ethanol solution at a current density 1 mA/cm² as a function of the ambient aging time The numbers represent the amount of etching time in min.

Fig. 3. Luminescence decay curves measured at 410 nm for the freshly prepared PS depicted as ox as well as 1 month ambient air aged PS marked as nox as room temperature and 20 K. The samples were prepared with photo-assisted 10% HF solution at a current density of 1 mA/cm².

of blue/violet and red PL of PS prepared in dilute HF do not show any shift with aging time, whereas the PS prepared in concentrated HF (thick films) show the blue shift as a function of etching time.
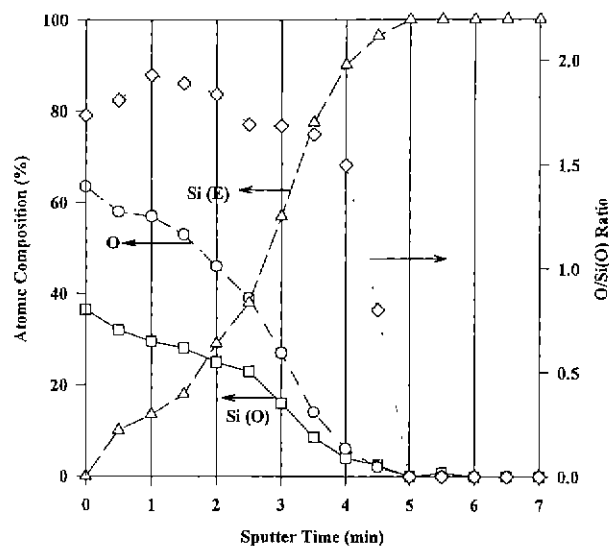
The knowledge of parameters that govern recombination process in PS is highly desirable in order to clarify the luminescence mechanism. The luminescence decay curves which are measured at 410 nm at room temperature and 20 K for the freshly prepared PS as well as one month ambient air aged thin PS, i.e. blue/violet luminescing PS, are depicted in Fig. 3. The decay dynamic is non-exponential and the curves cannot be fitted by a bimolecular recombination law nor by a stretched exponential function for the oxidized PS marked as ox as well as non-oxidized PS marked as nox at room temperature. These results indicate that the luminescence relaxation dynamics is more complicated compare to high optical quality semiconductors. However, the thorough inspection of Fig. 3 shows that there exist at least two main recombination channels. Specifically, the fast transition at 410 nm and slow decaying tail. The measured fast decay time constant is slightly less than 100 ps by $I_o(1/e)$ assumption at room temperature. However, the appreciable decrease of decay time is found at 20 K. The measured decay time constant of ambient air aged blue luminescing PS is substantially shorter than the lifetimes of red luminescing PS (typically 1~10 μs at room temperature).[14] However, analogous fast de-

cay in range of few ns has been reported for the blue-green band of strongly oxidized PS, i.e. rapid thermal oxidized PS at 1100°C.[2,13] The PL band of SiO₂ which falls in the same wavelength range, however, appears much slower in their decay characteristics. For the 1.9, 2.2, 2.7, and 3.1 eV transitions in silicon oxide, the decay constants of 12~14 μs, 60~80 ns, 9.4~10 ms, and 110 μs were reported, respectively.[15-18] As already mentioned, the blue PL band is related to the degree of oxidation in atmospheric aging of PS. Nonetheless, it seems unreasonable to consider transitions as they appear in SiO₂ as possible candidates to explain the observed blue/violet PL. The ambient air aged PS displays faster decay times at 410 nm than the freshly prepared PS regardless of measured temperature. Furthermore, the measured decay time of the ambient air aged PS is faster at room temperature than at 20 K. These abnormal behaviors are quite difficult to explain and are currently being studied. Judging from these results, it seems that the much faster blue/violet transitions deplete the reservoir of excited carriers, otherwise recombine via slow red channel. However, the detailed studies of the time resolved PL as a function of wavelength and temperature have to be done in order to gain the detailed relaxation mechanism.

Of particular interest is a study of the infrared vibrational spectra of blue luminescing ambient air aged PS. (There are ample reports of the vibrational spectra on the atmospheric aged red luminescing PS in the literature.[19,20]) The amount of stoichiometry or non-stoichiometry in SiOₓ for the blue/violet luminescing Si samples can be inferred by inspecting the Si-O stretching vibrations between 1050 and 1190 cm⁻¹ Fig. 4 dep-
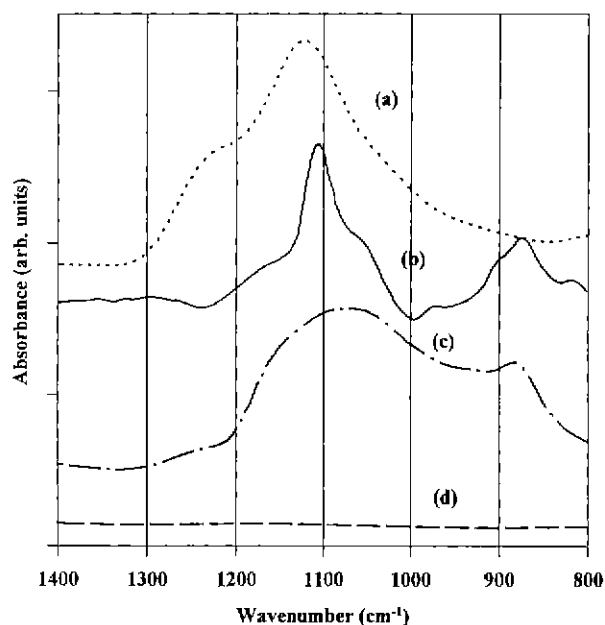
Fig. 4. Absorption Fourier transform infrared (FTIR) spectra of (a) fused SiO_2, (b) 1 month ambient air aged PS prepared with 10% HF solution, (c) vapor deposited SiO on Si, and (d) Si implanted by O (25 KeV, $2 \times 10^{16}/cm^2$).

Fig. 5. AES depth profile spectra of an ambient air aged PS prepared with photo-assisted anodic etching with 10% HF solution at a current density of 1 mA/cm^2 for the etching duration of 10 min.

icts a comparison of vibrational modes from fused SiO_2, ambient air aged thin PS, vapor deposition of SiO and Si in the range between 800~1400 cm^{-1}. Fused SiO_2 displays a vibrational mode near 1125 cm^{-1} with a shoulder at 1250 cm^{-1} which stand for asymmetric Si-O-Si stretchings and which are characteristics of stoichiometric SiO_2. In contrast, the absorption modes for ambient air aged PS (curve (b)), vapor deposited SiO (curve (c)) and for Si with implanted O (curve (d)) are shifted or show no particular features, respectively. Therefore, the ambient air aged PS is considered to possess a non-stoichiometric oxide, whereas rapid thermal oxidized PS which displays the blue luminescence is reported to possess a similar stoichiometric oxide.[3] In order to determine the oxide content as well as the thickness of thin PS, especially for PS which exhibit blue/violet PL, the depth profile of Auger electron spectroscopy (AES) has been performed on 10 min etched PS and the result is displayed in Fig.5. The thickness of PS which is electrochemically etched for 10 min with UV illumination is determined to be around 500 Å based on sputter rate calibration of 3 KV Ar^+ sputtering. The 60 min etched PS which is prepared under identical conditions yields the thickness of about 4000 Å. Thus, the relatively small growth rate of 65 Å/min is determined for photo-assisted etching in dilute solution. Fig.5 also depicts the O/Si ratio without the consideration of elemental silicon and shows the general agreement, which is drawn from infrared vibrational spectroscopy, i.e. non-stoichiometric Si suboxide (SiO_x). Finally, a brief discussion of blue/violet PL from ambient air aged PS will be attempted. The blue/violet band can

be easily obtained from thin PS as well as ambient aging of thin PS which leads to an increase of blue/violet band. In addition, the blue/violet PL band shows no peak energy shift with atmospheric aging as can be seen in Fig.1 and 2. Thus, a possible model is here reviewed which may lead to the observed blue/violet PL from ambient air aged PS. The blue/violet luminescence may originate from the silicon oxide itself. Despite the fact that silicon oxide possesses a wide band gap, there are various luminescence bands associated with different defect structures as already discussed, but these luminescence bands are quite slow in their decay times compared to the observed sub-nanosecond decay constants for the ambient aged PS. In addition to this fact, an excitation energy of at least 5.0 eV is necessary to activate various luminescence bands. The excitation energy of 5.0 eV that is used in literature is much higher than our excitation energy of 3.8 eV of He-Cd laser. Therefore the excitation energy of 3.8 eV is not enough to activate various luminescence bands associated with defects in SiO_2. However, different types of defects in silicon oxides may be present which are not yet revealed which can be excited by He-Cd laser. Our FTIR and AES analysis of ambient air aged PS suggest that the presence of a non-stoichiometric suboxide namely, SiO_x, is present. Indeed, the band gap of a non-stoichiometric suboxide (SiO_x) is smaller (Eg>3~4 eV for x=1.4~1.6) and near UV excitation may produce non-equilibrium carriers. Thus, the presence of this thin SiO_x film result in, though qualitatively, the evolution of the blue/violet PL band with aging time. Also, the saturation of the blue/violet PL band with extended aging, and the suppression of the blue/violet PL band by prolonged etching as can be seen in Fig.1 and Fig 2 may also originate from the SiO_x film. Although

further investigation is required to elucidate, the origin of the blue/violet PL band from ambient air aged PS seems to be associated with oxygen-related at our current understanding rather than quantum size effect.

IV. Summary

In conclusion, we observe that PS which has been ambient air aged leads to two PL band structures, namely blue/violet and red-orange PL. The blue/violet PL band is pronounced, especially for thin PS film, and displays a fast sub-nanosecond decay time at room temperature and shows an appreciably faster decay time than that of at 20 K. Atmospheric aging of this thin PS yields an increase of blue/violet luminescence band and leads to a non-stoichiometric oxide judging from vibrational spectra of Si-O and AES analysis. This blue/violet PL from ambient air aged PS seems to be associated with the oxygen-related origin.

References

1. X. Y. Hou, G. Shi, W. Wang, F. L. Zhang, P.H Hao, D. M. Huang and X. Wang, "Large Blue Shifts of Light Emitting Porous Silicon by Boiling Water Treatment", *Appl. Phys. Lett.* **62**, 1097-1099 (1993).

2. L. Tsybeskov, Ju. V. Vandyshev and P. M. Fauchet, "Blue Emission in Porous Silicon: Oxygen-related Luminescence", *Phys. Rev.* **B 49**, 7821-7824 (1994).

3. H. Mimura, T. Futagi, T. Matsumoto, T. Nakamura and Y. Kinemitsu, "Blue Light Emission from Rapid-Thermal-oxidized Porous Silicon", *Jpn. J. Appl. Phys.* **33**, 586-589 (1994).

4. A. Loni, A. J Simons, P. D. J. Calcott and L. T. Canham, "Blue Photoluminescence from Rapid Thermally Oxidized Porous Silicon Following Storage in Ambient Air", *J. Appl. Phys* **77**, 3557-3559 (1995).

5. R. E. Hummel, M. H. Ludwig, S.-S. Chang, P. M. Fauchet, Ju. V. Vandyshev and L. Tsybeskov, "Time Resolved Photoluminescence Measurements on Spark-processed Blue and Green Emitting Silicon", *Sol. State Commun.* **95** 553-557 (1995)

6. R. E. Hummel, M. H. Ludwig and S.-S. Chang, "Strong Blue Room Temperature Photoluminescence of Spark-

7. M. H. Ludwig, R. E. Hummel and S.-S. Chang, "Bright Visible Photoluminescence of Spark Processed Ge, GaAs, and Si", *J. Vac. Sci. Technol.* **B 12**, 3023-3026 (1994).

8. Y. Kinemitsu, T Futagi, T. Matsumoto and H. Mimura, "Origin of Blue and Red Photoluminescence from Oxidized Porous Silicon", *Phys. Rev.* **B 49**, 14732-14735 (1994).

9. M. K. Lee and K. R. Peng, "Blue Emission of Porous Silicon", *Appl. Phys. Lett.* **62**, 3159-3160 (1993).

10. H. Tamura, R Ruckschloss, T. Wirschem and S. Vepvek, "Origin of the Blue/green Luminescence from Nanocrystalline Silicon", *Appl. Phys. Lett.* **65**, 1537-1539 (1994).

11. H. Koyama, T. Nakagawa, T. Ozaki and N. Koshida, "Post-anodization Filtered Illumination of Porous Silicon in HF Solutions . An Effective Method to Improve Luminescence Properties", *Appl. Phys. Lett.* **65**, 1656-1658 (1993).

12. H. Koyama and N. Koshida, "Photo-assisted Tuning of Luminescence from Porous Silicon", *J. Appl. Phys.* **74** 6365-6367 (1993).

13. C. I. Harris, M. Syvajarvi, J. P. Bergman, O. Kordina, A. Henry and B. Monemar, "Time-resolved Decay of the Blue Emission in Porous Silicon", *Appl.Phys. Lett.* **65**, 2451-2453 (1994).

14. D. I. Kovalev, I. D. Yaroshetzkii, T. Muschik, V. Petrova-Koch and F. Koch, "Fast and Slow Visible Luminescence Bands of Oxidized Porous Silicon", *Appl. Phys Lett.* **64**, 214-216 (1994).

15. J H. Stathis and M A. Kastner, "Time-resolved Photoluminescence in Amorphous Silicon Dioxide", *Phys. Rev.* **B 35**, 2972 (1987).

16. H. Nishikawa, T. Shiroyama, R. Nakamura, Y. Ohki, K. Nagasawa and Y. Hama, "Photoluminescence from Defect Centers in High Purity Silica Glasses Observed Under 7~9 eV Excitation", *Phys. Rev.* **B 45**, 586 (1992).

17. L. N. Skuja, A. N. Streletstky and A. B. Pakovich, "A New Intrinsic Defect in Amorphous SiO_2 : Two Fold Coordinated Silicon", *Solid State Commun.* **50**, 1069 (1984).

18. L. N. Skuja, "Time Resolved Low Temperature Luminescence of Non-bridging Oxygen Hole Centers in Silica Glasss", *Solid State Commun.* **84**, 613 (1992).

19. Y. H. Xie, W. L. Wilson, F. M. Ross, J. A. Mucha, E.A. Fitzerald, J. M. Macaulay and T. D. Haris, "Luminescence and Structural Studies of Porous Silicon Films", *J. Appl. Phys* **71**, 2403-2407 (1992).

20. R. T. Collins, M. A. Tischler and J. H. Stathis, "Photoinduced Hydrogen Loss from Porous Silicon", *Appl. Phys. Lett.* **61**, 1649-1651 (1992).

processed Silicon", *Solid State Commun.* **93**, 237-241 (1995).