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Blue emission in porous silicon: Oxygen-related photoluminescence

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A blue-photoluminescence (PL) band, centered at 2.6 eV, was observed in thermally and chemically oxidized light-emitting porous silicon layers with an efficiency that can exceed 0.1%. The PL decay is found to be independent of excitation intensity and detection wavelength, and to be nonexponential with a characteristic time of ~1 nsec. A correlation between the intensity of the blue PL and the intensity of the infrared absorption related to bonded oxygen has been established. These results are examined in relation to the possible mechanisms for the blue-PL band.

Efficient photoluminescence (PL) in electrochemically anodized Si, which we call light-emitting porous silicon (LEPSi), has attracted much attention from the points of view of the origin of the luminescence and the possible applications in optoelectronics. The usual luminescence spectrum is a broad band centered around 1.7 eV.[1] The efficiency of this band is $\geq 1\%$ and its characteristic decay times are typically 1–10 μsec at room temperature.[2] Recently, orange PL with $h\nu_{\max} \geq 2$ eV and later green-blue PL with $h\nu_{\max} \approx 2.5$ eV were reported in oxidized porous silicon.[3] In contrast to the red and orange bands, the blue-PL band dynamics is in the nanosecond time domain.[3–5] The current interest in the blue PL is due to its importance for displays and fast optoelectronic devices applications. However, this PL band has been less investigated than its red counterpart.

In this paper we present time-resolved PL spectroscopic measurements of LEPSi layers prepared by different techniques. Time-resolved measurements make it possible to study in detail the two PL bands, in the red and blue spectral ranges. Since the photoluminescence properties of LEPSi are extremely sensitive to chemical modifications,[6,7] control and characterization of the surface chemistry are very important. Infrared absorption spectroscopy is used to investigate the correlation between PL and chemical composition. We will show that efficient blue PL in LEPSi does not require high-temperature treatments. Finally, possible mechanisms for the blue PL are discussed.

The time-resolved PL spectra were obtained using a gated optical multichannel analyzer after picosecond pulse excitation by the third harmonic of an actively-passively mode-locked Nd-YAG (yttrium aluminum garnet) laser ($\lambda = 355$ nm). The maximum pulse fluence was 1 mJ/cm^2 and the repetition rate was 10 Hz. The overall time resolution was 15 nsec. The PL dynamics at selected wavelengths was measured using a single photon-counting technique after excitation by the second harmonic of a synchronously pumped picosecond dye laser ($\lambda = 300$ nm). The average intensity was 2 W/cm^2 at a repetition rate of 2 MHz. The time resolution was ≤ 100 psec. Infrared absorption spectra were measured by a Fourier transform infrared (FTIR) spectrometer. The contribution from the silicon substrate was removed from the FTIR data using a difference method. All measurements were performed at room temperature.

LEPSi layers were formed by anodization of 5-Ω cm p-type silicon wafers in a methanol-HF-H_2O (2:1:1) solution. To change the sample's properties we varied the current density from 1 to 30 mA/cm^2. Anodization was performed in the dark or with light assistance using a white-light source (~100 mW/cm^2). Oxidization of the LEPSi layers was achieved in a tube furnace with a dry oxygen atmosphere.

The recent literature contains several reports of blue PL in LEPSi after rapid thermal oxidation at high temperature ($T_{\text{ox}} \geq 1000\,^\circ$C).[3,8] Therefore, the first type of sample we investigated was LEPSi anodized in the dark at a current density $j = 10$ mA/cm^2 and then oxidized for 2 min at 1100 °C in dry oxygen. These samples display the reported blue-PL band [Fig. 1(a)]. FTIR absorption measurements show a strong line at 1080 cm^{-1} related to the asymmetric stretching vibrational mode of the Si-O-Si oxygen bridge [Fig. 1(a), inset]. The second type of sample we investigated was LEPSi anodized at a smaller current density of 1 mA/cm^2 with light assistance. We have shown[9] that anodization with light assistance leads to the accumulation of oxygen on the nanocrystallite surface. In addition, FTIR data for this type of sample clearly display the presence of bonded oxygen and the almost complete absence of bonded hydrogen. There is only one strong peak at 1070 cm^{-1} which shows Si-O-Si bridges in a configuration close to stoichiometry [Fig. 1(b), inset]. Thus, the FTIR spectra show no significant difference in the chemical composition of these two types of samples. In the following we refer to these samples as "fully oxidized," since no Si-H bonds remain. This does not mean, however, that no silicon nanocrystallites are left in these samples.

The time-resolved PL spectra of these two types of samples are also similar: a broad PL band (full width at half maximum >0.5 eV) with a peak near 2.6 eV (Fig. 1). The PL spectra have not been corrected for the spectral sensitivity of our detection system. The blue-PL band decays with a characteristic time of ≈ 1 nsec (Fig. 2). The decay is nonexponential and we have been unable to fit the decay curve by a simple power law or by a stretched exponential. No significant wavelength dependence of the PL decay was observed from $\lambda = 440$ to 650 nm. The decay dynamics did not change when the excitation in-

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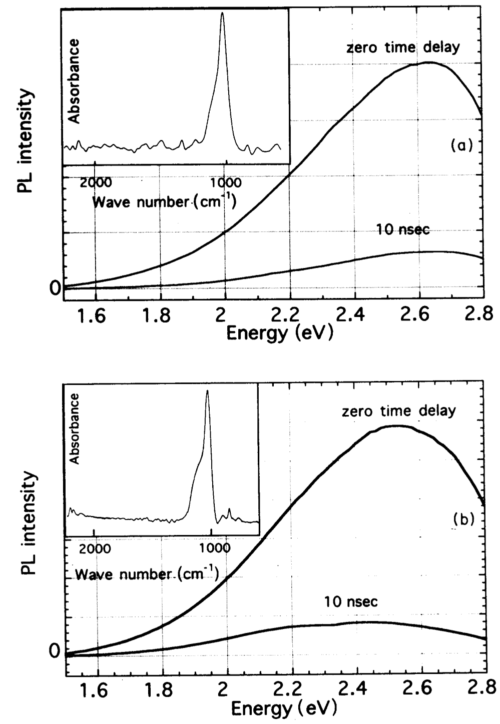

FIG. 1. Time-resolved PL spectra in fully oxidized LEPSi: sample after 1100 °C oxidation (a) and as anodized sample prepared at a current density $j = 1$ mA/cm^2 with light assistance (b). The excitation wavelength is 355 nm. The insets show the FTIR spectra.

tensity was varied by a factor of 10. The observed nonexponential decay may indicate a distribution of carrier lifetimes. Assuming monomolecular recombination and following the procedure outlined by Tsang and Street[10] we obtained the lifetime distribution shown in the inset of Fig. 2. We have performed the same experiments on a sample prepared for us by rapid thermal oxidation at 1100 °C.[3] The results are identical to those obtained in our samples. It is worth mentioning that the photoluminescence yield for the blue band of all the "fully oxidized" samples discussed above is quite high: after comparison with the brightest red-LEPSi samples we estimated the quantum efficiency to be more than 0.1%. As expected, immediately after excitation the intensity of the blue PL from "fully oxidized" samples is much higher than the intensity of the red PL from the most efficient red-LEPSi samples.

The next type of sample was anodized in the dark at a current density $j = 30$ mA/cm^2 and subsequently oxidized chemically by immersion in 10% HNO$_3$ for 2 min.[11] The FTIR spectrum clearly shows Si-O-Si bridges (1070 cm^{-1}) and in addition some oxidized Si-H bonds at 2250 and 880 cm^{-1} [Fig. 3(b)]. The presence of bonded hydrogen is accompanied by the appearance of the red-orange–PL component ($h\nu_{\text{max}} = 2.0$–2.2 eV). The decay of this PL component is also nonexponential, with a characteristic decay time in the microsecond range. Time-resolved PL spectra show the presence of a fast blue-PL component in these chemically oxidized samples right after excitation [Fig. 3(a)]. The broad PL band is in fact the superposition of two bands—a fast, blue band and a slow, red band. Measurements of the PL dynamics in the blue also show a nonexponential decay with a characteristic time close to those for the fully oxidized samples.

Finally, we present the results of measurements of freshly anodized ($j = 10$ A/cm^2) LEPSi samples. In agreement with previous works,[9,12,13] the FTIR spectrum (Fig. 4, inset) shows Si-H bonds in different

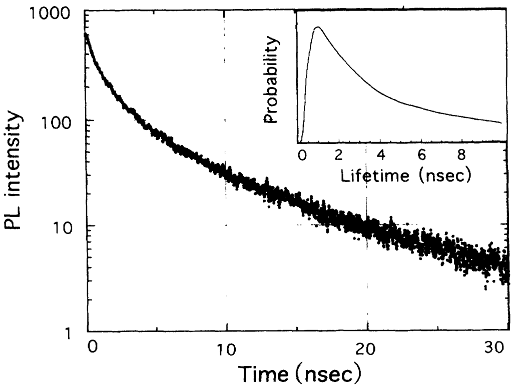

FIG. 2. PL decay for LEPSi sample oxidized at 1100 °C. The excitation wavelength is 300 nm. The inset shows the distribution of lifetimes.

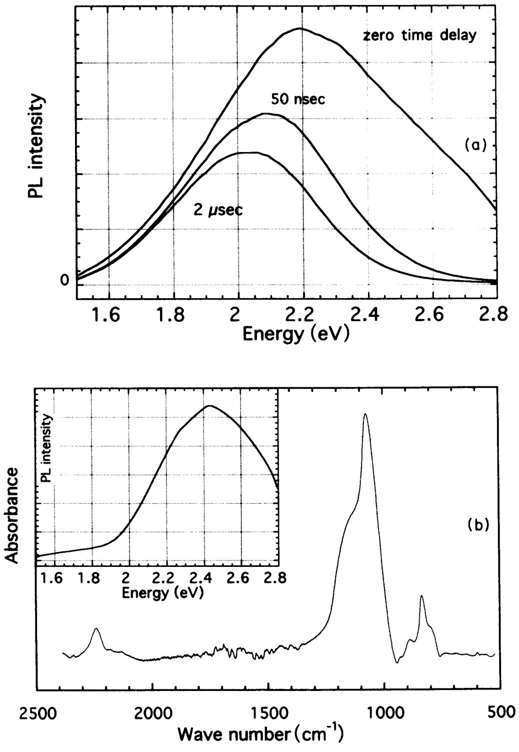

FIG. 3. Time-resolved PL spectra (a) and FTIR spectrum (b) in chemically oxidized LEPSi sample. The excitation wavelength is 355 nm. The inset of (b) shows the short-wavelength component of the PL obtained after subtraction of the PL spectrum measured at 50-nsec delay from the PL spectrum measured at zero delay.

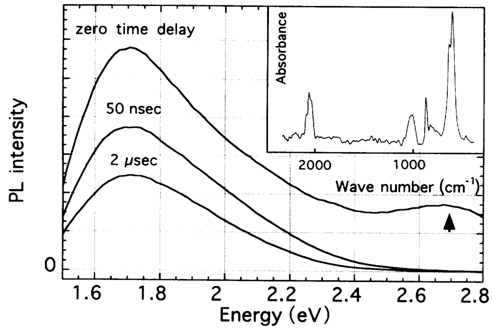

FIG. 4. Time-resolved PL spectra and FTIR spectrum (inset) for freshly anodized LEPSi. The excitation wavelength is 355 nm.

configurations (scissors at 910 cm^{-1}, stretching around 2100 cm^{-1}, and wagging modes at 630–670 cm^{-1}), no Si-O-H bonds (at 2250 or at 870 cm^{-1}) and only a small amount of Si-O-Si bridges at 1055 cm^{-1}. This small peak at 1055 cm^{-1} indicates the presence of nonstoichiometric suboxide presumably produced during handling of the sample in air. The main PL band peaks around 1.7 eV (Fig. 4). Time-resolved PL spectra right after excitation again show a weak but clearly observable blue-PL band (shown by the arrow), whose spectrum is similar to that of the "fully oxidized" samples. Due to the low intensity of this blue band we were not able to analyze the decay in detail, but the characteristic decay time is much less than 15 nsec.

In the following discussion, we consider three possible models for the blue emission from LEPSi: band-to-band recombination in silicon nanocrystals, emission from the oxide, and emission due to surface states. The quantum confinement model was proposed independently by Canham[1] and by Lehmann and Gosele[14] to explain the red luminescence and the opening of the band gap, respectively. In this model, PL is produced by band-to-band radiative transitions in nanocrystallites whose band structure is modified by quantum confinement and a reduction of the Si crystallite size below that of red-emitting LEPSi can lead to blue PL. Recent calculations suggest that the band gap is ≥ 2.5 eV for sizes below 2 nm.[15] However, our results show that the same fast and efficient blue PL is observed in samples prepared by different methods: high-temperature oxidation, when there are no Si crystallites larger than 1 nm left,[16] and anodization with light assistance, which does not lead to a significant reduction in crystallite size.[9] Thus an explanation of the blue-PL band in terms of the "pure" quantum confinement model is unlikely, since the PL spectrum and carrier lifetime should be very sensitive to the size of the crystallites.[17]

The second possibility is that the blue luminescence may originate from the silicon oxide itself. Indeed, SiO_2 is known to luminesce efficiently in the visible under appropriate conditions.[18] In nearly all reported cases, luminescence requires excitation with photon energies much larger than 3.5–4 eV, which is the excitation photon energy used in our experiments and is not enough to create nonequilibrium carriers across the band gap of SiO_2 ($E_g \geq 8$ eV). However, we cannot entirely rule out luminescence from the oxide for two reasons. First, in the nonstoichiometric suboxide SiO_x, the band gap is smaller ($E_g \geq 3$–4 eV for $x \approx 1.4$–1.6) (Ref. 19) and near UV excitation may produce nonequilibrium carriers. Because our FTIR spectra suggest the presence of a nearly stoichiometric oxide ($x \geq 1.8$) in blue-emitting LEPSi, we believe that this interpretation is unlikely. Second, different types of defects in silicon dioxide (e.g., nonbridging oxygen hole center) can be responsible for visible PL and it has been shown very recently that blue PL with a nanosecond decay time can be excited in high-purity wet synthetic silica by 4-eV light.[20]

The third model is related to the surface states model proposed by Koch.[21] Here, quantum confinement causes an opening of the band gap but radiative recombination involves carriers in surface states instead of free electrons and holes. In Ref. 21, it was proposed that the red-PL band involves surface states and that the blue-PL band corresponds to band-to-band recombination. This latter assignment appears implausible as discussed above. Instead the blue PL may also have a surface-related origin: it may involve states produced by the Si-O bonds at the surface of the nanocrystals or the interface between the silicon nanocrystals and the silicon dioxide. These oxygen-related states should be rather shallow, because the decay time of the blue PL and hence the carrier lifetime in these states is short (≈ 1 nsec). Similarly, the red PL may be related to deeper states produced by Si-H bonds on the surface: these states should have microsecond lifetimes as the red PL decays on the microsecond time scale. This model is supported by the correlation between PL spectra and surface chemistry that we recently observed.[22] The blue-PL band shifts slightly to longer wavelengths when the Si-O-H configuration is present in the IR absorption spectra and the red-PL band shifts to shorter wavelengths when the ratio of Si-O/Si-H bonds increases. These results are consistent with a modification of the spectrum of surface states when the nature and the amount of atoms bonded at the surface of silicon crystallites changes.

Both the surface state model and the model where the luminescence comes from the SiO_2 itself agree with the observed correlation between the intensity of the blue-PL band and the intensity of the Si-O infrared absorption. These models are only qualitative: the properties of the blue-PL band (peak position, decay law) are not explained in detail. Future work should strive to make the models more quantitative so that the microscopic origin of the blue PL can be established firmly.

In conclusion, we have observed blue photoluminescence in different types of LEPSi layers using time-resolved photoluminescence spectroscopy. This blue PL peaks near 2.6 eV and its characteristic decay time is approximately 1 nsec in all samples we have investigated. The efficiency of the blue PL exceeds 0.1% in the "fully oxidized" samples. We have demonstrated a correlation between the intensity of the blue-PL band and the intensity of the infrared absorption related to Si-O species.

After examination of several models, we suggest an oxygen-related origin for blue-PL band in LEPSi.

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[*] On leave from Moscow State University, Moscow 119899, Russia.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] N. Ookubo, H. Ono, Y. Ochiai, Y. Mochizuki, and S. Matsui, Appl. Phys. Lett. **61**, 940 (1992).

[3] V. Petrova-Koch, T. Muschik, D. I. Kovalev, F. Koch, and V. Lehmann, in *Microcrystalline Semiconductors: Materials Science & Devices,* edited by P. M. Fauchet, C. C. Tsai, L. T. Canham, I. Shimizu, and Y. Aoyagi, MRS Symposia Proceedings No. 283 (Materials Research Society, Pittsburgh, 1993), p. 178.

[4] A. V. Andrianov, D. I. Kovalev, V. B. Shuman, and I. D. Yaroshetskii, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 943 (1992) [JETP Lett. **56**, 236 (1992)].

[5] T. Miyoshi, K.-S. Lee, and Y. Aoyagi, Jpn. J. Appl. Phys. **31**, 2476 (1992).

[6] *Microcrystalline Semiconductors: Materials Science & Devices* (Ref. 3).

[7] M. A. Tischler and R. T. Collins, Solid State Commun. **81**, 307 (1992).

[8] Y. Kanemitsu, T. Masumoto, T. Futagi, and H. Mimura, in *Silicon-Based Optoelectronic Materials,* edited by M. A. Tischler, R. T. Collins, M. L. Thewalt, and G. Abstreiter, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993), p. 205.

[9] L. Tsybeskov, C. Peng, S. P. Duttagupta, E. Ettedgui, Y. Gao, P. M. Fauchet, and G. E. Carver, in *Silicon-Based Optoelectronic Materials* (Ref. 8), p. 307.

[10] C. Tsang and R. A. Street, Phys. Rev. B **19**, 3027 (1979).

[11] C. Peng, L. Tsybeskov, and P. M. Fauchet, in *Microcrystalline Semiconductors: Materials Science & Devices* (Ref. 3), p. 121.

[12] P. Gupta, V. L. Colvin, and S. M. George, Phys. Rev. B **37**, 8234 (1988).

[13] C. Tsai, K.-H. Li, J. Sarathy, S. Shin, J. C. Campbell, B. K. Hance, and J. M. White, Appl. Phys. Lett. **59**, 2814 (1991).

[14] V. Lehmann and U. Gosele, Appl. Phys. Lett. **58**, 856 (1991).

[15] M. S. Hybertsen, in *Light Emission from Silicon,* edited by S. S. Iyer, R. T. Collins, and L. T. Canham, MRS Symposia Proceedings No. 256 (Materials Research Society, Pittsburgh, 1992), p. 179.

[16] A. G. Cullis, L. T. Canham, G. M. Williams, P. W. Smith, and O. D. Doffer, J. Appl. Phys. **75**, 493 (1994).

[17] J. P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. **61**, 1948 (1992).

[18] J. H. Stathis and M. A. Kastner, Phys. Rev. B **35**, 2972 (1987).

[19] H. R. Philipp, J. Phys. Chem. Solids **32**, 1935 (1971).

[20] A. Anedda, G. Bongiovanni, M. Cannas, F. Congui, A. Mura, and M. Martin, J. Appl. Phys. **74**, 6993 (1993).

[21] F. Koch, in *Silicon-Based Optoelectronic Materials* (Ref. 8), p. 319.

[22] L. Tsybeskov and P. M. Fauchet, Appl. Phys. Lett. (to be published).